

UC San Diego

UC San Diego Electronic Theses and Dissertations

Title

Study of Perfluoropolyether Lubricant Transfer and Hydrocarbon Contamination at the Head/Disk Interface

Permalink

<https://escholarship.org/uc/item/92k7b3zh>

Author

Seo, Young Woo

Publication Date

2017

Peer reviewed|Thesis/dissertation

UNIVERSITY OF CALIFORNIA, SAN DIEGO

**Study of Perfluoropolyether Lubricant Transfer and Hydrocarbon
Contamination at the Head/Disk Interface**

A dissertation submitted in partial satisfaction of the requirements for the degree

Doctor of Philosophy

in

Engineering Sciences (Mechanical Engineering)

by

Young Woo Seo

Committee in charge:

Professor Frank E. Talke, Chair
Professor Gaurav Arya
Professor Yuri Bazilevs
Professor Mauricio de Oliveira
Professor Michael Tolley

2017

Copyright

Young Woo Seo, 2017

All rights reserved.

The dissertation of Young Woo Seo is approved, and it is acceptable in quality and form for publication on microfilm and electronically:

Chair

University of California, San Diego

2017

DEDICATION

To family and friends

TABLE OF CONTENTS

SIGNATURE PAGE	iii
DEDICATION	iv
TABLE OF CONTENTS	v
LIST OF FIGURES	ix
LIST OF TABLES	xx
ACKNOWLEDGEMENTS	xxi
VITA.....	xxiii
ABSTRACT OF THE DISSERTATION.....	xxv
Chapter 1 Introduction.....	1
1.1 History of Hard Disk Drives	1
1.2 Components in Hard Disk Drive.....	3
1.3 Principle of Magnetic Recording	5
1.3.1 Magnetic Materials	5
1.3.2 Write Process.....	7
1.3.3 Read Process.....	12
1.3.4 Magnetoresistive (MR) Heads.....	14
1.4 Tribology in Hard Disk Drives	17
1.4.1 Friction	18
1.4.2 Wear	23
1.4.3 Surface Interactions	28
1.4.4 Lubrication	38

1.4.5	Head-Disk Interface.....	48
1.5	Organization of Dissertation	53
Chapter 2	Experimental Techniques to Study Lubricant Transfer and	55
2.1	Spin Stand Tester	55
2.2	Experimental Techniques for Surface Characterization	58
2.2.1	Optical Surface Analysis (OSA)	59
2.2.2	Scanning Electron Microscopy (SEM).....	67
2.2.3	Atomic Force Microscopy (AFM).....	70
2.3	Experimental Techniques for Material Characterization	73
2.3.1	Energy-Dispersive X-ray Spectroscopy	73
2.3.2	Time-of-Flight Secondary Ion Mass Spectrometry	75
Chapter 3	Basics of Molecular Dynamics	79
3.1	Molecular Mechanics	79
3.1.1	Intramolecular Potential Functions.....	81
3.1.2	Intermolecular Potential Functions.....	84
3.2	Statistical Mechanics	89
3.2.1	Microcanonical Ensemble (NVE)	90
3.2.2	Canonical Ensemble (NVT)	91
3.2.3	Other Ensembles.....	94
3.3	Molecular Dynamics	96
3.4	Coarse-Grained Bead Spring Model	101
3.5	Molecular Dynamics Simulation using LAMMPS	104

Chapter 4	Hydrocarbon Contamination at the Head-Disk Interface	108
4.1	Introduction.....	108
4.2	Experimental Investigation	112
4.2.1	Hydrocarbon Contamination of Disk Surface	112
4.2.2	Slider Surface Contamination.....	126
4.3	Numerical Investigation.....	137
4.3.1	Molecular Dynamics Modeling.....	137
4.3.2	Simulation Results.....	142
4.3.3	Discussion.....	152
4.4	Summary and Conclusion	155
4.5	Acknowledgement	158
Chapter 5	Lubricant Transfer and Fragmentation at Head-Disk Interface ..	159
5.1	Introduction.....	159
5.2	Molecular Dynamics Simulation Model.....	161
5.3	Results and Discussion	163
5.3.1	Lubricant Transfer	166
5.3.2	Lubricant Fragmentation	168
5.4	Summary	170
5.5	Acknowledgement	171
Chapter 6	Lubricant Depletion under Pulsed Laser Irradiation.....	172
6.1	Introduction.....	172
6.2	Molecular Dynamics Simulation	176
6.2.1	Disk-Lubricant Modeling	176

6.2.2	Potential Functions	177
6.2.3	Pulsed Laser Modeling	181
6.2.4	Molecular Dynamics Simulation.....	182
6.3	Results.....	186
6.4	Discussion	194
6.5	Summary	198
6.6	Acknowledgement	199
Chapter 7	Summary and Conclusions	200
	Bibliography	203

LIST OF FIGURES

Figure 1.1 Photos [2] of RAMAC at (a) U.S. Army Red River Arsenal and (b) Computer History Museum.....	2
Figure 1.2 Photo of Ultrastar He 10, the first 10 TB HDD [3].....	2
Figure 1.3 Mechanical components of a hard disk drive [4].....	3
Figure 1.4 (a) Schematic of a typical head gimbal assembly (HGA) in a hard disk drive [5]. (b) Photo of an actual air bearing surface [6].....	4
Figure 1.5 B-H hysteresis loop of a ferromagnetic material [10].....	6
Figure 1.6 Schematic of the writing process in longitudinal magnetic recording (LMR)	8
Figure 1.7 Schematic of the writing process in perpendicular magnetic recording (PMR)	9
Figure 1.8 Schematic of (a) heat assisted magnetic recording head-disk interface and (b) the recording process in heat assisted magnetic recording [19].....	11
Figure 1.9 Schematic of the reading process in perpendicular magnetic recording (PMR)	12
Figure 1.10 Resistance in material due to the giant magnetoresistive effect [33].....	16
Figure 1.11 Transmission electron microscope (TEM) image of a tunneling magnetoresistive sensor in a hard disk drive and [35]	17
Figure 1.12 Solid body on an inclined slope	19
Figure 1.13 Schematic of two sliding bodies at (a) macroscopic scale and (b) microscopic scale	21

Figure 1.14 Schematic illustrating adhesive wear at the contact interface with tangential loading on the bottom material [46].....	23
Figure 1.15 Two modes of abrasive wear showing (a) two-body mode and (b) three-body mode [59]	25
Figure 1.16 Schematic illustrating abrasive wear (in courtesy of [46])	26
Figure 1.17 Mechanism behind abrasive wear by (a) cutting, (b) fracturing, (c) ploughing and (d) pulling out grains (after [59])	27
Figure 1.18 Schematic of “exaggerated” surface profile with length L	28
Figure 1.19 Schematic showing the difference between the apparent area of contact A_a and the real area of contact A_r	31
Figure 1.20 Schematic of two spheres in contact with each other	32
Figure 1.21 Schematic of a smooth surface contacting a rough surface [70].....	33
Figure 1.22 Schematic of a liquid droplet on a solid surface	36
Figure 1.23 The Stribeck curve showing the friction coefficient to be a function of the lubrication parameter ηVP [77]	38
Figure 1.24 Schematic of (a) boundary lubrication, (b) mixed lubrication and (c) hydrodynamic lubrication	39
Figure 1.25 Chemical diagrams for (a) methane, (b) ethylene, and (c) acetylene	41
Figure 1.26 Three types of synthetic oils: (a) polyalphaolefin (PAO), (b) polyolester (POE), and (c) silicone.....	43
Figure 1.27 Chemical formula for (a) Fomblin Z and (b) Demnum	45
Figure 1.28 An example of a poly-alpha-olefin, hex-1-ene or 1-hexene (C_6H_{12})	47
Figure 1.29 Chemical structure of an additive, X-1P (cyclic phosphazene)	48

Figure 1.30 Head-disk interface in hard disk drives.....	49
Figure 1.31 (a) Finite element mesh of a typical air bearing pressure and (b) finite element simulation result showing pressure distribution on the air bearing surface	52
Figure 1.32 Schematic of the thermal flying height control where (a) 0 mW electric power is applied to the heater element and (b) the full touch down power is applied to the heater element	53
Figure 2.1 Schematic of VENA spin stand tester setup	56
Figure 2.2 Photo of a commercially available spin-stand tester (VENA – VS90) [97]	57
Figure 2.3 Schematic showing the main components of a commercially available optical surface analyzer [123]	59
Figure 2.4 Schematic of p-polarization, s-polarization, and q-polarization of a laser beam [124].	60
Figure 2.5 Schematic of scattered laser due to the presence of a particle on the disk surface [123].	61
Figure 2.6 Optical surface analysis image of a disk surface contaminated with small particles [97]	61
Figure 2.7 Schematic of an optical surface analyzer detecting a layer of foreign liquid, or stain, on the disk surface [124].	62
Figure 2.8 Schematic showing the principle of ellipsometry [124]	63
Figure 2.9 Schematic of laser path through air (Layer #0), lubricant film (Layer #1) and carbon overcoat (Layer #2) [127]	64

Figure 2.10 Optical surface analysis image of a disk surface with different lubricant thickness measured. Q-polarized light is used [128]	66
Figure 2.11 Schematic of components in a scanning electron microscope [129]	67
Figure 2.12 Images of an air bearing surface contaminated with hydrocarbon oil near the read/write element using (a) optical microscopy and (b) scanning electron microscopy [97].	69
Figure 2.13 Schematic of atomic force microscopy [133]	70
Figure 2.14 Schematic of (a) contact mode, (b) non-contact mode and (c) tapping mode of atomic force microscopy [134].....	71
Figure 2.15 Atomic force microscopy image of a crystallized hydrocarbon on the disk surface [97]	72
Figure 2.16 Schematic of the working principle behind EDX [140]	74
Figure 2.17 EDX analysis of an alkane crystal on the air bearing surface [97]	75
Figure 2.18 Schematic of time-of-flight secondary ion mass spectrometry [141]	76
Figure 2.19 Typical ToF-SIMS spectrum showing (a) aluminum and (b) PFPE lubricant fragments and organic compounds [144].....	78
Figure 3.1 Schematic illustrating intramolecular interactions of (a) stretching, (b) bending, and (c) twisting (torsion).....	81
Figure 3.2 Schematic illustrating intermolecular interactions of (a) van der Waals, (b) electrostatic, and (c) polarization.....	84
Figure 3.3 (a) Three potential functions approximating van der Waals attraction and repulsion. (b) Minimum energy for 12-6 LJ potential function and truncated	

12-6 LJ potential function. (c) Comparison of three mathematical models at $r = 2.5\sigma$. All three plots are generated using MATLAB.	86
Figure 3.4 Comparison of the 12-6 LJ potential function, the Coulomb potential function and the EXP potential function. The plot was generated using MATLAB.	87
Figure 3.5 An example of an ensemble showing different configurations: (a) Configuration 1, (b) Configuration 2, and (c) Configuration 3	89
Figure 3.6 Schematic illustrating an NVT system in an infinitely large bath with the bath energy E_B and the system energy E_v	92
Figure 3.7 Schematic of (a) an $N\phi T$ ensemble and (b) a μVT ensemble	95
Figure 3.8 Schematic of a Verlet neighbor list with (a) the central atom, (b) atoms inside the cut-off distance r_c , (c) atoms inside the “skin region” r_s , and (d) atoms not interacting with the central atom	100
Figure 3.9 Schematic of (a) an atomic model of a PFPE lubricant and (b) a CG-BS model of a PFPE lubricant [189].....	102
Figure 3.10 Schematic of the CG-BS model of a Zdol 2000 lubricant molecule [93]	103
Figure 3.11 A disk surface consisting of a diamond-like carbon overcoat and a layer of perfluoropolyether lubricants.....	104
Figure 3.12 Molecular dynamics simulation of perfluoropolyether lubricants on the diamond-like carbon overcoat.....	107
Figure 4.1 (a) Outgassing of hydrocarbon oil from the pivot actuator arm (b) Mechanism of hydrocarbon contamination at the head-disk interface.....	111

Figure 4.2 Schematic of hydrocarbon oil outgassing procedure (temperature: 60°C, 70 °C, 80 °C; time: 2 hours, 4 hours, 8 hours, 12 hours)	113
Figure 4.3 Disk surface (Side B) analyzed using an optical surface analyzer (a) before and (b) after hydrocarbon contamination. The disk was baked at 80°C for 12 hours in the presence of hydrocarbon oil mixture.	116
Figure 4.4 Effect of heat exposure time on the number of scatter sites at 80°C	117
Figure 4.5 Optical surface analysis measurements of disk surface with hydrocarbon oil mixture condensed at 60°C, 70°C, and 80°C for 8 hrs. and 12 hrs.....	118
Figure 4.6 OSA images of a disk exposed to heat at 80°C for (a) 8 hours and (b) 12 hours	119
Figure 4.7 AFM scan on a disk after heat exposure for 8 hours at 60°C (a) 3D image and (b) cross-section of contaminant	120
Figure 4.8 Crystallization of C ₂₄ H ₅₀ (tetracosane) using molecular dynamics simulation.	121
Figure 4.9 Schematic of “United Atom Model” of a linear hydrocarbon chain.....	121
Figure 4.10 Droplet-like contaminant: (a) 3D image and (b) cross-section of typical droplet observed.....	124
Figure 4.11 (a) Schematic of contact angle measurement. Contact angle measurements on 0.5 µL droplets of (b) pivot base oil, and (c) pivot base oil mixed with four linear hydrocarbons. Dashed line represents the disk surface.....	125
Figure 4.12 (a) Spin-stand tester (VENA-VS90). (b) Schematic of “sweep test” using the spin-stand tester.....	126

Figure 4.13 Slider surface after sweeping over a contaminated disk surface at a temperature of 50°C for 4 hours. (a) Contaminated air bearing surface. (b) Droplets formed at the trailing edge. (c) and (d) Contaminants in the air bearing cavities. Prior to the sweep test, the disk surface.....	129
Figure 4.14 SEM analysis of the slider surface shown in Figure 4.13. (a) SEM image of the entire air bearing surface, (b) Signs of “smearing” and droplet formation near the pole-tip region, (c) Crystallized hydrocarbon in the air bearing cavity, (d) EDX analysis of droplets shown in (b).....	130
Figure 4.15 Slider surface after sweep testing at 60°C for 4 hours. (a) Optical microscope image of the slider air bearing surface. (b) SEM image of the slider air bearing surface. (c) Droplet on the trailing edge near the pole tip region. (d) Crystallized hydrocarbon	131
Figure 4.16 EDX analysis of the crystals shown in Figure 4.15(d)	132
Figure 4.17 Slider surface after sweep testing for 4 hours at 60°C. (a) Optical microscope image of the slider surface. (b) SEM image of the entire air bearing surface. (c) Droplets formed on the trailing edge near the pole-tip region. (d) Droplets formed in the air bearing cavity	133
Figure 4.18 ToF-SIMS results of contaminants on different slider surfaces of the same air bearing design (a) Slider 1, (b) Slider 2, (c) Slider 3, and (d) reference ToF-SIMS result of pivot base oil	134
Figure 4.19(a) Schematic of the simulation for a typical air bearing step and (b) coarse-grained bead spring model of disk, slider, lubricant, and hydrocarbon	

molecules, in which intermolecular and intramolecular interactions are modeled using	138
Figure 4.20 Molecular dynamics simulation with parameters $T = 1.6\epsilon/k_B$, $V_d = 2.5\sigma/\tau$, $H_{\min} = 10\sigma$, and $\alpha = 45^\circ$ for C_{24} contamination at (a) $t = 0$, (b) $t = 445\tau$, and (c) $t = 490\tau$	143
Figure 4.21 Schematic of the molecular dynamics simulation with parameters of $T = 1.6\epsilon/k_B$, $V_d = 2.5\sigma/\tau$, $H_{\min} = 30\sigma$, and $\alpha = 45^\circ$ for C_{24} contamination at (a) $t = 0$ and (b) $t = 445\tau$	144
Figure 4.22 Molecular dynamics simulation of C_{24} transfer and the effect of C_{24} on lubricant transfer at the V_d of $2.5\sigma/\tau$	146
Figure 4.23 Molecular dynamics simulation of C_{36} transfer and the effect of C_{36} on lubricant transfer at the V_d of $2.5\sigma/\tau$	147
Figure 4.24 “Long time” ($t = 7,820\tau$) simulation results showing hydrocarbon transfer in which the PFPE layer was contaminated with C_{24} and C_{36} , receptively. Simulations were performed at $T = 1.2\epsilon/k_B$, $1.4\epsilon/k_B$, and $1.6\epsilon/k_B$, respectively, at $H_{\min} = 100\sigma$ and $V_d = 2.5\sigma/\tau$	148
Figure 4.25 “Long time” ($t = 7,820\tau$) simulation results showing PFPE lubricant transfer in which the PFPE layer was contaminated with C_{24} and C_{36} , receptively. Simulations were performed at $T = 1.2\epsilon/k_B$, $1.4\epsilon/k_B$, and $1.6\epsilon/k_B$, respectively, at $H_{\min} = 100\sigma$ and $V_d = 2.5\sigma/\tau$	149
Figure 4.26 Schematic of molecular dynamics simulation with parameters of $T = 1.6\epsilon/k_B$, $V_d = 2.5\sigma/\tau$, $H_{\min} = 100\sigma$, and $\alpha = 45^\circ$ for C_{24} contaminations. A	

monolayer of PFPE lubricant was deposited on the slider surface prior to the molecular dynamics simulation.....	150
Figure 4.27 Molecular dynamics simulation after depositing a monolayer of PFPE on the slider surface prior to simulating lubricant and hydrocarbon transfer. Simulations were performed at $H_{\min}=100\sigma$, $t=7,820\tau$, and $V_d = 2.5\sigma/\tau$ with C_{24} hydrocarbon contaminants.....	151
Figure 4.28 Molecular dynamics simulation after depositing a monolayer of PFPE on the slider surface prior to simulating lubricant and hydrocarbon transfer. Simulations are run at $H_{\min}=100\sigma$, $t=7,820\tau$, and $V_d = 2.5\sigma/\tau$ with C_{36} hydrocarbon contaminants	152
Figure 5.1 Four different types of lubricant molecules used in the present molecular dynamics simulation.	161
Figure 5.2 Schematic of simplified head-disk interface.	162
Figure 5.3 Molecular dynamics simulation results at different times: (a) $t = 0 \tau$, (b) $t = 100 \tau$, (c) $t = 200 \tau$, (d) $t = 300 \tau$, (e) $t = 400 \tau$, and (f) $t = 500 \tau$	165
Figure 5.4 Molecular dynamics simulation of lubricant transfer versus (a) temperature, (b) local pressure change, and (c) disk velocity.....	166
Figure 5.5 Molecular dynamics simulation of lubricant fragmentation versus (a) temperature, (b) local pressure change and (c) disk velocity.....	168
Figure 6.1 Schematic of the modeling process: (a) typical magnetic disk with diameter of 3.5 inches, (b) cross-section of the disk, and (c) coarse-grained bead spring model of the carbon overcoat with a thin lubricant layer.	177

Figure 6.2 Schematic of intermolecular and intramolecular interactions among the modeled coarse-grained beads.	178
Figure 6.3 Illustration of a Gaussian pulse laser over space at different times (a) $t = 0\tau$, (b) 1.0τ , (c) 2.0τ , (d) 3.0τ , (e) 4.0τ , and (f) 5.0τ	182
Figure 6.4 Molecular dynamics simulation model: (a) the laser spot region, (b) the intermediate Newtonian region, and (c) the outer thermostat region.	183
Figure 6.5 Molecular dynamics simulation with $P_{\text{peak}} = 1,400\epsilon/\tau$ (≈ 14 nW), FWHM = 2.35τ (≈ 235 ps), and $f_{\text{pulse}} = 0.2\tau^{-1}$ (≈ 2 GHz) for pulsed laser irradiation on the disk surface at (a) $t = 0\tau$, (b) $t = 150\tau$, and (c) $t = 300\tau$	186
Figure 6.6 Molecular dynamics results showing (a) the maximum temperature in the lubricant layer versus time and (b) lubricant height distribution as a function position at time $t = 300\tau$	187
Figure 6.7 Effect of laser peak power on (a) maximum temperature, (b) lubricant depletion width, (c) number of evaporated lubricant beads, and (d) number of fragmented lubricant chains.....	188
Figure 6.8 Effect of pulse duration on (a) maximum temperature in the lubricant layer, (b) depletion width, (c) number of evaporated lubricant beads, and (d) number of fragmented lubricant chains.	189
Figure 6.9 Effect of repetition rate on (a) maximum temperature, (b) lubricant depletion width, (c) number of evaporated lubricant beads, and (d) number of fragmented lubricant chains.	190
Figure 6.10 Laser power versus time for (a) Continuous-wave laser, (b) Gaussian pulse laser, and (c) square pulse laser.	191

Figure 6.11 Comparison between a continuous-wave laser and a Gaussian pulse laser.	
Effect of laser peak power on (a) maximum temperature, (b) lubricant depletion width, (c) number of evaporated lubricant beads, and (d) number of fragmented lubricant chains.....	192
Figure 6.12 Comparison between a square pulse laser and a Gaussian pulse laser. Effect of pulse duration on (a) maximum temperature, (b) lubricant depletion, (c) number of evaporated lubricant beads, and (d) number of fragmented lubricant chains.	193
Figure 6.13 Laser pulse power as a function of time with $\text{FWHM} = 2.35\tau$ (≈ 235 ps) at the repetition rate (a) $f_{\text{pulse}} = 0.2\tau^{-1}$ (≈ 2 GHz) and (b) $f_{\text{pulse}} = 0.5\tau^{-1}$ (≈ 5 GHz).	
.....	195
Figure 6.14 Molecular dynamics simulation with a moving laser source with a radius $r_{\text{laser}} = 20\sigma$ and $V_{\text{laser}} = 1.0\sigma/\tau$ (approximately 7 m/s).....	196
Figure 6.15 Number of evaporated lubricant beads as a function of laser peak power for a moving laser source.....	197

LIST OF TABLES

Table 1.1 Straight hydrocarbons – alkanes [76, 78]	40
Table 1.2 Homologous series of hydrocarbons [76, 79]	41
Table 3.1 Ensembles and related equations: probability distribution, partition function, and bridge equation [169]	96
Table 4.1 Physical data of hydrocarbons used [203-204]	115
Table 4.2 Sweep Test Conditions	128
Table 4.3 Parameters for the molecular dynamics simulation model	142
Table 6.1 Potential Function Coefficients	180

ACKNOWLEDGEMENTS

First, I would like to express my gratitude to my academic advisor Professor Frank E. Talke. Without his guidance, support, and mentorship, this dissertation would not have been possible. Since 2012, Professor Talke always challenged me to be better a better engineer and researcher worthy of a doctorate degree. He not only guided me through my academic career but also opened many future opportunities for me as well. I will always be grateful for his unending support and guidance.

I would like to thank my committee members Professor Gaurav Arya, Professor Yuri Bazilevs, Professor Mauricio de Oilieveira and Professor Michael Tolley.

I would also like to thank Dr. Andrey Ovcharenko, Dr. Raj Thangaraj, Dr. Daniel Bilich, Dr. Jih-Ping Peng, Dr. Min Yang, and Dr. Ralf Brunner for their support and guidance during my two summer internships at Western Digital Corporation, as well as when I was back at UC San Diego.

I would like to thank two alumni from Professor Talke's lab, Dr. Youyi Fu and Dr. Liane Matthes, for their advice and discussions during my Ph.D. study.

I would also like to express my thanks to my lab mates Karcher Morris, Anay Pandit, Alex Phan, Dr. Andreas Rosenkranz, Benjamin Suen, Tan Trinh, and Phuong Truong. They helped me greatly during my Ph.D. study. I would also like to thank Iris Villanueva and Ray Descoteaux from the Center for Memory and Recording Research for their help during my study.

Lastly, I would like to thank my family: my parents and sister. Despite being in Mongolia for their missionary work, my parents always believed in me and loved me. I

will never forget their support and trust. My sister, living on the other side of the country, always made me proud of her achievement.

Chapter 4, in part is a reprint of the material as it appears in "Experimental Investigation of Hydrocarbon Contamination at the Head–Disk Interface," Seo, Young Woo, Andrey Ovcharenko, Daniel Bilich, and Frank E. Talke, *Tribology Letters* 65, no. 2 (2017): 54. The dissertation author was the primary investigator and author of this paper.

Chapter 4, in part is a reprint of the material as it appears in "Simulation of hydrocarbon oil contamination at the head–disk interface using molecular dynamics," Seo, Young Woo, Andrey Ovcharenko, and Frank E. Talke, *Tribology Letters* 61, no. 3 (2016): 28. The dissertation author was the primary investigator and author of this paper.

Chapter 5, in part is a reprint of the material as it appears in "Molecular Dynamics Simulation of Lubricant Transfer at the Head-Disk Interface Considering Lubricant Fragmentation," Seo, Young Woo, Andreas Rosenkranz, and Frank E. Talke, *In Preparation for Publication*. The dissertation author was the primary investigator and author of this paper.

Chapter 6, in part is a reprint of the material as it appears in "Molecular Dynamics Simulation Study on the Effect of Laser Pulse Peak Power, Pulse Duration, and Repetition Rate on Lubricant Depletion," Seo, Young Woo, Andreas Rosenkranz, and Frank E. Talke, *In Preparation for Publication*. The dissertation author was the primary investigator and author of this paper.

VITA

06/2012	B.S., Mechanical Engineering, University of California, San Diego, La Jolla, CA, USA
06/2012-08/2017	Research and Teaching Assistant Center for Memory and Recording Research, University of California, San Diego, La Jolla, CA, USA
06/2013-09/2013	Tribology Software Intern, Full-Time Western Digital Corporation, San Jose, CA, USA
04/2014	M.S., Mechanical Engineering University of California, San Diego, La Jolla, CA, USA
06/2014-09/2014	Tribology Intern, Full-Time Western Digital Corporation, San Jose, CA, USA
2017	Doctor of Philosophy in Engineering Sciences (Mechanical Engineering) University of California, San Diego, La Jolla, CA, USA

PUBLICATIONS

Seo, Young Woo, Deng Pan, Andrey Ovcharenko, Min Yang, and Frank E. Talke. "Molecular dynamics simulation of lubricant transfer at the head-disk interface." *IEEE Transactions on Magnetics* 50, no. 11 (2014): 1-4.

Zhang, Chuanwei, Alex Phan, Young Woo Seo, Andrey Ovcharenko, Min Yang, and Frank E. Talke. "Effect of a void on the heat transfer in the head disk interface." *Microsystem Technologies* 21, no. 12 (2015): 2597-2603.

Seo, Young Woo, Andrey Ovcharenko, and Frank E. Talke. "Simulation of hydrocarbon oil contamination at the head-disk interface using molecular dynamics." *Tribology Letters* 61, no. 3 (2016): 28.

Seo, Young Woo, Andrey Ovcharenko, Daniel Bilich, and Frank E. Talke. "Experimental Investigation of Hydrocarbon Contamination at the Head-Disk Interface." *Tribology Letters* 65, no. 2 (2017): 54.

Seo, Young Woo, Andreas Rosenkranz, and Frank E. Talke. "Investigation of Lubricant Transfer and Lubricant Degradation in a Hard Disk Drive." *In Preparation for Publication*

Seo, Young Woo, Andreas Rosenkranz, and Frank E. Talke. "Molecular Dynamics Study of Lubricant Depletion by Pulsed Laser Heating." *In Preparation for Publication*

ABSTRACT OF THE DISSERTATION

**Study of Perfluoropolyether Lubricant Transfer and Hydrocarbon
Contamination at the Head/Disk Interface**

by

Young Woo Seo

Doctor of Philosophy in Engineering Sciences (Mechanical Engineering)

University of California, San Diego, 2017

Professor Frank E. Talke, Chair

To achieve an areal density of 1 terabit per square inch (1 Tb/in²) in hard disk drives, the mechanical spacing between the flying slider and the rotating disk has decreased to approximately 1 nm. With this decrease in spacing, the head-disk interface has become increasingly more susceptible to slider-disk contacts, wear, and lubricant transfer from the disk to the slider. Contamination at the head-disk interface can cause “flying stiction”, flying instability, and read/write errors, leading ultimately to failure of the disk drive. It is essential to understand perfluoropolyether lubricant transfer and

hydrocarbon contamination at the head-disk interface to improve the tribological performance and the reliability of hard disk drives.

In this dissertation, perfluoropolyether lubricant transfer and lubricant fragmentation at the head-disk interface are investigated numerically as a function of temperature, local pressure change, and disk velocity. Molecular dynamics is used to study the effect of laser pulse peak power, pulse duration, and repetition rate on lubricant depletion. Hydrocarbon contamination at the head-disk interface is modeled experimentally by assuming a three-step mechanism for hydrocarbon contamination, consisting of evaporation, transfer, and condensation. In addition, a numerical investigation of hydrocarbon contamination at the head-disk interface is performed using molecular dynamics simulations.

The results of this dissertation provide guidance in the design of perfluoropolyether and hydrocarbon lubricants to improve the tribological performance and reliability of the head-disk interface in hard disk drives.

Chapter 1

Introduction

1.1 History of Hard Disk Drives

Digital data are created in the form of videos, music, pictures, smartphone messages, E-mails, credit card transactions, etc. In 2015, Forbes [1] estimated that by the year 2020, 1.7 megabytes (MB) of new data will be created every second by every person alive. This would amount to a total of 44 zettabytes (ZB), or 44×10^{21} bytes. In order to store such a huge amount of data, hard disk drives (HDD) are needed due to their high storage capacity and low cost per gigabyte compared to other storage devices such as magnetic tapes or solid-state drives (SSD).

In 1956, IBM announced the IBM 305 RAMAC, the first commercial computer storage system [2]. At the time, RAMAC stored approximately 5 megabytes of data and was leased monthly for \$3,200 (equivalent to \$28,827 in 2016). Figure 1.1 shows some of the first commercial hard disk drives developed by IBM.

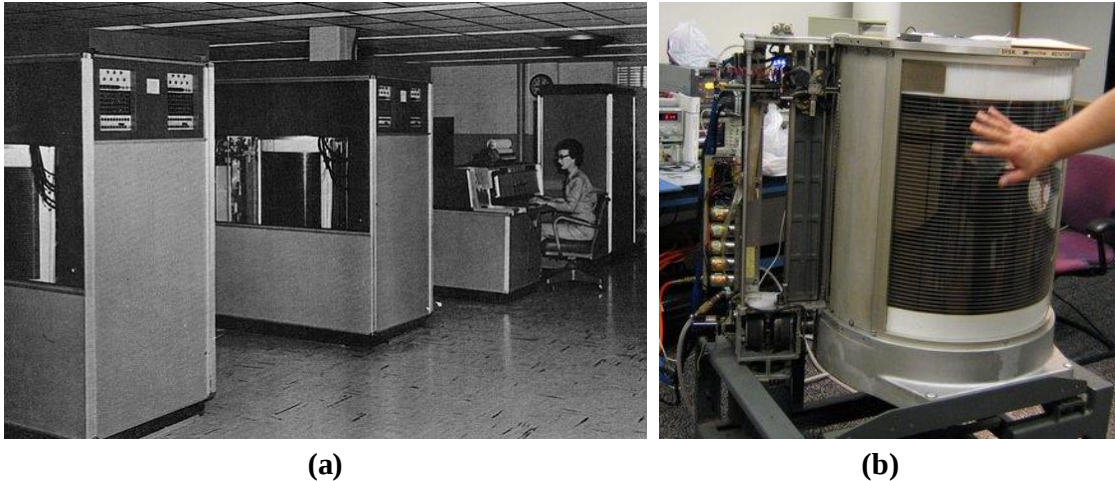


Figure 1.1 Photos [2] of RAMAC at (a) U.S. Army Red River Arsenal and (b) Computer History Museum

Over the past sixty years, hard disk drive technology has developed at a rapid rate. In 2015, HGST, a Western Digital (WD) company, announced the first HDD with 10 terabytes (TB), or 10^{13} bytes of storage, “Ultrastar He 10” [3]. This is roughly 2 million times larger in storage capacity compared to RAMAC’s 5 MB in 1956. From a device that occupied a room of 9 m x 15 m x 25 m, a hard disk drive can now store up to 10 TB in an enclosure of 146 mm x 101 mm x 25 mm (5.75 in x 4 in x 1 in). Figure 1.2 shows Ultrastar He 10 from HGST.



Figure 1.2 Photo of Ultrastar He 10, the first 10 TB HDD [3]

In order to understand how hard disk drives achieve such high storage capacity, it is necessary to look closely at the mechanical components of HDDs.

1.2 Components in Hard Disk Drive

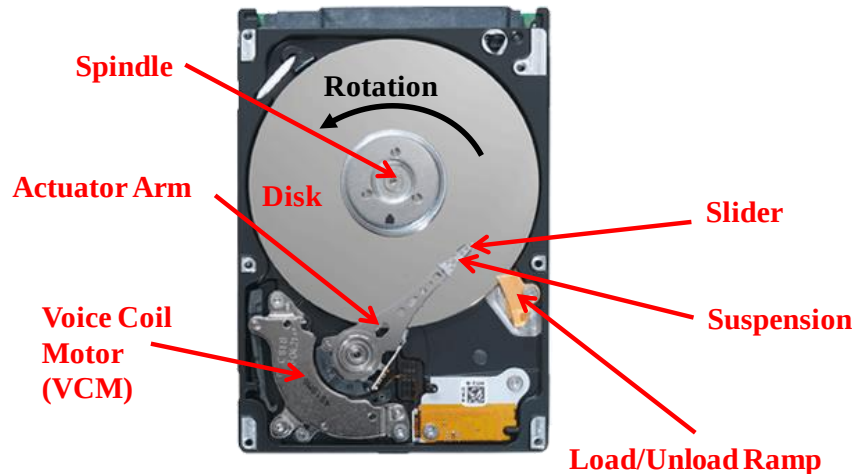


Figure 1.3 Mechanical components of a hard disk drive [4]

Figure 1.3 shows the mechanical components inside a hard disk drive. A conventional hard disk drive has multiple disks mounted on a spindle in the disk drive enclosure. A magnetic recording slider, that reads and writes magnetic bits on the disks, is attached to a suspension (Figure 1.3). The suspension is fixed to the actuator arm. If the hard disk drive is not in operation, the slider is lifted off from the disk by means of the “load/unload ramp.” During actual operation, the disk rotates at high rotational speed and the slider flies over the disk supported by an air bearing. During start-up, a current flows to the voice coil motor, inducing a magnetic force on the actuator arm. This moves the slider from the resting position on the ramp onto the rotating disks. When the hard disk drive shuts down, the slider is moved back to the ramp. The process of moving the

slider on the rotating disks during the operation and withdrawing the slider on the ramp during shutdown is called “loading” and “unloading”, respectively.

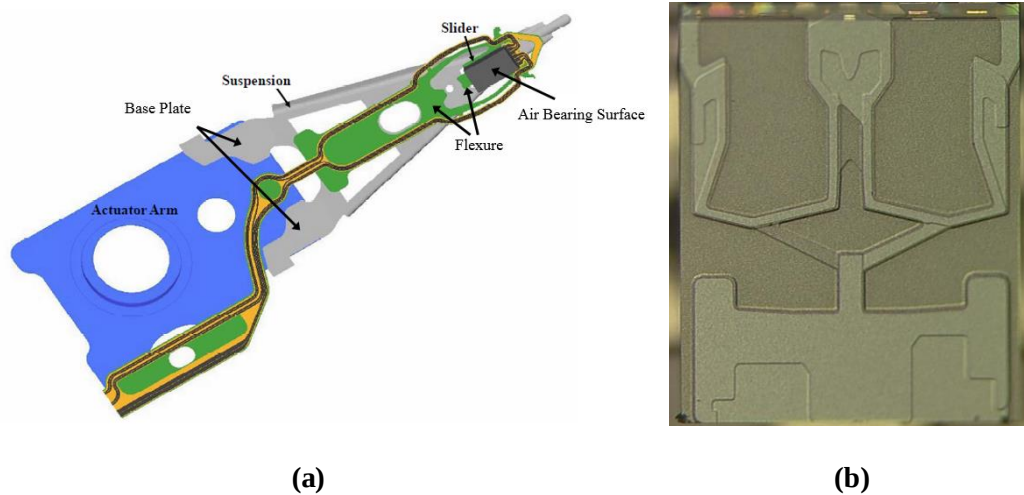


Figure 1.4 (a) Schematic of a typical head gimbal assembly (HGA) in a hard disk drive [5]. (b) Photo of an actual air bearing surface [6]

Figure 1.4(a) shows a schematic of a typical head gimbal assembly in a hard disk drive [5]. It consists of the suspension, the flexure, and the slider. The slider is bonded to the flexure, which is welded to the suspension. Between the flexure and the suspension is the “dimple-gimbal” interface. The dimple-gimbal interface allows the slider to roll and pitch while it flies over the rotating disk. The disk-facing surface of the slider is called the air bearing surface (ABS). As shown in Figure. 1.4(b), the air bearing surface has regions of different depths allowing the slider to generate the desired pressure distribution over the surface to allow flying height on the order of 1nm [6]. The pressure distribution generated over the air bearing contour allows the slider to fly over the rotating disk in a stable manner. This interface is called the head-disk interface.

1.3 Principle of Magnetic Recording

In hard disk drives, information is stored in the form of magnetic bits. The magnetic bits are recorded in the magnetic layer of a hard disk. The magnetic layer is composed of fine grains. Several grains form one magnetic domain where one bit is stored. This section discusses the magnetic material, the write process, and the read process in hard disk drives.

1.3.1 Magnetic Materials

In general, magnetic materials can be categorized into three groups: diamagnetic, paramagnetic and ferromagnetic [7-8]. “Diamagnetic” materials are materials that are weakly repelled in the presence of an external magnetic field. Diamagnetic materials include carbon, copper, water and plastic. When an external magnetic field is applied to a diamagnetic material, the material is weakly magnetized. However, once the external magnetic field is removed, the magnetic properties of the material return to their original state.

“Paramagnetic” materials are materials that are weakly attracted in the presence of an external magnetic field. Paramagnetic materials include platinum, aluminum, magnesium, lithium and tantalum. When an external magnetic field is applied to a paramagnetic material, the material is weakly magnetized. However, once the external magnetic field is removed, the magnetic properties of the paramagnetic material return to their original state, similar to diamagnetic materials.

“Ferromagnetic” materials are materials that are “magnetic” in general. Ferromagnetic materials exhibit strong attraction in the presence of an external magnetic

field. Ferromagnetic materials include iron, nickel and cobalt. When an external magnetic field is applied to a ferromagnetic material, the material is magnetized as the magnetic domains are aligned. Once all the domains are aligned, the material is “saturated” and exhibits strongest internal magnetization.

In hard disk drives, ferromagnetic materials are used to manufacture the magnetic layer in which data is stored. The magnetic layer is composed of many magnetic grains. These magnetic grains can be magnetized in two orientations by applying a proper magnetic field [9]. In order to understand this process, the B-H hysteresis loop needs to be considered (Figure 1.5) [10].

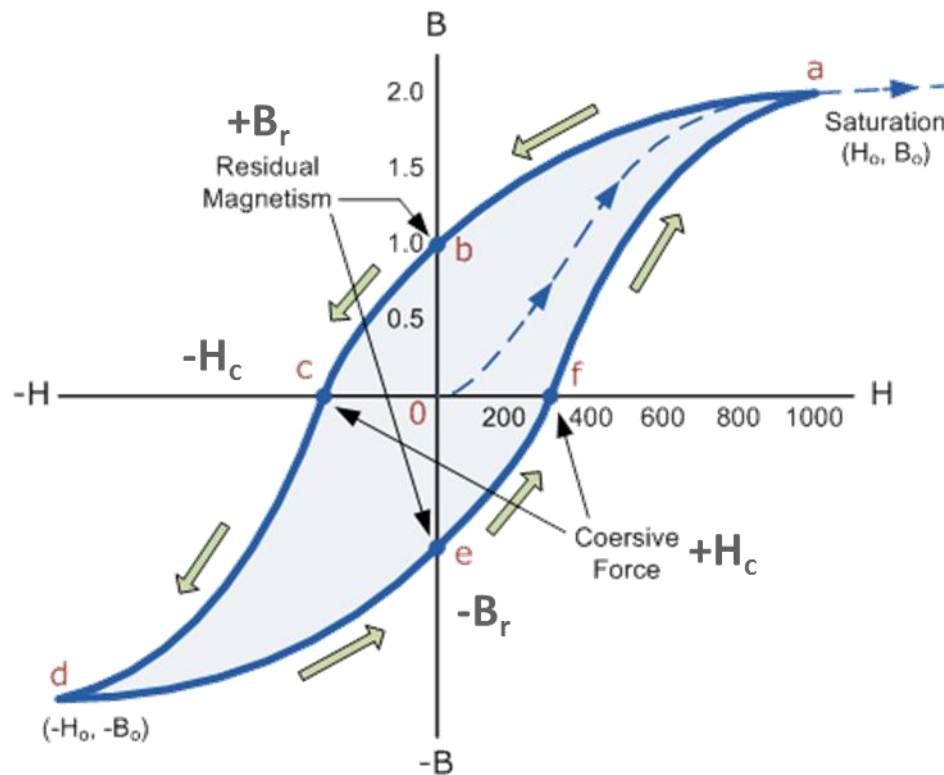


Figure 1.5 B-H hysteresis loop of a ferromagnetic material [10]

Figure 1.5 illustrates a B-H hysteresis loop. The vertical axis B represents the magnetic flux density, or magnetization, and the horizontal axis H represents the

magnetic field strength. A ferromagnetic material holds *zero* magnetization in the absence of an external magnetic field (Figure 1.5(0)). When an external magnetic field with the magnetic strength of positive H is applied, the material is magnetized in one orientation. As H is increased, the magnetization of the ferromagnetic material reaches saturation (Figure 1.5(a)). When the magnetic field H is decreased to *zero*, the magnetization does not return to *zero*, but reaches the residual magnetization, or residual inductance of $+B_r$ (Figure 1.5(b)). To achieve *zero* magnetization, the magnetic field with magnetic strength of $-H_c$ in the negative direction is needed (Figure 1.5(c)). H_c represents the coercivity of the magnetic material. When an even stronger magnetic field is applied, the magnetization reaches saturation in the negative orientation (Figure 1.5(d)). When the magnetic field is removed, the magnetization of the material will reach residual magnetization of $-B_r$ (Figure 1.5(e)). $+B_r$ and $-B_r$ represent two stable magnetization states of a ferromagnetic material.

In hard disk drives, the magnetic layer needs to have high magnetic coercivity H_c in order to store data reliability. If the magnetic coercivity is low, magnetization of the magnetic domains can easily change due to slight changes in temperature, leading to a loss of data.

1.3.2 Write Process

Longitudinal Magnetic Recording (LMR)

Until 2005, data in commercially available disk drives was stored as a collection of magnetic bits written horizontally on the recording media. This method of storing

data is called *longitudinal magnetic recording* (LMR) [11-14]. Figure 1.6 shows a schematic of longitudinal magnetic recording.

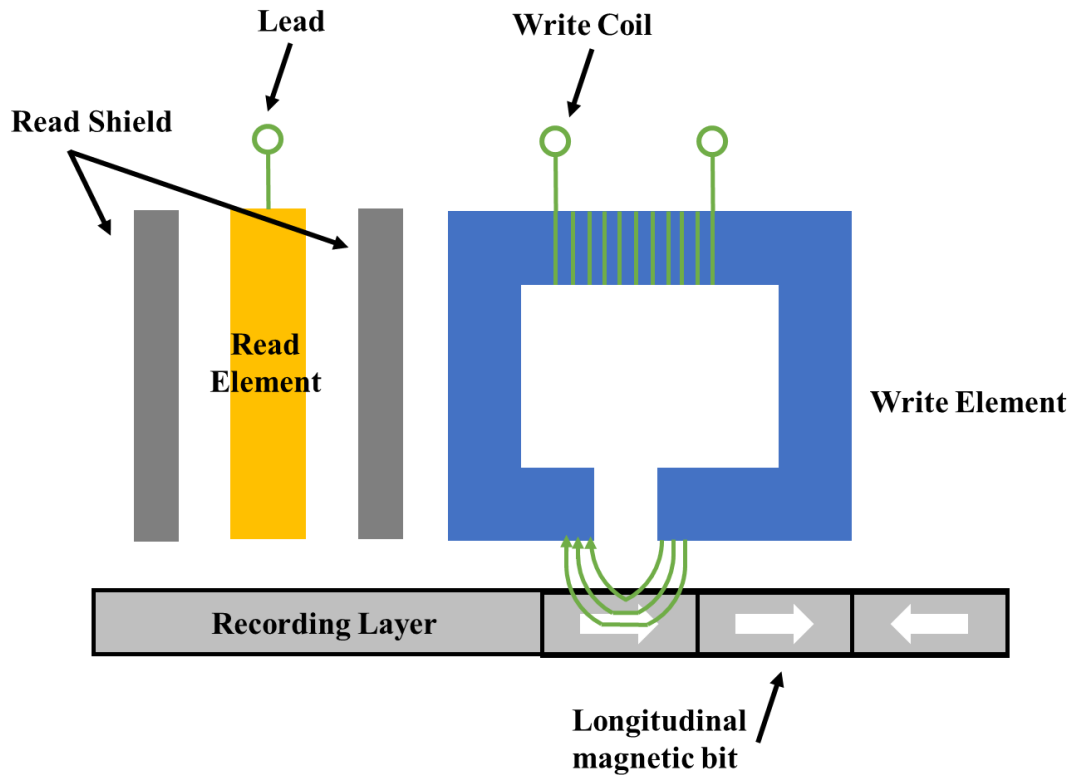


Figure 1.6 Schematic of the writing process in longitudinal magnetic recording (LMR)

The magnetic head in longitudinal magnetic recording consists of a write coil, a write element, read shields, and a read element (Figure 1.6). The write coil wraps around an inductive ferromagnetic element called “write element”. During the write process, data is treated as either “0” or “1”, i.e., as binary numbers. This is passed down to the write coil in the form of an alternating electrical current called the “write current”. As the current passes through the write coil, a magnetic field is created by the write element. The magnetic field is applied to the recording layer and “writes” the data in the form of magnetization *parallel* to the disk surface, thus the name *longitudinal magnetic*

recording. Longitudinal magnetic recording reached its super-paramagnetic limit in the early 2000's. The super-paramagnetic limit is reached when the stored magnetic bits can randomly flip even by a slight change in temperature [15-16]. To overcome this problem, *perpendicular magnetic recording (PMR)* has been used since 2005 [13, 17].

Perpendicular Magnetic Recording (PMR)

The main difference between longitudinal magnetic recording disks and perpendicular magnetic recording disks is the presence of a so-called “soft magnetic layer” as shown in Figure 1.7. The soft magnetic layer allows perpendicular magnetic recording to achieve high signal-to-noise ratio (SNR) with smaller magnetic grain sizes that those of longitudinal magnetic recording.

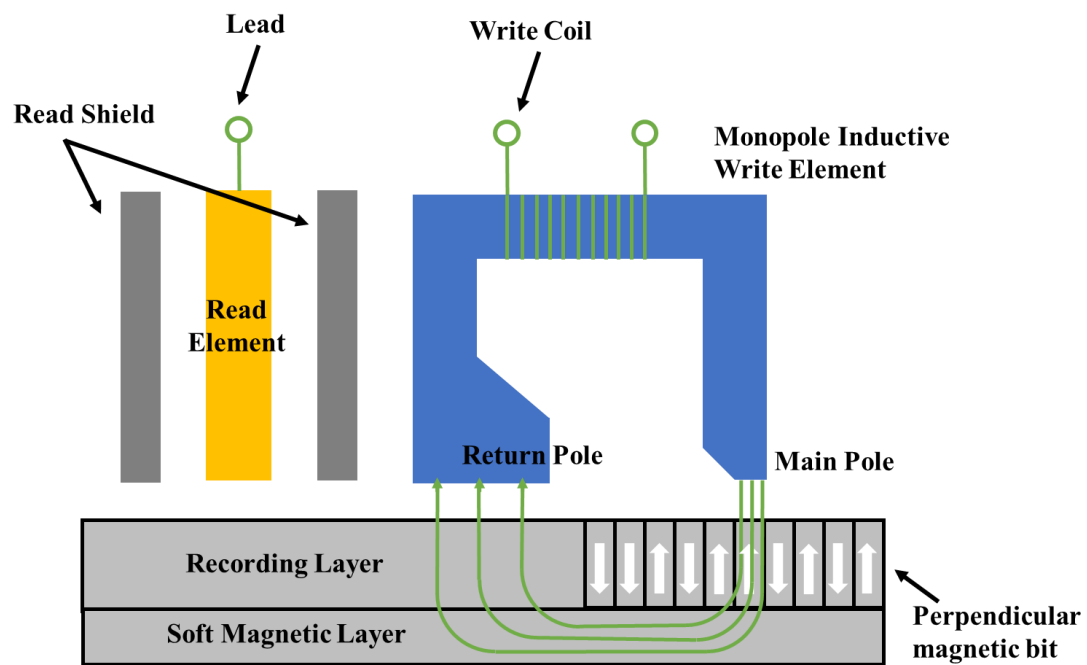


Figure 1.7 Schematic of the writing process in perpendicular magnetic recording (PMR)

The magnetic head in perpendicular magnetic recording consists of a write coil, a monopole inductive write element, read shields, and a read element (Figure 1.7). Data

is treated in the form of “0” or “1”, i.e., as binary numbers. The write coil wraps around the inductive ferromagnetic write element. The data passes the write coil in the form of alternating current. As the current flows through the write coil, the write element produces a magnetic field as shown in Figure 1.7. The magnetic field passes through both the recording layer and the soft magnetic layer. The perpendicular magnetic recording layer has two stable magnetization orientations *perpendicular* to the disk surface (Figure 1.7), thus the technology is called *perpendicular magnetic recording*. The soft magnetic layer is used to “close” the magnetic flux from the main pole to the return pole as shown in Figure 1.7. An ideal soft magnetic layer has infinite thickness and infinite permeability [13].

Heat Assisted Magnetic Recording (HAMR)

In order to achieve an areal density greater than 1 Tb/inch², very small magnetic grains (grain size < 6nm) are required. When the grain size is reduced, conventional perpendicular magnetic recording reaches its super-paramagnetic limit. The super-paramagnetic limit is reached when even small thermal fluctuations induce random flipping of the magnetization of magnetic domains. In order to avoid the super-paramagnetic limit, a magnetic layer with high coercivity is needed. To allow writing data on a high coercivity magnetic layer, heat assisted magnetic recording (HAMR) is researched as an alternative to perpendicular magnetic recording [18]. Figure 1.8 shows the schematic of heat assisted magnetic recording.

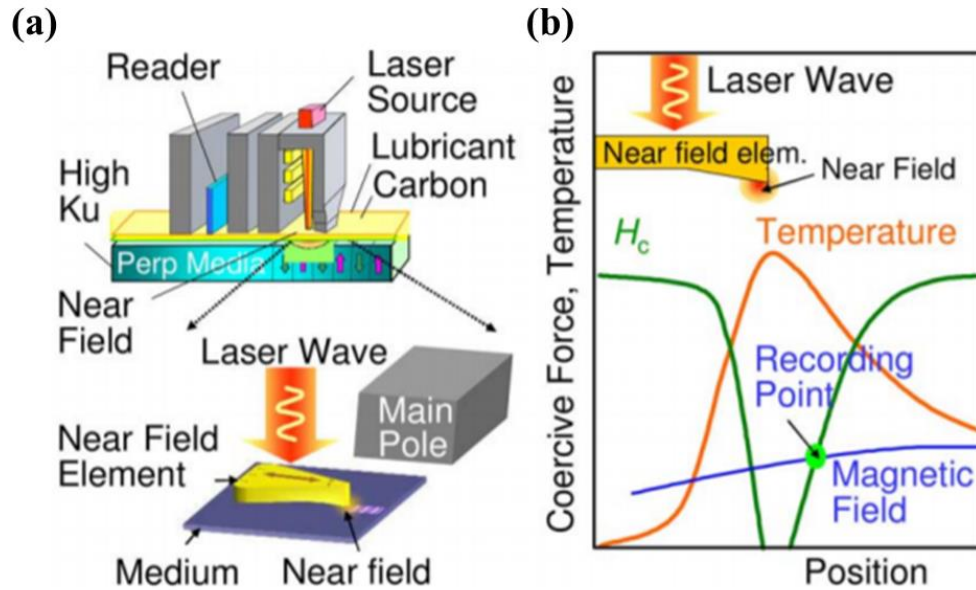


Figure 1.8 Schematic of (a) heat assisted magnetic recording head-disk interface and (b) the recording process in heat assisted magnetic recording [19]

In heat assisted magnetic recording, laser heating is used in conjunction with a high coercivity magnetic layer. The recording process proceeds as follows. First, a laser is focused on the disk surface using a waveguide and a near-field transducer (Figure 1.8(a)). The laser heats the irradiated spot to a temperature slightly below its Curie temperature, lowering the coercivity of the magnetic layer. Data is recorded at the low coercivity level and “frozen” during subsequent cooling down (Figure 1.8(b)).

Shiroish et al. [19] discussed the implementation and the associated challenges of heat assisted magnetic recording technology in hard disk drives, including efficient light delivery to the near-field optical transducer, the magnetic medium with high magnetic coercivity and thermal stability, and carbon overcoat and lubricant films that can withstand high thermal stress from laser irradiation. Also, due to high thermal cycling from high heating and cooling, the magnetic material needs high thermal

stability [20-21]. In addition, the cooling time of the magnetic medium must be shorter than 1 ns in order to ensure similar read/write speed as in conventional perpendicular magnetic recording hard disk drives [22]. Due to these technical difficulties, heat assisted magnetic recording hard disk drives are not yet commercially available.

1.3.3 Read Process

The read process of stored data on the recording layer is explained in Figure 1.9.

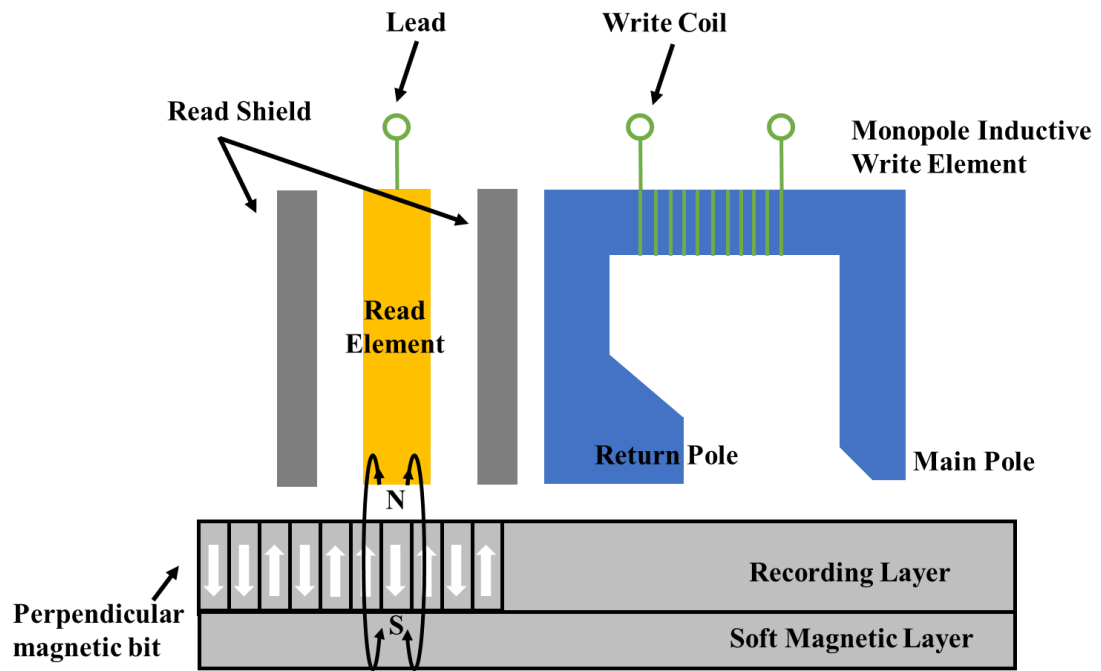


Figure 1.9 Schematic of the reading process in perpendicular magnetic recording (PMR)

Figure 1.9 shows a perpendicular magnetic recording head with read shields, a read element and a write element. As the magnetic head flies over the disk surface, the change in magnetic flux induced by the magnetic field from the recording layer (Figure 1.9) generates a voltage signal (read voltage), as given by Faraday's law [23], i.e.,

$$V = -N \frac{d\phi}{dt} \quad (1.1)$$

where V is the voltage generated, N is the number of windings of the coil, and $\frac{d\phi}{dt}$ is the change in the magnetic flux. The magnitude of the read voltage $e(t)$ depends on many parameters, as derived by Wallace [24-25]:

$$e(t) = 4\pi(10^{-8})N\alpha W \left(\frac{\mu}{\mu + 1} \right) Mv(1 - e^{-2\pi\delta/\lambda})G(\lambda) \cdot e^{-2\pi d/\lambda} \cos\left(\frac{2\pi vt}{\lambda}\right) \quad (1.2)$$

where e is the readback signal in volts, t is time, N is the number of coils, α is the head efficiency, W is the width of the read head, μ is core permeability, M is the residual magnetization of the magnetic material, v is the tangential velocity, δ is the thickness of the medium, λ is the wavelength of the signal read from the recorded data, $G(\lambda)$ is the gap factor, and d is the spacing between the read/write head and the recording medium. Equation 1.2 can be simplified as [25]:

$$E = F(M, \delta)e^{-2\pi d/\lambda} \quad (1.3)$$

where E represents the magnitude of $e(t)$ and F is a function of peak residual magnetization M and medium thickness δ . In order to obtain highest readback signal magnitude E , the optimum spacing d between the read/write head and the recording medium is *zero*. However, *zero* spacing indicates continuous contact between two surfaces, leading to high frictional heat, wear particle generation, and ultimately failure of a hard disk drive. For this reason, current hard disk drives have a spacing of a few nanometers between the read element and the magnetic layer in order to achieve high readback signal-to-noise ratio. Still, spacings on the order of nanometers leads to

tribological issues at the head-disk interface, including lubricant transfer from the disk to the head and hydrocarbon contamination.

1.3.4 Magnetoresistive (MR) Heads

In order to increase the storage capacity, the magnetic bit size has to be reduced. A reduction in bit size causes the read-back signal amplitude of an inductive read element to decrease, resulting in low signal-to-noise ratio (SNR). To increase the signal-to-noise ratio, magnetoresistive (MR) heads were introduced in the 1990s for the read process [26]. Magnetoresistive heads are based on the principle of the magnetoresistive effect, which states that the electrical resistance of a magnetoresistive material changes if a magnetic field is applied [27]. Three types of magnetoresistive heads have been used in hard disk drives [28]: anisotropic magnetoresistive (AMR) heads (1990), giant magnetoresistive (GMR) heads (1997), and tunneling magnetoresistive (TMR) heads (2004).

Anisotropic Magnetoresistive Effect

In 1856, Thomson [29] discovered the anisotropic magnetoresistive effect. The anisotropic magnetoresistive effect describes the dependence of electrical resistance of a material on the orientation of the applied magnetic field. The anisotropic magnetoresistive effect follows Equation 1.4 [30]:

$$\rho(\xi) = \rho_{\perp} \sin^2 \xi + \rho_{\parallel} \cos^2 \xi \quad (1.4)$$

where $\rho(\xi)$ is the resistivity of the material, $\rho_{\perp}$ and $\rho_{\parallel}$ are resistivities perpendicular and parallel, respectively, to the magnetic moment, and ξ is the angle between the electric current and the magnetic field. In general, $\rho_{\parallel}$ is greater than $\rho_{\perp}$ [30].

Equation 1.4 shows that the electrical resistance of the material $\rho(\xi)$ is maximum when the angle ξ between the electric current and the magnetic field is 0 or π and minimum when the angle ξ is $-\pi/2$ or $+\pi/2$.

Giant Magnetoresistive Effect

In 1988, Fert [31] and Grunberg [32] discovered the giant magnetoresistive effect. The giant magnetoresistive effect is a type of magnetoresistive effect in which a substantial change in resistivity is observed when a magnetic field is applied to a multilayer structure that is composed of alternating ferromagnetic and non-magnetic layers. Equation 1.5 [27] describes the giant magnetoresistive effect. In the equation, the magnitude of the giant magnetoresistive effect is denoted as $(\rho_{AP} - \rho_P)/\rho_P$, the so-called “magnetoresistive ratio”:

$$\frac{\rho_{AP} - \rho_P}{\rho_P} = \frac{(\rho_+ - \rho_-)^2}{4\rho_+\rho_-} = \frac{(1 - \alpha)^2}{4\alpha} \quad (1.5)$$

where ρ_P and ρ_{AP} are total electrical resistivities of the material in the direction parallel and antiparallel to the magnetization, ρ_+ and ρ_- are electrical resistivities for electron spins parallel and antiparallel, respectively, to the magnetization, and α is ρ_-/ρ_+ . From Equation 1.5, one could see that when $\alpha \ll 1$ or $\alpha \gg 1$, the magnitude of the giant magnetoresistive effect becomes large. Due to this effect, giant magnetoresistive heads were used in hard disk drives until replaced recently by tunneling magnetoresistive heads.

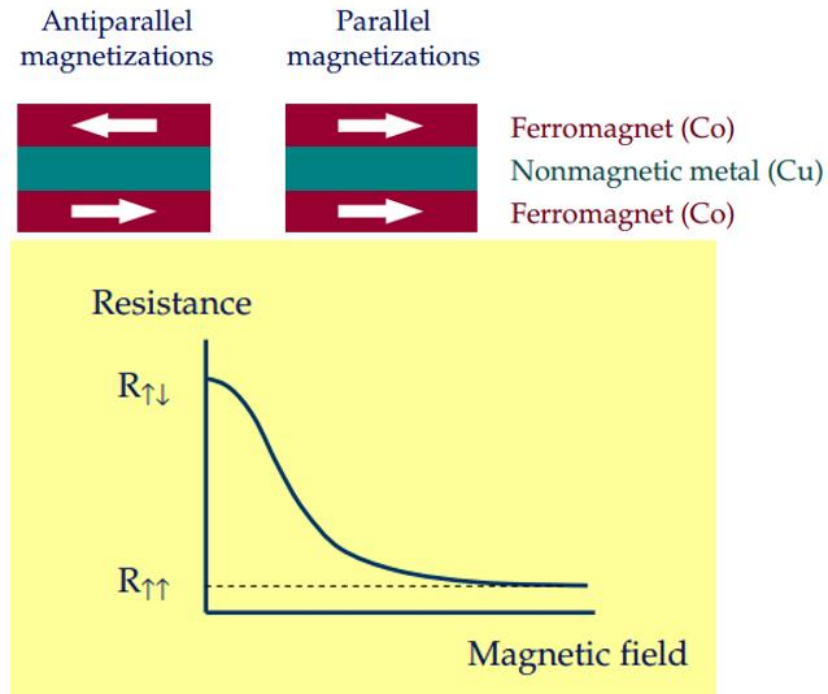


Figure 1.10 Resistance in material due to the giant magnetoresistive effect [33]

Figure 1.10 shows an example of the giant magnetoresistive effect in a multilayer structure composed of two cobalt layers (ferromagnetic) separated by one copper layer (non-magnetic).

Tunneling Magnetoresistive Effect

Since their introduction in 2004, tunneling magnetoresistive heads have been used in hard disk drives. The tunneling magnetoresistive effect was first observed in 1975 by Julliere [34]. It occurs in a multilayer structure composed of two ferromagnetic layers separated by a thin magnetic insulator, as shown in Figure 1.11. This structure is called a magnetic tunnel junction (MTJ). If the magnetic tunnel junction layer is thin enough (typically on the order of a few nanometers), electrons can “tunnel” from one ferromagnetic layer to the other.

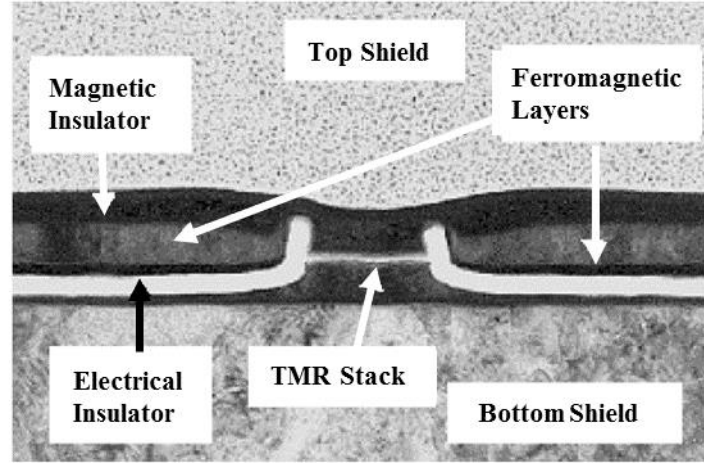


Figure 1.11 Transmission electron microscope (TEM) image of a tunneling magnetoresistive sensor in a hard disk drive and [35]

The tunneling magnetoresistance effect can be described using the magnetoresistive ratio [27]:

$$\frac{R_{AP} - R_P}{R_P} = \frac{2P_1P_2}{1 - P_1P_2} \quad (1.6)$$

where R_P and R_{AP} are the resistivities of the material in the case of parallel and antiparallel magnetization, respectively. P_1 and P_2 are spin polarization factors for the two ferromagnetic layers. When the two ferromagnetic layers spin perfectly polarized ($P_1 = P_2 = 1$), the resistance in the material would reach infinity in theory, i.e., the infinite tunneling magnetoresistive ratio can be achieved.

1.4 Tribology in Hard Disk Drives

In order to develop a reliable interface between a flying slider and a high-speed rotating disk surface, it is necessary to minimize friction and wear at the interface. Understanding of tribology, the study of friction, wear, and lubrication, is needed. In this section, a review of friction, wear, and lubrication is presented.

1.4.1 Friction

Friction is defined as resistance at the contact interface between materials that are in sliding or rolling motion [36-44]. In 1699, Amonton published his observations of friction, which are known as Amonton's laws of dry friction [38]:

1. Friction force is directly proportional to the normal load (Amonton's 1st Law)
2. Friction force is independent of apparent contact area (Amonton's 2nd Law)
3. Kinetic friction force is independent of the sliding velocity (Coulomb's Law)

Based on his laws, Amonton proposed the following equation for a solid body sliding against a contacting surface:

$$F_{friction} = \mu N_{force} \quad (1.7)$$

where $F_{friction}$ is the friction force, μ is the friction coefficient, and N_{force} is the applied normal force. In classical tribology, a number of theories exist that are used to describe frictional forces between two surfaces [36].

Interlocking Theory

The first mathematical approach to friction was suggested by Leonard Euler in the case of “dry” friction. He assumed a solid body on an inclined slope, considering both static and dynamic friction force. Figure 1.12 shows a schematic of Euler's model.

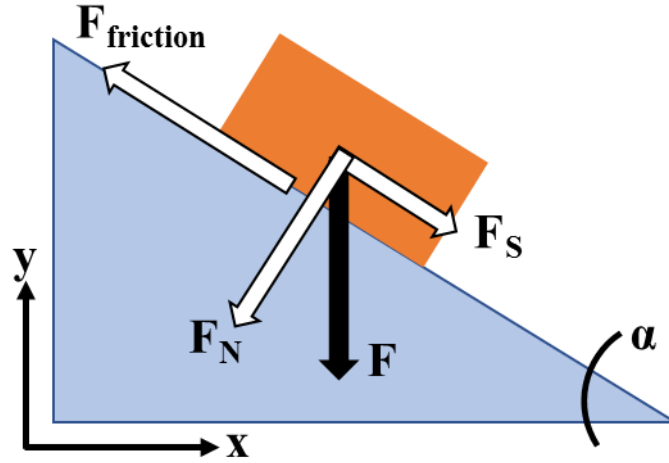


Figure 1.12 Solid body on an inclined slope

Euler first assumed the model in Figure 1.12 to be in static equilibrium. Then, the following relationships can be derived:

$$F_{friction} = F \sin(\alpha) - F_S \quad (1.8.1)$$

$$F_N = F \cos(\alpha) \quad (1.8.2)$$

where $F_{friction}$ is the friction force, F is the weight of the solid body, F_S is the component of F in the direction of the slope, F_N is the component of F normal to the inclined slope, and α is the angle of the inclination. Then, the friction coefficient μ can be derived as follows:

$$\mu = \frac{F_{friction}}{F_N} = \tan(\alpha) - \frac{F_S}{F \cos(\alpha)} \quad (1.8.3)$$

where α is greater than 0 and less than 90°. When $F_S = 0$, Equation (1.8.3) gives the static friction coefficient μ_{static} , and when $F_S \neq 0$, Equation (1.8.3) gives the dynamic friction coefficient $\mu_{dynamic}$.

Rolling Friction

Rolling friction occurs due to energy dissipation at the rolling contact interface [42]. Dissipated energy is associated with

1. Micro-slip at the interface
2. Inelastic deformation
3. Surface roughness

Coulomb proposed that rolling friction $F_{friction}$ in the case of a cylinder on a flat surface is proportional to the normal load P and inversely proportional to the radius of the cylinder, as shown in Equation (1.9.1)

$$F_{friction} \propto \frac{P}{R} \quad (1.9.1)$$

In 1840, Dupuit proposed that material after rolling contact would plastically deform. He argued that the friction force would be inversely proportional to the square root of the radius of the cylinder, as shown in Equation (1.9.2).

$$F_{friction} \propto \frac{P}{\sqrt{R}} \quad (1.9.2)$$

In 1955, Tabor [43] experimentally confirmed Dupuit's argument and observed the friction force to have the following relationship.

$$F_{friction} \propto \frac{P^{3/2}}{\sqrt{R}} \quad (1.9.3)$$

Inelastic Adhesion

In 1954, Bowden and Tabor realized that friction behaved differently at the macroscopic scale than at the microscopic scale. Amonton's law states that friction is independent of contact area, which provides the macroscopic scale of friction. However,

to further understand friction, one needs to look at this also at the microscopic scale. Figure 1.13 shows both the macroscopic and microscopic scales of contacting solid bodies.

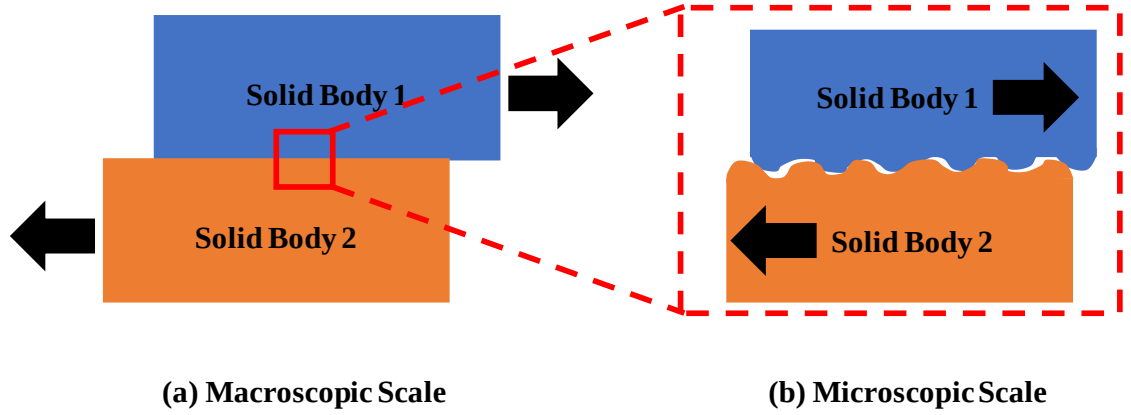


Figure 1.13 Schematic of two sliding bodies at (a) macroscopic scale and (b) microscopic scale

Bowden and Tabor realized that the contact area shown in Figure 1.13(a) is the *apparent* contact area. The *real* contact interface would be closer to what is shown in Figure 1.13(b). This yields the conclusion that the total real contact area is the sum of all individual asperity contact areas:

$$A_r = \sum_i a_i \quad (1.10.1)$$

where A_r is the total real contact area and a_i is the contact area of individual asperities. By assuming that the actual contact radius r is much smaller than the asperity radius R , the Hertz theory can be used to determine the contact radius:

$$r^3 = \frac{3PR}{4E^*} ; E^* = \left(\frac{1 - \nu_1^2}{E_1} + \frac{1 - \nu_2^2}{E_2} \right) ; r \ll R \quad (1.10.2)$$

where P is the contact load, E^* is the equivalent elastic modulus, E_1 and ν_1 are the elastic modulus and Poisson ratio, respectively, for material 1, and E_2 and ν_2 are the elastic

modulus and Poisson ratio, respectively, for material 2. Assuming that the two surfaces are in a sliding motion, then the kinetic friction coefficient can be determined to be a function of interfacial stress σ , real contact area A_r , and mean contact pressure p_m . Bowden and Tabor proposed that sliding motion occurs when the following two conditions are met:

1. Plastic deformation of the asperities, corresponding to $p_m = 2.8Y$ (Y is the yield pressure)
2. Interfacial stress σ must overcome the shear strength of the softer material: $\sigma = \sigma_{crit}$

The above conditions yield the kinetic friction coefficient to be as shown in Equation (1.10.3).

$$\mu = \frac{F_{friction}}{P} = \frac{\sigma_{crit} A_r}{p_m A_r} \approx \frac{\sigma_{crit}}{2.8Y} \quad (1.10.3)$$

Archard's Elastic Friction Model

Bowden and Tabor (1954) assumed that the asperities in sliding motion undergo plastic deformation. However, Archard [45] argued that sliding motion could occur in the presence of elastic deformation as well. By modifying the equation of Bowden and Tabor, Archard proposed a mathematical model of friction assuming elastic deformation:

$$F_{friction} = \tau \pi \left(\frac{3R}{4E^*} \right)^{2/3} P^{2/3} \quad (1.11)$$

where $F_{friction}$ is the friction force, τ is the shear stress at the contact interface, R is the asperity radius, E^* is the equivalent elastic modulus as shown in Equation (1.10.3), and P is the contact load.

1.4.2 Wear

In his book [46], Rabinowicz defined wear as “the removal of material from solid surfaces as a result of mechanical action or chemical reaction”. Some common types of wear include adhesive wear, abrasive wear, corrosive wear and surface fatigue and more. In this section, two types of wear are discussed: adhesive and abrasive wear.

Adhesive Wear

Adhesive wear is the most commonly observed type of wear [46]. It occurs when the surface of a solid is normally or tangentially loaded onto another surface. When loaded, atoms in both surfaces will experience attractive force toward the other surface. This is commonly referred as adhesive force. Material failure during loading will result in particle generation. When wear particles are generated, they can transfer to the adjacent surface [47].

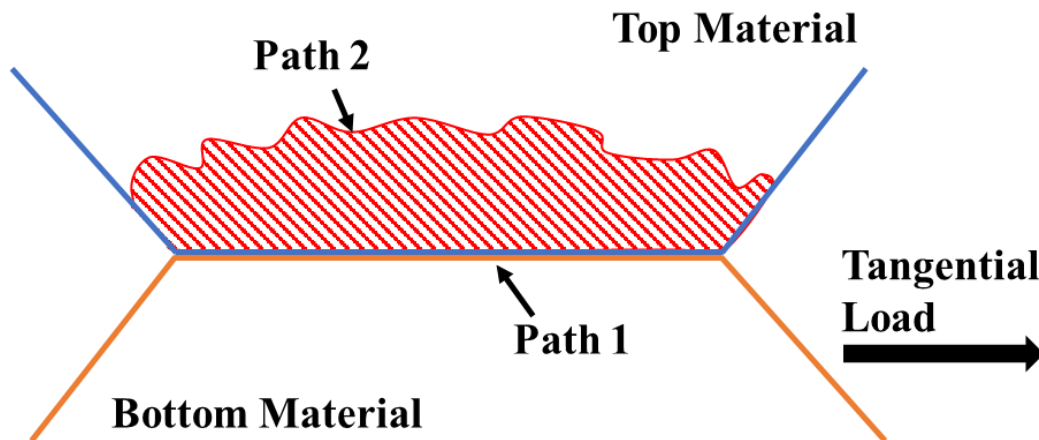


Figure 1.14 Schematic illustrating adhesive wear at the contact interface with tangential loading on the bottom material [46]

Figure 1.14 shows a junction that is being sheared. When the shear stress at the junction is greater than the material strength of the top material, adhesive wear will

occur along Path 2. The shaded part of the top material will fail, leading to particle generation and possibly material transfer from the top to the bottom. Greenwood and Tabor (1955, 1957) [48-49] showed that when the plane of the junction (Path 1) is not parallel to the direction of the tangential load, then material transfer would more likely to occur. Several theories concerning material wear along Path 2 have been developed, including [46]:

1. IBM fatigue theory [50-51]: This theory states that for cyclic sliding motion, materials at the junction undergo fatigue, eventually leading to fatigue failure and material transfer.
2. Statistical theory of wear [52]: This theory assumes asperity contact at the junction interface and that stress in the material has a statistical distribution. Wear particle generation occurs when the material strength along Path 2 is lower than along Path 1.
3. Delamination theory of wear [53]: During sliding contact, a crack parallel to the surface will form. Over time, the crack will grow and lead to material failure.
4. The approach of Komvopoulos, Saka, and Suh [54]: The theory discusses the detrimental consequences that can occur when Path 1 is not parallel to the direction of the sliding motion.

To quantify adhesive wear, the Holm-Archard equation is commonly used [55-56].

$$W = \frac{kNL}{H} \quad (1.12)$$

where W is the wear volume on the softer material, H is the hardness, N is the normal load, L is the sliding distance, and k is the dimensionless wear coefficient.

Abrasive Wear

Abrasive wear occurs when a rough surface slides against a softer surface (two-body mode of abrasion) [57] or when rough, abrasive particles are present between two sliding surfaces (three-body mode of abrasion) [58]. The two modes of abrasive wear are illustrated in Figure 1.15.

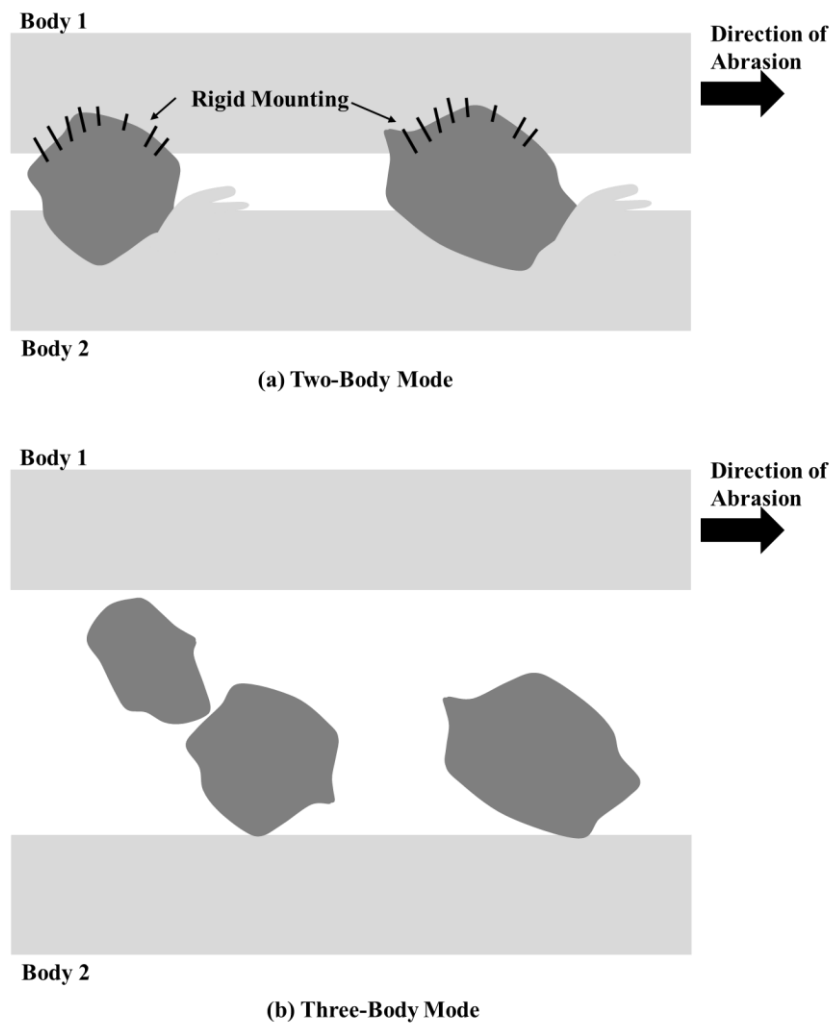


Figure 1.15 Two modes of abrasive wear showing (a) two-body mode and (b) three-body mode [59]

As shown in Figure 1.15(a), two-body abrasive wear occurs when the hard, sliding body has a rough surface. In other words, if the contact interface is smooth, abrasive wear would not occur [46]. Similarly, three-body abrasive wear occurs when particles between the two sliding bodies (Figure 1.15) are harder than the contacting surfaces [46].

To quantify abrasive wear, a hard, conical surface is assumed as shown in Figure 1.16. As the cone moves from left to right, some volume of material will be removed. Abrasive wear volume can be defined as the following equation [46]:

$$V = \frac{Px \tan \theta}{\pi H} \quad (1.13)$$

where V is the wear volume, P is the load, H is the hardness of the softer material, and x is the distance traveled by the cone. For both abrasive and adhesive wear, a simple form of mathematical model is considered:

$$V = \frac{k_{abr}Px}{H} \quad (1.14)$$

where k_{abr} is the abrasive wear coefficient that physically represents the geometry of the conical asperity divided by π [46]. Abrasive wear coefficients are found for various material contacts for both two-body and three-body modes [60-67].

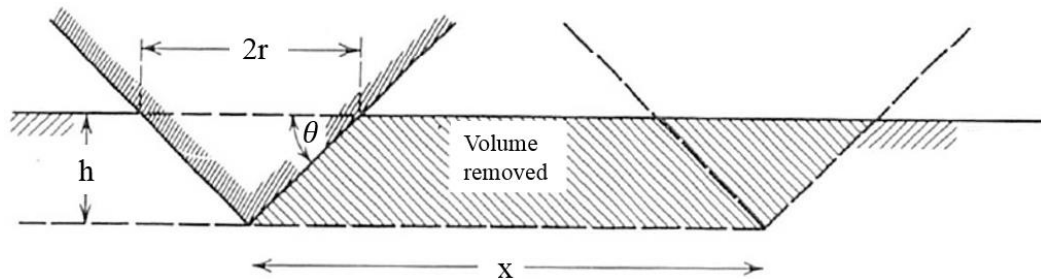


Figure 1.16 Schematic illustrating abrasive wear (in courtesy of [46])

Abrasive wear was originally considered to be due to *cutting* of material, similar to machining. However, microscopic studies revealed that there are, in general, four types of abrasive wear: cutting, fracturing, repeated ploughing, and pulling grains out of material (Figure. 1.17) [59].

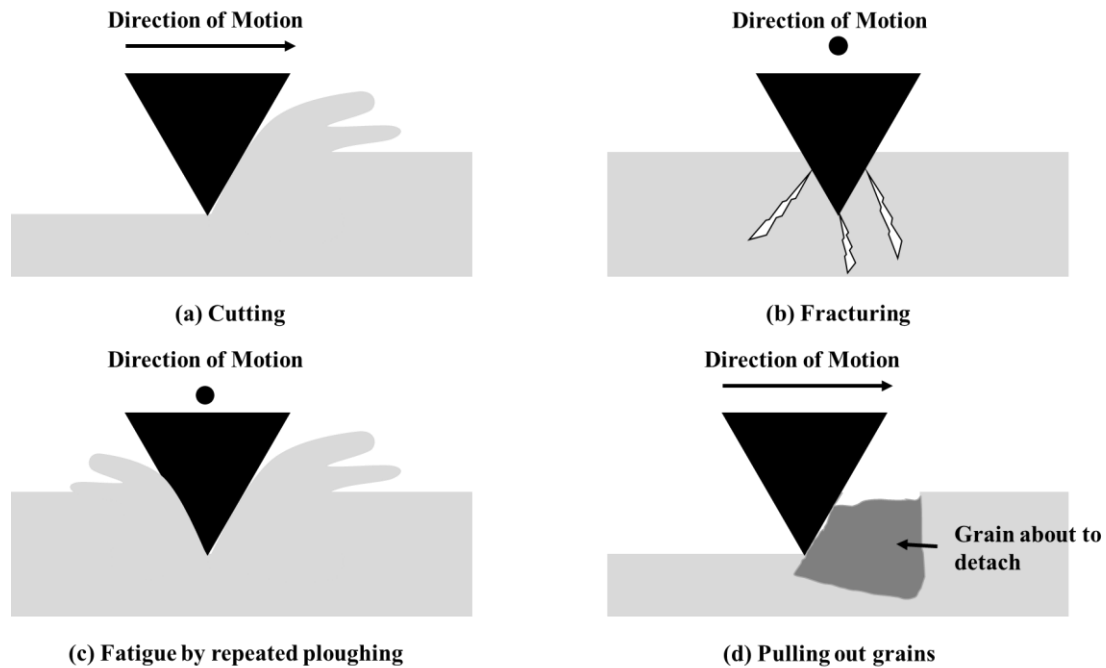


Figure 1.17 Mechanism behind abrasive wear by (a) cutting, (b) fracturing, (c) ploughing and (d) pulling out grains (after [59])

The most common mechanism of abrasive wear is micro-cutting as illustrated in Figure 1.17(a). If a hard, conical body abrades against a softer surface, some part of the latter is removed, forming material debris. The second mechanism of abrasive wear is observed when a brittle material (such as glass, ceramic, etc.) is abraded. Instead of material removal, formation of cracks can be observed as shown in Figure 1.17(b). Figure 1.17(c) displays material failure due to fatigue from repeated abrasion. This type of wear occurs when the worn material is ductile, such as metal alloys. Lastly, when

brittle materials are abraded by hard material, grains can be pulled out since grain boundaries are observed to be weak in brittle materials such as ceramics (Figure 1.17(d)).

1.4.3 Surface Interactions

In order to understand how two surfaces interact, it is essential to know how to characterize surfaces and how two rough surfaces contact each other. This section describes characterization of surface roughness, surface contact, and surface energy.

Surface Roughness

All surfaces, regardless of how smooth they are on a macro-scale, are rough on the nano-scale. Surface roughness on nano-scale dominates tribology of contact surfaces. Figure 1.18 shows a schematic of a surface profile.

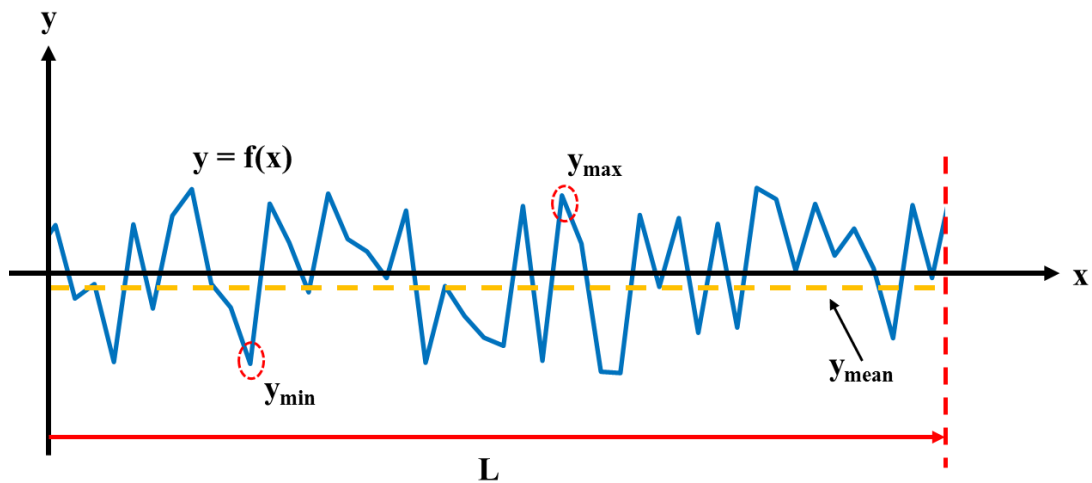


Figure 1.18 Schematic of “exaggerated” surface profile with length L

Figure 1.18 shows a surface profile with length L where y represents height as a function of x . There exist several ways to characterize the surface profile such as the one shown in Figure 1.18 [68]. Equation 1.15 shows the *peak-to-valley distance* y_p :

$$y_p = |y_{max} - y_{min}| \quad (1.15)$$

where y_{max} and y_{min} represent the maximum and the minimum height, respectively. The mean value of surface roughness $y(x)$ is defined as:

$$y_{mean} = \frac{1}{L} \int_0^L y dx \quad (1.16.1)$$

$$y_{mean} = \frac{1}{n} \sum_{i=1}^n y \quad (1.16.2)$$

where L is the length of the surface profile and n is the number of data points. Then, the arithmetic mean roughness R_a (first moment of height distribution) is given by:

$$R_a = \frac{1}{L} \int_0^L |y - y_{mean}| dx \quad (1.17.1)$$

$$R_a = \frac{1}{n} \sum_{i=1}^n |y_i - y_{mean}| \quad (1.17.2)$$

where Equation 1.17.1 denotes the analytical form while Equation 1.17.2 denotes the digital form. The surface roughness can be also evaluated by looking at the root-mean square (RMS) R_q (second moment of height distribution) given by:

$$R_q = \left(\frac{1}{L} \int_0^L (y - y_{mean})^2 dx \right)^{1/2} \quad (1.18.1)$$

$$R_q = \left(\frac{1}{n} \sum_{i=1}^n (y_i - y_{mean})^2 \right)^{1/2} \quad (1.18.2)$$

Both R_a and R_q give an idea of how rough a surface is but it has been known that two difference surfaces can have the same R_a and R_q . In order to characterize surface

roughness accurately, two more parameters need to be obtained, namely skewness (third moment of height distribution) and kurtosis (fourth moment of height distribution) as:

$$Sk = \frac{1}{R_q^3} \frac{1}{L} \int_0^L (y - y_{mean})^3 dx \quad , \quad Sk = \frac{1}{nR_q^3} \sum_{i=1}^n (y_i - y_{mean})^3 \quad (1.19)$$

$$K = \frac{1}{R_q^4} \frac{1}{L} \int_0^L (y - y_{mean})^4 dx \quad , \quad K = \frac{1}{nR_q^4} \sum_{i=1}^n (y_i - y_{mean})^4 \quad (1.20)$$

where R_q is the root-mean square value evaluated using Equation 1.18. Skewness corresponds to what kind of asperities make up the surface, e.g. negative skewness indicates that a surface consists mostly of valleys while positive skewness indicates that a surface consists mostly of peaks. Kurtosis is a measurement of sharpness of surface roughness.

Surface Contact

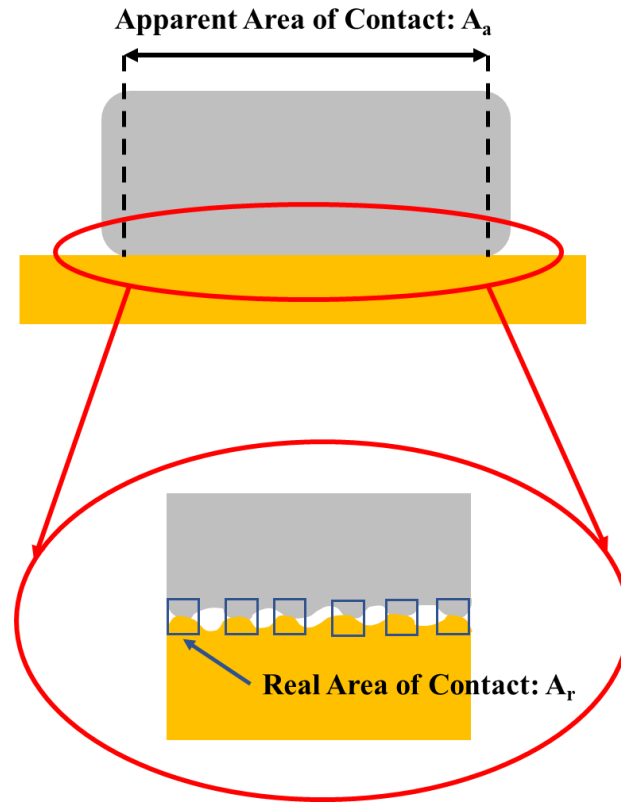


Figure 1.19 Schematic showing the difference between the apparent area of contact A_a and the real area of contact A_r .

Figure 1.19 shows the apparent area of contact A_a and the real area of contact A_r . The apparent area of contact denotes an area that two surfaces “seem” to make contact on the macro-scale. However, when investigated on a smaller scale, the real contacts are made by asperities of the two surfaces. As the load is carried on the asperities, it is important to consider asperity contact when studying surface contact.

The Hertzian contact model [69] describes an asperity contact assuming that two elastic spheres are in contact. The model was developed by Hertz in 1881. He assumed

that the two spheres in contact are deformed elastically and that the real area of contact is much smaller than the actual size of the spheres. Figure 1.20 illustrates the Hertzian contact model.

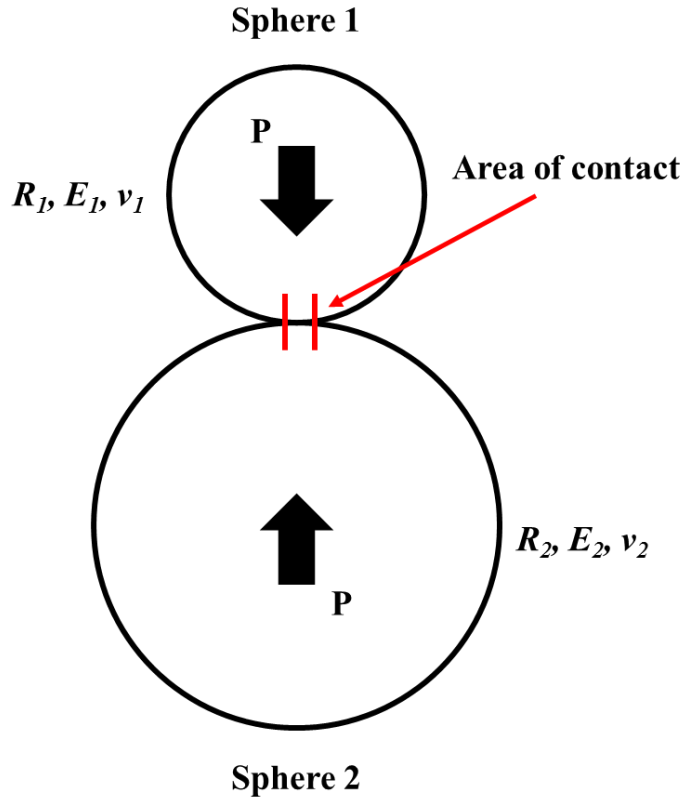


Figure 1.20 Schematic of two spheres in contact with each other

Figure 1.20 shows two spheres loaded onto each other with the area of contact much smaller than the size of the spheres. R_1 , E_1 , and ν_1 denote the radius, the elastic modulus, and the Poisson's ratio, respectively, of *Sphere 1*, while R_2 , E_2 , and ν_2 denote the radius, the elastic modulus, and the Poisson's ratio of *Sphere 2*, respectively [69].

The radius of the contact area is given by:

$$a = \left(\frac{3PR^*}{4E^*} \right)^{1/3} \quad (1.21)$$

where P is the load on the spheres, R^* is the effective radius, and E^* is the effective elastic modulus. R^* and E^* are defined as:

$$\frac{1}{R^*} = \frac{1}{R_1} + \frac{1}{R_2} \quad (1.22)$$

$$\frac{1}{E^*} = \frac{1 - \nu_1^2}{E_1} + \frac{1 - \nu_2^2}{E_2} \quad (1.23)$$

Then, the contact interference and the maximum pressure between two spheres are given by:

$$\delta = \left(\frac{9p^2}{16R^*E^{*2}} \right)^{1/3} \quad (1.24)$$

$$p_{max} = \left(\frac{6PE^{*2}}{\pi^3 R^{*2}} \right)^{1/3} \quad (1.25)$$

where δ is the contact interference between two spheres and p_{max} is the maximum pressure.

The Hertzian contact model illustrates an asperity contact, but does not provide a model for surface-to-surface contact with consideration of surface roughness. In 1966, Greenwood and Williamson developed a contact model that describes a contact between two rough surfaces, also known as *Greenwood-Williamson contact model* [70]. Figure 1.21 illustrates contact between a perfectly flat surface and a rough surface.

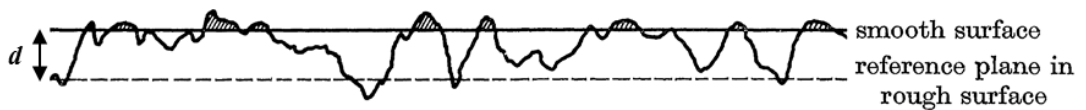


Figure 1.21 Schematic of a smooth surface contacting a rough surface [70]

The Greenwood-Williamson contact model assumes that all asperities are spherical near their summits with a radius of β and randomly distributed heights, following a Gaussian distribution. The probability of height distribution is given by [70]:

$$\text{probability}(z > d) = \int_d^{\infty} \phi(z) dz \quad (1.26)$$

where z is the height of asperities, d is the distance between the rough surface and the smooth surface, and $\phi(z)$ is a Gaussian distribution. If there are N asperities on the rough surface, the expected number of contacts between two surfaces is given by:

$$n = N \int_d^{\infty} \phi(z) dz \quad (1.27)$$

where n is the expected number of contacts and N is the total number of asperities. The mean contact area between two surfaces is given by:

$$A_{mean} = \pi\beta \int_d^{\infty} (z - d)\phi(z) dz \quad (1.28)$$

where β is the radius of the asperities. The expected total area of contact is given by:

$$A_{total} = NA_{mean} = N\pi\beta \int_d^{\infty} (z - d)\phi(z) dz \quad (1.29)$$

Then, the expected total contact load is:

$$P = \frac{4}{3}NE^*\beta^{\frac{1}{2}} \int_d^{\infty} (z - d)^{\frac{3}{2}}\phi(z) dz \quad (1.30)$$

where E^* is the effective elastic modulus shown in Equation 1.23.

Surface Energy

Surface energy and intermolecular forces are important parameters for characterizing the tribological performance of a material. In hard disk drives, the recording disk is coated with a thin film of diamond-like carbon and a thin film of perfluoropolyether lubricants. In order to determine the tribological performance of a hard disk, it is essential to measure surface energy.

Surface energy of a thin-film coated disk is governed by a disjoining pressure that is given by [71]:

$$\Pi = \Pi_d + \Pi_p = -\frac{d\gamma_s^d}{dh} - \frac{d\gamma_s^p}{dh} \quad (1.31)$$

where Π is the total disjoining pressure of the surface, Π_d and Π_p are dispersive and polar components of the disjoining pressure, respectively, $\frac{d\gamma_s^d}{dh}$ is the change in dispersive surface energy with respect to thin film thickness, and $\frac{d\gamma_s^p}{dh}$ is the change in polar surface energy with respect to thin film thickness. Then, the total surface energy can be determined by:

$$\gamma = \gamma_s^d + \gamma_s^p \quad (1.32)$$

where γ is the total surface energy, γ_s^d is the dispersive component of the surface energy, and γ_s^p is the polar component of the surface energy. The dispersive surface energy γ_s^d results from van der Waals interaction, while the polar surface energy γ_s^p results from Lewis acid-base interactions [72]. Lewis acid-base interactions describe an interaction between an electron-pair acceptor (Lewis acid) and an electron-pair donor (Lewis base).

One common method for measuring surface energy is contact angle measurement. Figure 2 shows a schematic of a liquid droplet on a hard disk [73].

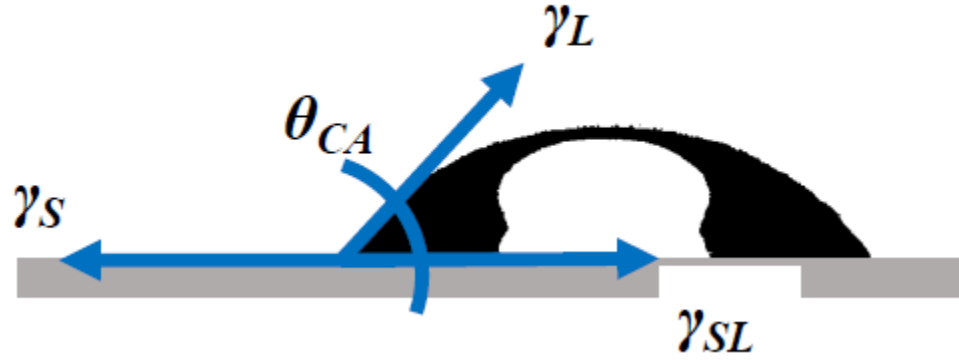


Figure 1.22 Schematic of a liquid droplet on a solid surface

Figure 1.22 shows a liquid droplet on a solid surface where γ_S is the surface energy of the solid surface, γ_L is the surface energy of the liquid droplet, γ_{SL} is the surface energy of the solid-liquid interface, and θ_{CA} is the contact angle between the liquid droplet and the solid surface. The relationship among the four parameters is given by Young's equation:

$$\gamma_{SL} = \gamma_S - \gamma_L \cos(\theta_{CA}) \quad (1.33)$$

In order to measure the surface energy of the solid surface γ_S , the “Owens, Wendt, Rabel, and Kaelbe” (OWRK) method can be used [74]. As shown in Equation 1.32, the total surface energy is composed of the dispersive and the polar components. The OWRK method uses pure hexadecane ($C_{16}H_{34}$) that is purely dispersive and distilled water that is both dispersive and polar. Pure hexadecane has purely dispersive surface energy γ_S^d of 27.5 dynes/cm. Distilled water has dispersive surface energy γ_S^d of

51.0 dynes/cm and polar surface energy γ_s^p of 21.8 dynes/cm. The interfacial surface energy γ_{SL} can be approximated by the following equation [75]:

$$\gamma_{SL} = \gamma_s + \gamma_L - 2\sqrt{\gamma_s^d \gamma_L^d} - 2\sqrt{\gamma_s^p \gamma_L^p} \quad (1.34)$$

Then, Equation 1.33 and 1.34 can be used to determine the surface energy of the solid surface. To determine the dispersive component of the surface energy γ_s^d , the following equation is used in conjunction with a pure hexadecane droplet:

$$\gamma_s^d = \frac{\gamma_L^d (1 + \cos \theta_{CA}^{hexadecane})^2}{4} \quad (1.35)$$

where γ_s^d is the dispersive component of the solid surface, γ_L^d is the surface energy of the hexadecane droplet, and $\theta_{CA}^{hexadecane}$ is the contact angle between the solid surface and the hexadecane droplet. Then, the polar component of the surface energy γ_s^p is determined by using the following equation in conjunction with a droplet of distilled water:

$$\gamma_s^p = \frac{\left(\gamma_L \cos \theta_{CA}^{water} + \gamma_L - 2\sqrt{\gamma_s^d \gamma_L^d} \right)^2}{4\gamma_L^p} \quad (1.36)$$

where γ_s^p is the polar component of the surface energy, γ_L is the surface energy of the distilled water droplet, γ_L^p is the polar component of the surface energy for the distilled water droplet, γ_s^d is the dispersive component of the surface energy determined using Equation 1.35, and γ_L^d is the dispersive component of the surface energy for the distilled water droplet. Then, the surface energy for the solid surface can be obtained.

1.4.4 Lubrication

General Theory of Lubrication

Lubricants are used at the interface between two surfaces in order to reduce friction and decrease generation of wear particles. A lubricant is any substance, fluid or solid, that is used to reduce friction and wear at the contact interface [76]. Lubricants can be in the form of gas (such as air), liquid (such as mineral oils, esters, etc.), and solid (such as Teflon or polytetrafluoroethylene). The Stribeck curve (Figure 1.23) shows how lubrication between two solid surfaces affects the friction coefficient based on the lubrication parameters of the lubricant viscosity η , sliding velocity V , and normal load P [77].

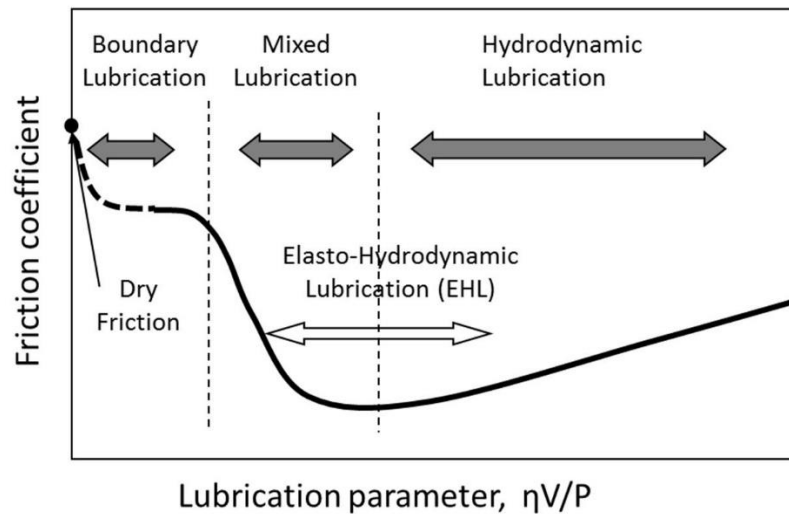


Figure 1.23 The Stribeck curve showing the friction coefficient to be a function of the lubrication parameter $\frac{\eta V}{P}$ [77]

As illustrated in Figure 1.23, lubrication can be divided into three regimes: boundary lubrication, mixed lubrication, and hydrodynamic lubrication. The Stribeck curve shows that dry friction, or dry contact, has the highest friction coefficient. Figure

1.24 shows a schematic of boundary lubrication, mixed lubrication, and hydrodynamic lubrication.

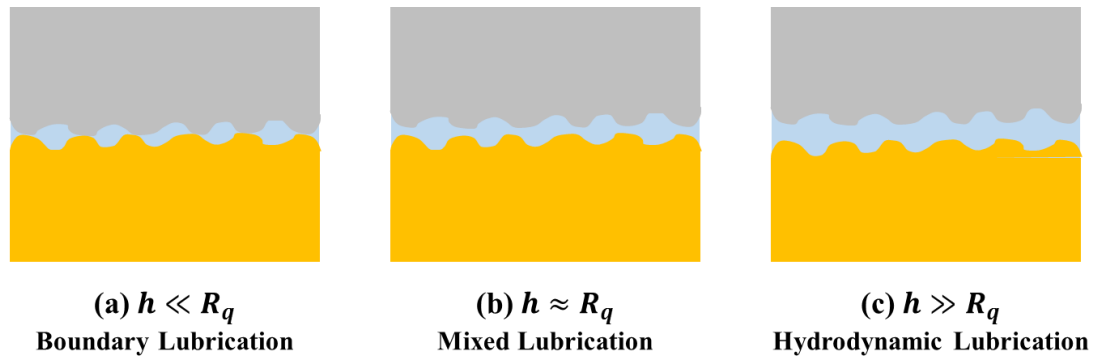


Figure 1.24 Schematic of (a) boundary lubrication, (b) mixed lubrication and (c) hydrodynamic lubrication

In boundary lubrication (Figure 1.24(a)), the spacing h between two surfaces is much smaller than the root-mean square (RMS) surface roughness. In the case of boundary lubrication, friction is reduced as lubricants reduce shear stress and wear particle generation. With an increase in lubrication, the contact interface experiences mixed lubrication (Figure 1.24(b)), in which the spacing h is similar to the RMS surface roughness. In this case, friction is further reduced as the real contact area is decreased compared to the case of boundary lubrication. In hydrodynamic lubrication (Figure 1.24(c)), the spacing h is much larger than the RMS surface roughness. In hydrodynamic lubrication, a decrease in friction coefficient (Figure 1.23) as a function of lubrication parameter is observed as the load is carried fully by the lubricant film. However, with an increase in fluid viscosity and sliding velocity, friction coefficient increases as the viscous resistance in the lubricant film increases (Figure 1.23) [77].

Basic Chemistry of Liquid Lubricants

Lubricants, in any form, are used to reduce friction and wear. However, liquid lubricants have special physical and chemical properties [77]. They can provide cooling between sliding surfaces and can be mixed with other chemicals to meet desired physical properties such as viscosity and corrosion resistance. Liquid lubricants can be divided into two types: organic and synthetic lubricants. In order to understand them, it is necessary to study lubricants from a basic chemistry point of view [76].

One type of liquid lubricants are *hydrocarbons*, organic compounds composed of carbon and hydrogen in covalent bonds. The simplest form of a hydrocarbon is methane with the chemical formula of CH₄. Carbon atoms can easily form bonds. Hydrocarbons linked in a straight chain are commonly referred as alkanes or paraffins. Table 1.1 shows straight hydrocarbons.

Table 1.1 Straight hydrocarbons – alkanes [76, 78]

Number of carbon atoms	Name	Chemical Formula	Boiling Point °C	Specific Gravity
1	Methane	CH ₄	-161.5	_____
2	Ethane	C ₂ H ₆	-88.3	_____
3	Propane	C ₃ H ₈	-44.5	_____
4	Butane	C ₄ H ₁₀	-0.5	_____
5	Pentane	C ₅ H ₁₂	36.2	0.626
6	Hexane	C ₆ H ₁₄	69.0	0.660
7	Heptane	C ₇ H ₁₆	98.4	0.684
8	Octane	C ₈ H ₁₈	125.8	0.704
9	Nonane	C ₉ H ₂₀	150.6	0.718
10	Decane	C ₁₀ H ₂₂	174.0	0.730

Due to its valency of 4, carbon can form single bonds, double bonds, and triple bonds. Figure 1.25 shows methane (CH₄), ethylene (C₂H₄), and acetylene (C₂H₂), which are the simplest single-bond hydrocarbons, double-bond hydrocarbons, and triple-bond hydrocarbons, respectively.

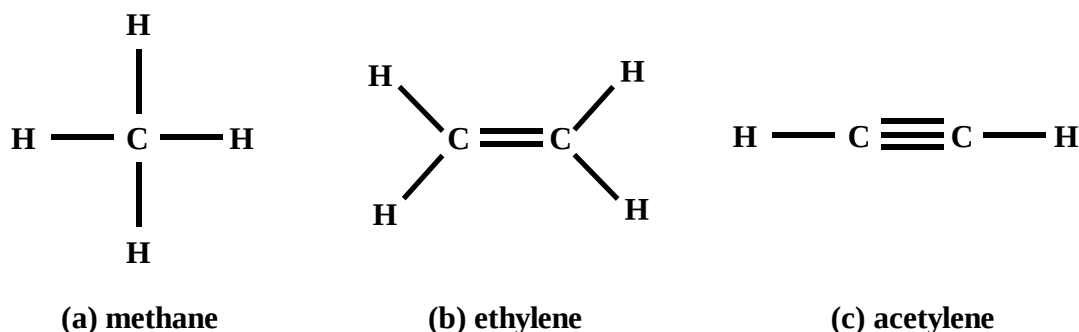


Figure 1.25 Chemical diagrams for (a) methane, (b) ethylene, and (c) acetylene

Based on the different bonds, hydrocarbons can be categorized into the following homologous series, as shown in Table 1.2.

Table 1.2 Homologous series of hydrocarbons [76, 79]

Name	Chemical Formula	Sample Hydrocarbon
Alkane or paraffin	C_nH_{2n+2}	CH_4
Olefin or alkene	C_nH_{2n}	C_2H_4
Acetylene or alkyne	C_nH_{2n-2}	C_2H_2
Cycloparaffin or naphthene	C_nH_{2n}	C_5H_{10}
Aromatic	C_nH_{2n-6}	C_6H_6

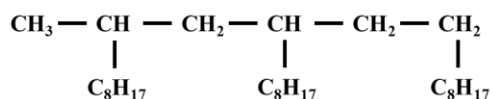
When one hydrogen atom in methane is replaced with the hydroxyl group OH, it becomes methyl alcohol (methanol: CH_3OH). In a similar manner, ethane can also be modified to become ethyl alcohol (ethanol: C_2H_5OH) when one hydrogen atom is replaced with the hydroxy group OH. The family of alcohol compounds has the chemical structure of $C_nH_{2n+1}OH$, i.e., alcohols have backbone atoms of carbon and the functional groups of OH. The hydroxyl group is known to be highly polar. High polarity influences the physical and chemical properties of the attached molecules, resulting in

strong polar attraction toward molecules with opposite polarity [80]. In hard disk drives, many of the popular lubricants are terminated with the hydroxyl group OH to increase bonding to the disk surface that has a carbon overcoat with functional groups of opposite polarity to the hydroxyl group [81].

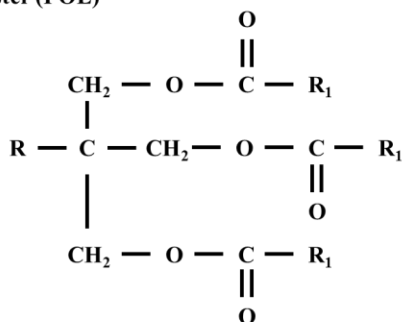
When the methyl (CH_3) end group for a paraffin is replaced with a carboxyl (CO_2H) group, it becomes a fatty acid [81]. For example, when an ethane (C_2H_6) chain is terminated with a carboxyl group, an ethanoic acid, or acetic acid, with the chemical formula of CH_3COOH is formed. When a carboxylic acid group reacts with a chain of alcohol, an ester and a water molecule are formed [82]. Likewise, if an acetic acid (CH_3COOH) meets an ethanol ($\text{C}_2\text{H}_6\text{O}$), an ethyl acetate ($\text{CH}_3\text{COOCH}_2\text{CH}_3$ or $\text{C}_4\text{H}_8\text{O}_2$) and a water molecule are formed.

Another type of liquid lubricants is synthetic oil, which is an artificially made oil for turbines and compressors. Synthetic oils are synthesized to meet desired physical properties. Thus, they prove to have superior performance than mineral oils. One disadvantage is that synthetic oils are typically costly compared to mineral oils, so synthetic oils are used when performance is more important than cost, e.g., in hard disk drives. Compared to mineral oils, synthetic oils have better thermal stability, lower pour point, higher viscosity index, and lower volatility [83].

(a) Polyalphaolefin (PAO)



(b) Polyolester (POE)



(c) Silicone

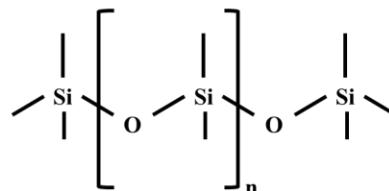


Figure 1.26 Three types of synthetic oils: (a) polyalphaolefin (PAO), (b) polyolester (POE), and (c) silicone

In general, synthetic oils can be categorized into hydrocarbon-based oils, ester-based oils, and silicon-based oils [83]. One hydrocarbon-based oil is polyalphaolefin (PAO). Polyalphaolefin (Figure 1.26(a)) lubricants are used as industrial lubricants in aviation and automobile industries since they have high pressure stability, high thermal stability, high viscosity index, and low volatility. Another type of synthetic oils is ester-based oil such as polyolester (POE). Polyolester (Figure 1.26(b)) lubricants are used in jet engines and marine gas turbines as they have very high thermal stability, very low volatility, high viscosity index, and high biodegradability. A third type of synthetic oils is silicon-based oil, such as silicone. Silicone (Figure 1.26(c)) lubricants have very high viscosity index and high resistant to thermal degradation. However, they do not provide good lubrication, for example, between two steel surfaces. For this reason, silicone lubricants have restricted usage, such as hydraulic fluids in liquid dampers in automobiles. In the hard disk drive industry, perfluoropolyether lubricants, a type of

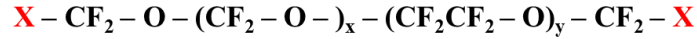
synthetic oils, are used to protect the disk surface since they have low vapor pressure and low surface energy.

Perfluoropolyether Lubricants

In order to protect the disk surface from possible wear and corrosion, a thin film of perfluoropolyether lubricant is applied [84-88]. Mate [84] states that effective lubricants must have the following properties:

1. Good boundary lubrication to provide protection against possible wear
2. High mobility for lubricant replenishment
3. Good surface adhesion to reduce loss of lubricants
4. Low volatility to prevent lubricant evaporation
5. Low surface energy to decrease stiction and minimize adsorption of contaminants
6. Good thermal and chemical stability

Some of the properties mentioned above contradict each other. Historically, the challenge in lubricant design for the head-disk interface has always focused on optimizing the chemical structure to find the best compromise. One of the most popular lubricant types used in the hard disk drive industry is perfluoropolyether. Examples of these lubricants include Fomblin Z and Demnum [86-87].



(a) Fomblin Z



(b) Demnum

Figure 1.27 Chemical formula for (a) Fomblin Z and (b) Demnum

Figure 1.27 shows the chemical formula for two popular lubricant backbone structures. “X” represents the functional end groups. Fomblin Z can be terminated with two functional end groups while Demnum can only be terminated with one group. Depending on the functional end groups, different derivatives of the Fomblin Z can form: Z-15 (X = CF₃), Zdol (X = CH₂OH: hydroxyl group), and Zdiac (X = COOH: carboxyl group). This is similar to the Demnum backbone. Demnum SA (X = hydroxyl group) and Demnum SP (X = phenyl ester ether) can be obtained. From their experiments, Tyndall et al. [86] concluded that the polar functional groups determine the bond strength between the lubricant and the disk surface.

However, durability of the head-disk interface is not only determined by the bonding strength, but also by the mobility of lubricants [88]. While a substantial portion of the lubricant molecules are bonded to the disk surface, the remaining lubricant molecules are considered to be “mobile”. Mobile lubricants “reflow and replenish” the lubricant layer in the case of lubricant depletion.

Since liquid lubricants are used to protect the disk surface, lubricant transfer at the head-disk interface is an inevitable consequence. Lubricant transfer is undesirable as it can cause flying instability, stiction at the head-disk interface, and error in

read/write operations [89-91], ultimately leading to hard disk drive failure. Lubricant transfer can occur even in the absence of actual head-disk contacts [92-93]. Lubricant transfer is a complicated phenomenon. It occurs in the molecular regime but its effect is observed at the macroscale level.

Fluid Bearing Oil in Hard Disk Drives

Apart from perfluoropolyether lubricants used to protect the disk surface, other liquid lubricants are used in fluid bearings for the spindle motor and pivot actuator arm in a hard disk drive. Until early 2000s, ball bearings were dominantly used for spindle motors in hard disk drives. However, for decreased run-out and increased rotational velocity, fluid bearings replaced ball bearings [94-96]. One of the primary reasons for the transition to fluid bearings was to reduce the so-called “non-repeatable runout”. Non-repeatable runout is “the radial displacement of the spindle that is not repeatable at each revolution” [95]. For similar reasons, fluid bearings are used for the pivot actuator arm in hard disk drives. The key component of the fluid bearing that allows for improved hard disk drive performance is the fluid bearing oil.

For both the motor spindle and the pivot actuator arm, organic compounds are used as fluid bearing oils. A mixture of mineral oils, a type of hydrocarbons – explained in the previous section, and poly-alpha-olefins (POA) is used to lubricate the pivot actuator arm [97]. A poly-alpha-olefin is a polymer chain composed of alpha-olefins. An alpha olefin is a type of organic compound chain made of alkenes with a double bond at the alpha position. Figure 1.28 shows an example of a poly-alpha-olefin, hex-1-ene.

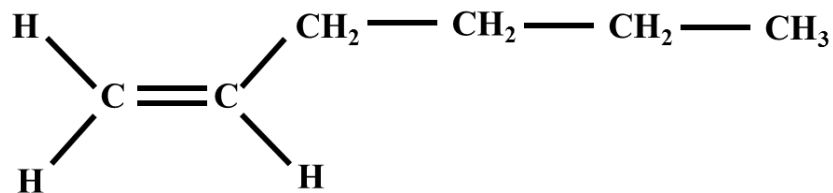


Figure 1.28 An example of a poly-alpha-olefin, hex-1-ene or 1-hexene (C_6H_{12})

To lubricate the motor spindle, a mixture of esters (cetyl palmitate – $\text{C}_{32}\text{H}_{64}\text{O}_2$ and cetyl stearate – $\text{C}_{34}\text{H}_{68}\text{O}_2$) is used. While reducing the non-repeatable runout as well as noise, and providing mechanical shock resistance, fluid bearing oil has become of increasing concern to the head-disk interface as a source of contaminants [98-103]. In 1999, Fowler et al. [98] reported that they observed hydrocarbon oil droplets on the slider surface. They concluded that hydrocarbon oil molecules use the disk as intermediary medium before transferring to the slider surface. Fowler and Geiss [99] observed from their experimental study that even a small amount of organic compounds, such as alkanes, can cause detrimental damage to the head-disk interface. Akamatsu and Ohtani [100] used thermal desorption spectroscopy to study how hydrocarbons contaminate the head-disk interface. They concluded that with appropriate surface treatment, hydrocarbon contamination at the head-disk interface can be controlled. In 2012, Sonoda [101] investigated flying instability due to contamination at the head-disk interface from organic compounds. He concluded that organic compounds evaporate and condense inside a hard disk drive and accumulate on the flying head. In 2013 and 2014, Raman et al. [102] and Kasai et al. [103], respectively, stated that hydrocarbon contamination at the head-disk interface is largely influenced by physical properties of the lubricants and environmental conditions. However, the actual mechanism behind

hydrocarbon contamination at the head-disk interface is still not fully understood. In Chapter 7 of this dissertation, hydrocarbon contamination at the head-disk interface will be investigated in detail.

Additives

As lubricants are used in extreme conditions, such as high temperature and high pressure, additives have been developed in order to improve lubricant properties [104].

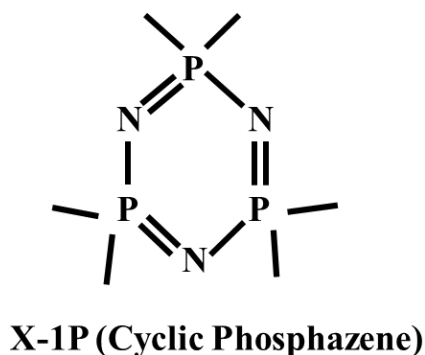


Figure 1.29 Chemical structure of an additive, X-1P (cyclic phosphazene)

Figure 1.29 shows X-1P (cyclic phosphazene) additive that was developed for perfluoropolyether lubricants. When added, X-1P increases perfluoropolyether lubricants' mobility and prevents catalytic reaction between the slider surface and the lubricants, improving the tribological performance of perfluoropolyether lubricant at the head-disk interface.

1.4.5 Head-Disk Interface

As described in the previous section, a hard disk drive is a mechanical system in which a read/write head (slider) flies over the magnetic medium (disk) in close proximity. The interface between the flying head and the rotating disk is called the *head-disk interface*. Figure 1.30 shows a schematic of the head-disk interface.

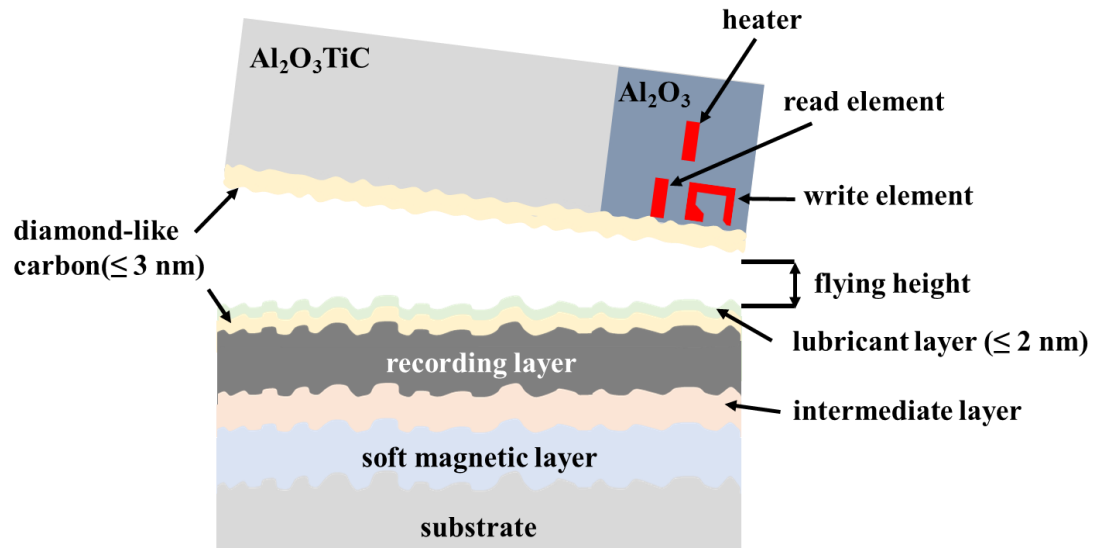


Figure 1.30 Head-disk interface in hard disk drives

During the write process, the minimum flying height at the head-disk interface is on the order of 1 nm. At such low spacing, intermittent contacts at the interface are inevitable. In order to reduce friction and wear, layers of protection are applied on both the disk and slider surface. On both the disk and the slider, a thin film (≤ 3 nm) of diamond-like carbon is deposited [105-109]. On the disk surface, on top of the carbon overcoat, a thin layer (≤ 2 nm) of perfluoropolyether (PFPE) lubricant is applied as shown in Figure 1.30.

Air Bearing Surface – Reynolds Equation

As explained in the previous section, the head flies over the disk surface in close proximity by forming a so-called “air bearing” by creating a pressure distribution under the air bearing surface. The fundamental principle of an air bearing is described by the Reynolds equation [6, 110-113], which is derived from the continuity equation and the

Navier-Stokes equation under the assumption that viscous forces are balanced by pressure forces. The two-dimensional compressible Reynolds equation is given by:

$$\frac{\partial}{\partial x} \left(p h^3 \frac{\partial p}{\partial x} \right) + \frac{\partial}{\partial y} \left(p h^3 \frac{\partial p}{\partial y} \right) = 6\mu \left(U \frac{\partial p h}{\partial x} + V \frac{\partial p h}{\partial y} \right) + 12\mu \frac{\partial p h}{\partial t} \quad (1.37)$$

where p is pressure, h is the spacing, μ is the fluid viscosity, U is the velocity of the moving surface in the x-direction, and V is the velocity of the moving surface in the y-direction. The above equation assumes that the spacing between the two adjacent surfaces in relative motion is very small, and that there is no-slip at the boundary. However, the spacing at the head-disk interface is in the nanoscale regime, hence the no-slip boundary condition is no longer valid if the spacing h is smaller than the mean free path λ of air. The mean free path is defined as the average distance a particle travels from one impact to the next one [114]. Thus, in current hard disk drives, the air flow at the head-disk interface is rarefied. When the rarefaction effect is considered, Equation 1.37 is modified as shown below.

$$\frac{\partial}{\partial x} \left(Q p h^3 \frac{\partial p}{\partial x} \right) + \frac{\partial}{\partial y} \left(Q p h^3 \frac{\partial p}{\partial y} \right) = 6\mu \left(U \frac{\partial p h}{\partial x} + V \frac{\partial p h}{\partial y} \right) + 12\mu \frac{\partial p h}{\partial t} \quad (1.38)$$

where Q is the non-dimensional, correction factor that represents the flow rate of air based on the Knudsen number $K_n = \lambda / h$. The relationship between Q and K_n is given by Fukui and Kaneko [115]:

$$Q = \begin{cases} -2.22919D + 2.10673 + \frac{0.01653}{D} - \frac{0.0000694}{D^2} & (0.01 \leq D \leq 0.15) \\ 0.13852D + 1.25087 + \frac{0.15653}{D} - \frac{0.00969}{D^2} & (0.15 \leq D \leq 5) \\ \frac{D}{6} + 1.0162 + \frac{1.0653}{D} - \frac{2.1354}{D^2} & (D \geq 5) \end{cases} \quad (1.39)$$

where D is the inverse Knudsen number.

Since Equation 1.38 is a non-linear partial derivative equation, its solution can only be obtained using numerical schemes such as finite difference methods [111], finite element methods [116], or finite volume methods [117]. Students in Prof. Talke's lab at the Center for Memory and Recording Research, UC San Diego developed a simulation package named the *CMRR Air Bearing Simulator* over many years using the finite element method [111-112, 118-119]. Figure 1.31 shows the discretized air bearing surface and the pressure distribution obtained using the *CMRR Air Bearing Simulator*. Further details of the derivation of Equation 1.38 and the numerical implementation can be found in Wahl [111] and Duwensee [112].

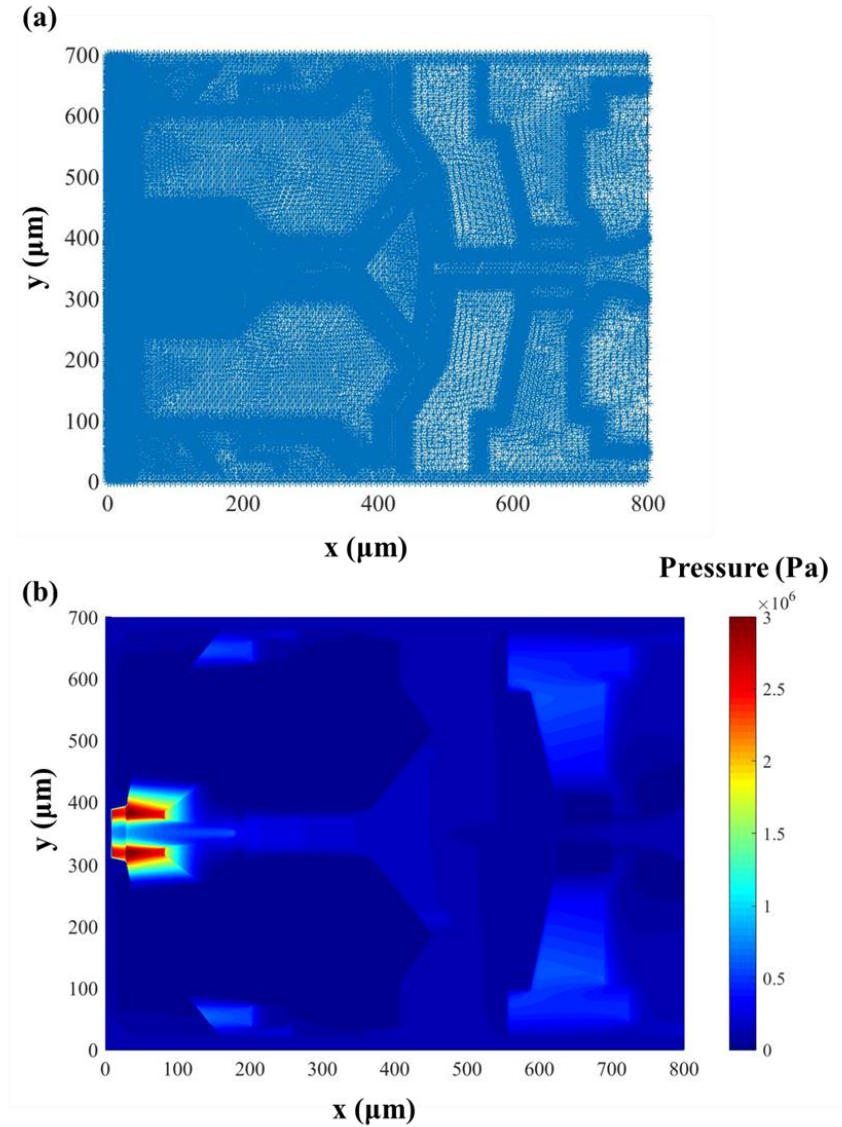


Figure 1.31 (a) Finite element mesh of a typical air bearing pressure and (b) finite element simulation result showing pressure distribution on the air bearing surface

Thermal Flying Height Control

Current hard disk drives have a flying height at the head-disk interface on the order of 1 nm. This flying height can be achieved using the so-called “thermal flying height control” (TFC) [120-122]. In this technology, an electric current is used to heat up a so-called “heater element”, which causes the read and write elements to protrude

toward the disk surface. Figure 1.32 shows a schematic of thermal flying height control technology.

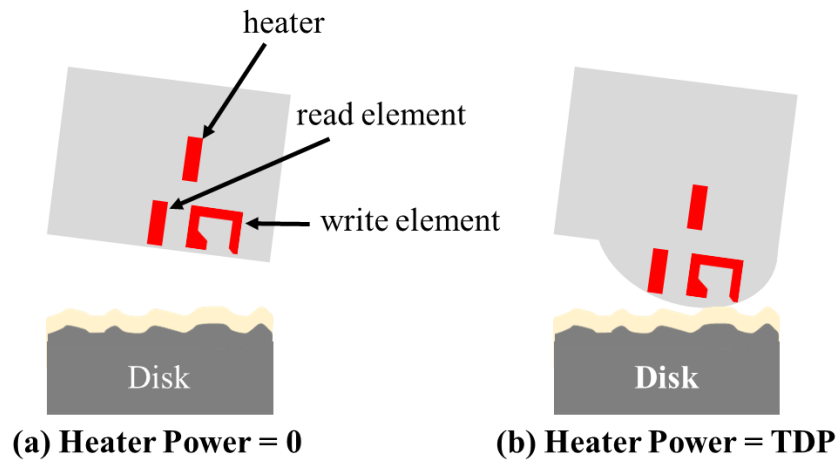


Figure 1.32 Schematic of the thermal flying height control where (a) 0 mW electric power is applied to the heater element and (b) the full touch down power is applied to the heater element

The nominal flying height of a head without thermal protrusion is approximately 10 nm. During the write and read process, the write and read elements must fly very close to the disk [120]. To reliably reduce the spacing, electric power is applied to the heater element, causing a thermal protrusion of the material around it and lowering the read and write elements toward the disk. The electric power at which contact occurs is known as the “touch down power” (TDP). By applying electric power a few milli-watts below the touchdown power, the head-disk spacing can be reduced to 1 nm [122].

1.5 Organization of Dissertation

This dissertation focuses on the investigation of lubricant transfer and hydrocarbon contamination at the head-disk interface in hard disk drives.

Chapter 1 gives a brief history of hard disk drives and the corresponding technology. The principle of magnetic recording is explained in this chapter. The importance of tribology in hard disk drives is also briefly discussed.

Chapter 2 explains various experimental techniques used to investigate contamination at the head-disk interface.

Chapter 3 provides a brief history of molecular dynamics. The fundamentals of molecular dynamics simulation are also explained in the chapter.

Chapter 4 investigates hydrocarbon contamination at the head-disk interface. An experimental investigation of hydrocarbon contamination is first discussed. Then, a molecular dynamics simulation of hydrocarbon contamination at the head-disk interface is performed to further understand the problem.

Chapter 5 investigates lubricant transfer at the head-disk interface using molecular dynamics. Lubricant transfer was studied as a function of local pressure change, disk velocity, air bearing design, lubricant-disk bond ratio, head-disk spacing, and finite width of air bearing surface. Also, transfer and fragmentation of four different types of lubricant molecules were studied as a function of temperature, local pressure change, and disk velocity.

Chapter 6 investigates lubricant evaporation and fragmentation under laser irradiation using molecular dynamics simulation. In this study, a pulsed laser was modeled as a non-moving heat source on the disk surface. Evaporation and fragmentation of lubricant molecules were studied as a function of laser peak power, pulse duration and repetition rate.

Chapter 7 presents the conclusions and summary of the dissertation.

Chapter 2

Experimental Techniques to Study Lubricant Transfer and Hydrocarbon Contamination

In this dissertation, lubricant transfer and hydrocarbon contamination of the head-disk interface is studied using commercially available equipment. A number of high resolution analytical instruments such as optical surface analyzer, scanning electron microscope, and atomic force microscope are used to analyze the head-disk interface.

In the following, we describe the experimental set-up and equipment used in this thesis, followed by a discussion of the analytical methods used to investigate the slider surface and the disk surface.

2.1 Spin Stand Tester

To study the reliability of the head-disk interface in the presence of contaminants, a commercially available “spin stand tester (VENA)” was used (Figure 2.1).

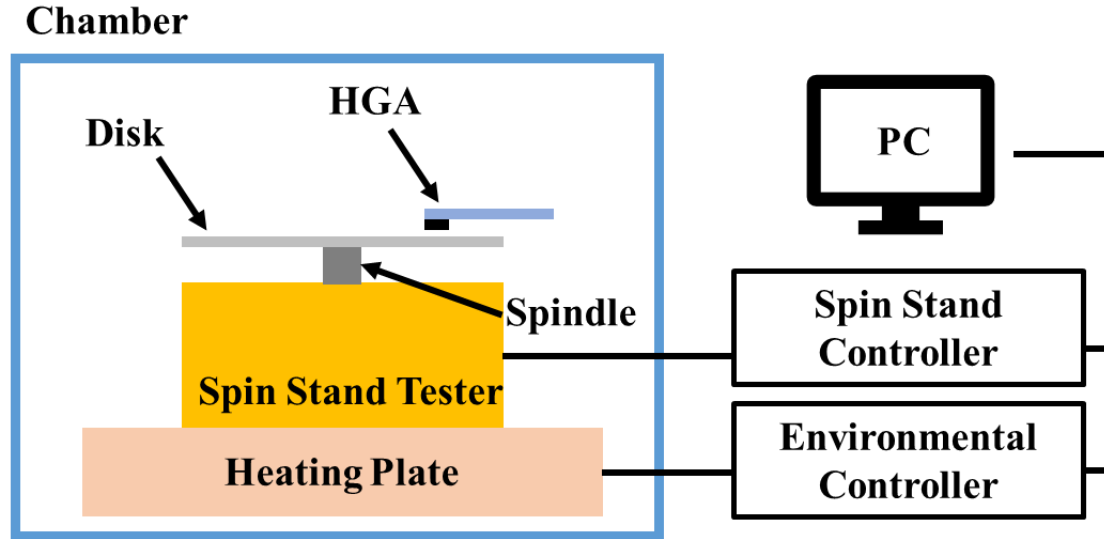


Figure 2.1 Schematic of VENA spin stand tester setup

Figure 2.1 shows a schematic of the spin stand tester, consisting of a spindle, a chamber, and a heating plate. The spin stand tester is connected to a controller box (spin stand controller) and a computer in order to adjust the spindle speed and the head-gimbal assembly (HGA) actuation. The heating plate is connected to an environmental controller and a computer. The heating plate is used to control the temperature inside the chamber since temperature is an important parameter for studying contamination at the head-disk interface. The chamber is needed to ensure that no foreign particles contaminate the head-disk interface.

Using this spin stand tester, we have investigated various combinations of disks and head-gimbal assemblies to study the effect of airborne contaminants on the reliability of the head disk interface. Figure 2.2 shows a close-up photograph of the spin stand tester [97].

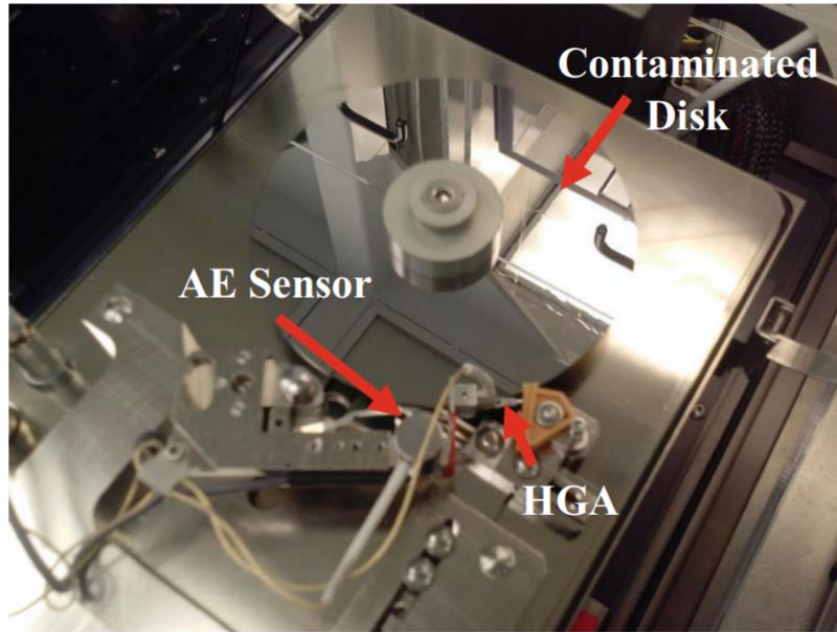


Figure 2.2 Photo of a commercially available spin-stand tester (VENA – VS90) [97]

To study contamination at the head-disk interface, a disk was first contaminated with a small amount of hydrocarbon oil and placed in the spin stand tester (Figure 2.2). A clean head-gimbal assembly was used as shown in Figure 2.2. Then, the heating plate (Figure 2.1) was energized to reach an environmental temperature of 60°C. The disk was controlled to rotate at 7,200 rpm. The head-gimbal assembly was adjusted to fly the head over the disk. After flying for 4 hours, both the disk and the head-gimbal assembly were removed to be analyzed using the optical surface analyzer, the scanning electron microscope, the atomic force microscope, and the time-of-flight ion mass spectrometry.

2.2 Experimental Techniques for Surface Characterization

Lubricant and hydrocarbon contamination at the head-disk interface can be using optical surface analysis (OSA), scanning electron microscopy (SEM), and atomic force microscopy (AFM).

To investigate disk surface contamination, optical surface analysis is typically used. Optical surface analysis provides information about lubricant degradation, lubricant depletion, and carbon overcoat defects. For inspecting the disk surface at much finer resolution, atomic force microscopy is commonly used. An atomic force microscope can detect surface changes on the order of nanometers, or even Angstroms.

For inspecting contamination on the head surface, both scanning electron microscopy and atomic force microscopy are commonly used. Both methods provide lateral resolution on the order of nanometers. Scanning electron microscopy provides two-dimensional images of the scanned surface, while atomic force microscopy provides three-dimensional information, such as surface roughness.

2.2.1 Optical Surface Analysis (OSA)

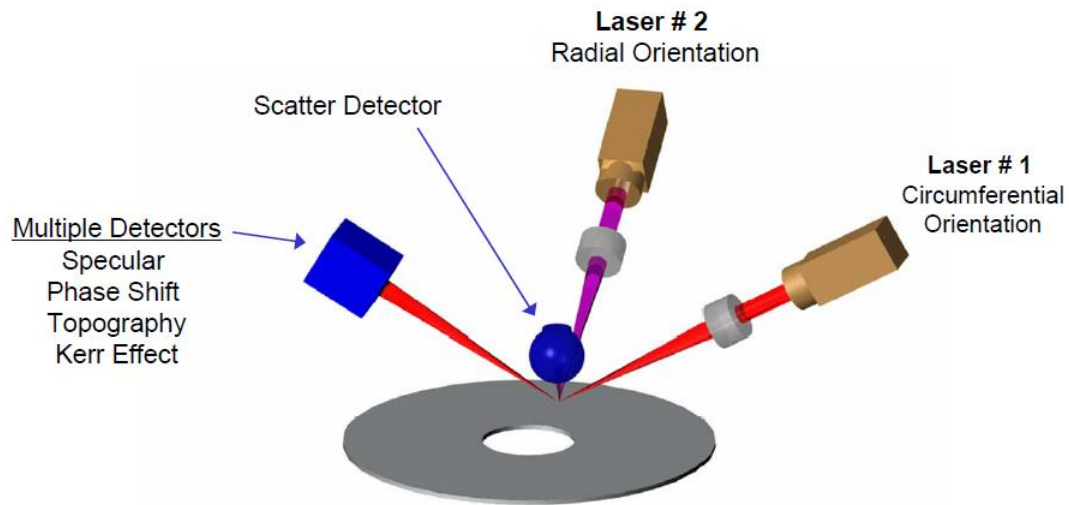


Figure 2.3 Schematic showing the main components of a commercially available optical surface analyzer [123]

Figure 2.3 shows the principle of an optical surface analyzer that consists of multiple detectors and two lasers for studying circumferential and radial orientation of the surface, respectively. An optical surface analyzer directs a laser on the disk surface and collects reflected and scattered electromagnetic waves. Laser beams for optical surface analysis can be polarized in three different directions, i.e., p-polarization, s-polarization, and q-polarization. Figure 2.4 illustrates the different polarization direction of a laser as used for optical surface analysis.

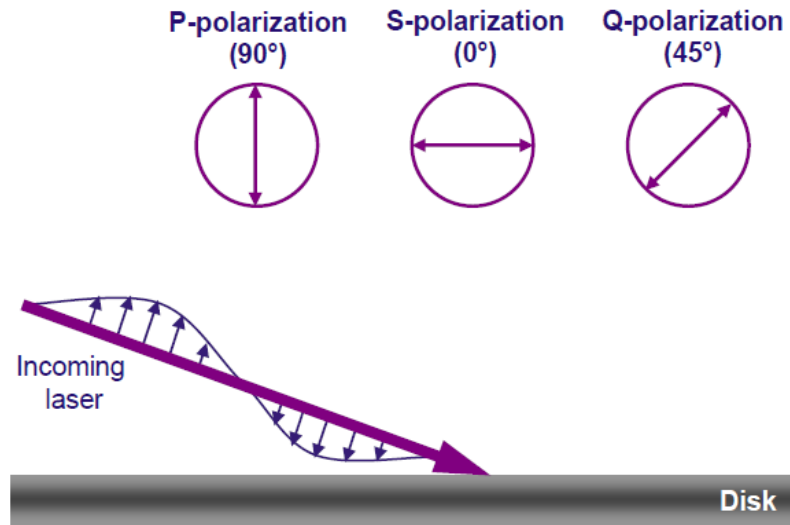


Figure 2.4 Schematic of p-polarization, s-polarization, and q-polarization of a laser beam [124].

As shown in Figure 2.4, a beam polarized parallel to the plane of incidence is denoted as p-polarized, a beam normal to the plane of incidence is denoted as s-polarized, and a beam 45° from the plane of incidence is denoted as q-polarized (Figure 2.4). By measuring p-, s-, and q-polarization, particle contamination and lubricant degradation on the disk surface can be detected.

Figure 2.5 shows the schematic of a laser beam scattered due to the presence of particles on the disk surface.

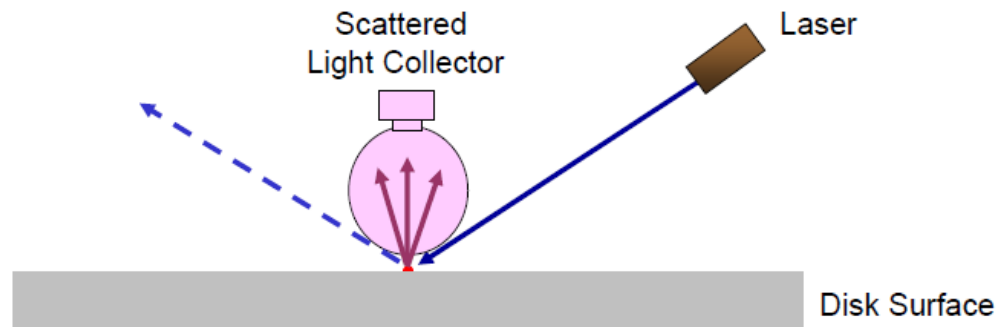


Figure 2.5 Schematic of scattered laser due to the presence of a particle on the disk surface [123].

In the presence of a solid particle, the incoming laser scatters in many directions (Figure 2.5). The scattered light is collected by the scatter detector and analyzed. A contamination particle will typically show a high reflectivity compared to the disk surface, i.e., particles show up on the optical surface analyzer as bright dots or spots. Figure 2.6 shows a typical image obtained by using the scatter detector [97].

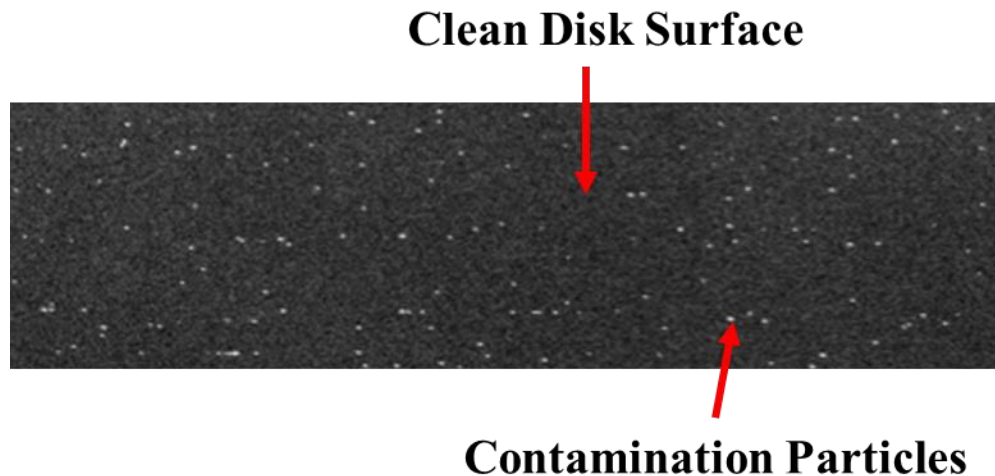


Figure 2.6 Optical surface analysis image of a disk surface contaminated with small particles [97]

Figure 2.6 shows a disk surface contaminated with small particles, or hydrocarbon crystals. The optical surface analyzer produced an image in which the clean part of the disk surface appears as dark area and the contaminants as bright dots. Using optical surface analysis measurements, one can detect and measure large particles accurately [124]. However, alternative methods, such as atomic force microscopy, are needed to measure particles on the order of nanometers.

Another valuable information optical surface analysis provides is lubricant film thickness. This information can be used to check lubricant film uniformity and formation of a foreign liquid layer (stain) on the disks surface [124]. Figure 2.7 shows a schematic of an optical surface analyzer with the phase shift detector.

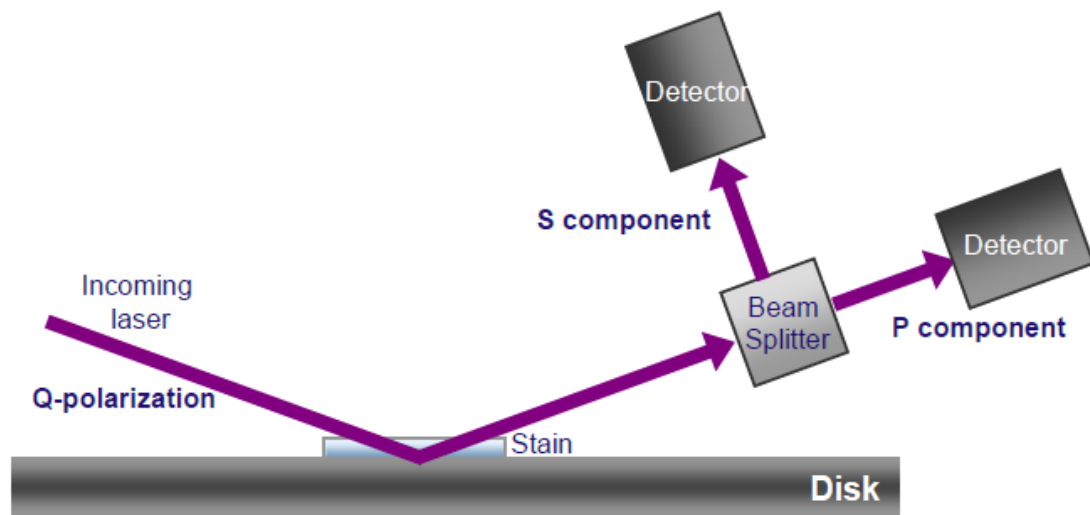


Figure 2.7 Schematic of an optical surface analyzer detecting a layer of foreign liquid, or stain, on the disk surface [124].

The incoming laser is q-polarized, 45° from the plane of incidence. Once the laser beam is reflected and refracted through the thin film layer, it is split into s-polarization component and p-polarization component (Figure 2.7). By measuring the

phase difference between the s-polarization component and p-polarization component, the optical surface analyzer can measure the thickness of the thin film. This method is based on ellipsometry.

Ellipsometry is a non-invasive, optical technique that is used to measure dielectric properties of thin films by looking at the changes in the polarization of light [125]. The technique has been known since 1888 [126]. Figure 2.8 shows a schematic of the principle of ellipsometry.

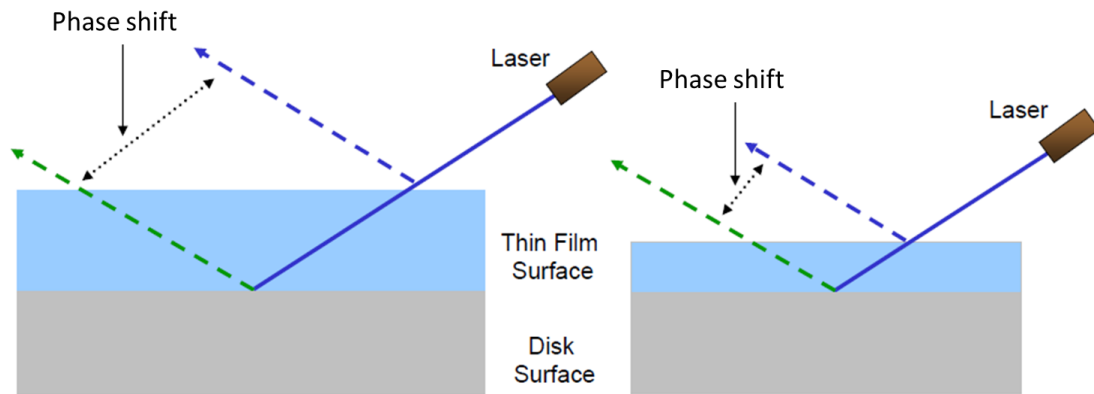


Figure 2.8 Schematic showing the principle of ellipsometry [124]

When meeting a thin film surface, a portion of the incoming laser beam is reflected, while the remaining laser penetrates the thin film layer. When meeting the disk surface, some portion of the laser beam is reflected (Figure 2.8). By measuring the phase difference, the thickness of the thin film layer can be calculated. Figure 2.9 shows a detailed image of ellipsometry on a three-layer surface that consists of air (layer #0), lubricant film (layer #1), and carbon overcoat (layer #2) [127]

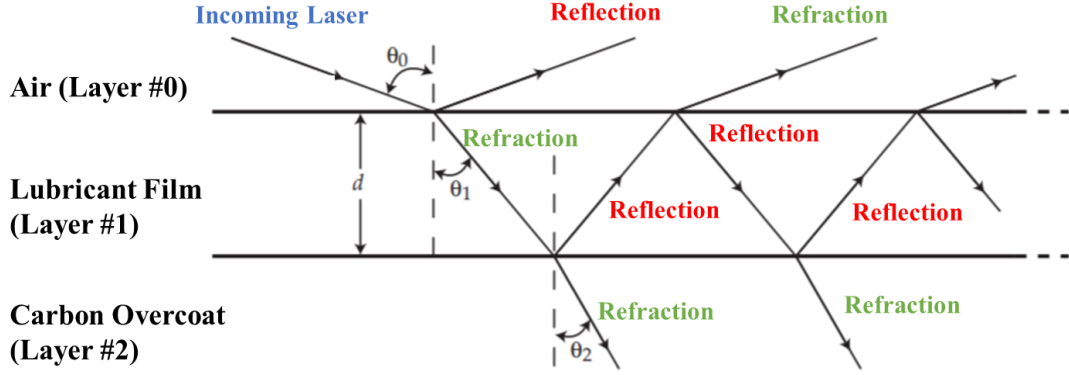


Figure 2.9 Schematic of laser path through air (Layer #0), lubricant film (Layer #1) and carbon overcoat (Layer #2) [127]

Figure 2.9 shows a schematic of the path of a laser beam reflecting from the disk surface. The beam is reflected at the air-lubricant interface and the lubricant-carbon overcoat interface. θ_0 is the angle of reflection at the air-lubricant interface, θ_1 is the angle of refraction at the air-lubricant interface, and θ_2 is the angle of refraction at the lubricant-carbon overcoat interface. d is the thickness of the lubricant film.

By using both Snell's law of refraction and Fresnel equations, one can determine the thickness of the thin film on a thick substrate.

$$\begin{aligned}
 r_{01}^p &= \frac{n_1 \cos(\theta_0) - n_0 \cos(\theta_1)}{n_1 \cos(\theta_0) + n_0 \cos(\theta_1)} \\
 r_{01}^s &= \frac{n_0 \cos(\theta_0) - n_1 \cos(\theta_1)}{n_0 \cos(\theta_0) + n_1 \cos(\theta_1)} \\
 r_{12}^p &= \frac{n_2 \cos(\theta_1) - n_1 \cos(\theta_2)}{n_2 \cos(\theta_1) + n_1 \cos(\theta_2)} \\
 r_{12}^s &= \frac{n_1 \cos(\theta_1) - n_2 \cos(\theta_2)}{n_1 \cos(\theta_1) + n_2 \cos(\theta_2)}
 \end{aligned} \tag{2.1}$$

where n_0 , n_1 , and n_2 are refractive indices for the air, the lubricant film, and the carbon overcoat substrate, respectively. r is the Fresnel reflection coefficients where the

subscript represents the interface between two layers. For example, r_{12} represents the Fresnel reflection coefficient associated with the interface between the lubricant film and the carbon overcoat substrate. The superscript s and p represent senkrecht and parallel (German for perpendicular and parallel) light waves, respectively. Once the reflection coefficients are known for each interface, the total reflection coefficients can be calculated using the following equations:

$$\begin{aligned} R^p &= \frac{r_{01}^p + r_{12}^p \exp(-j2\beta)}{1 + r_{01}^p r_{12}^p \exp(-j2\beta)} \\ R^s &= \frac{r_{01}^s + r_{12}^s \exp(-j2\beta)}{1 + r_{01}^s r_{12}^s \exp(-j2\beta)} \end{aligned} \quad (2.2)$$

where R^p and R^s are the total reflection coefficients of the surface for the s-wave and the p-wave, respectively. j is the complex number and β is a coefficient related to phase change from top to bottom of the film. β is related to the film thickness d by the following equation:

$$\beta = 2\pi \frac{d}{\lambda} \sqrt{n_1^2 - n_2^2 \sin^2 \theta_0} \quad (2.3)$$

Once the total reflection coefficients are known, the film thickness d can be determined by the following relationship:

$$R = \frac{R^p}{R^s} = \tan(\psi) e^{j\Delta} \quad (2.4)$$

where $\tan(\psi)$ is the amplitude ratio of the reflected over the incident light and Δ is the phase shift between the incident and reflected light. If the refractive index of the film is known, then the film thickness can be solved analytically. If the refractive index of the

film is not known, then the film thickness must be determined iteratively through numerous iterations [127].



Figure 2.10 Optical surface analysis image of a disk surface with different lubricant thickness measured. Q-polarized light is used [128]

Figure 2.10 shows optical surface analysis measurement of lubricant thickness on the disk surface after flying a slider slowing from the inner diameter to the outer diameter of the disk [128]. As shown in the image, the lubricant layer is not uniformly distributed but disturbed with different thickness in the radial direction.

2.2.2 Scanning Electron Microscopy (SEM)

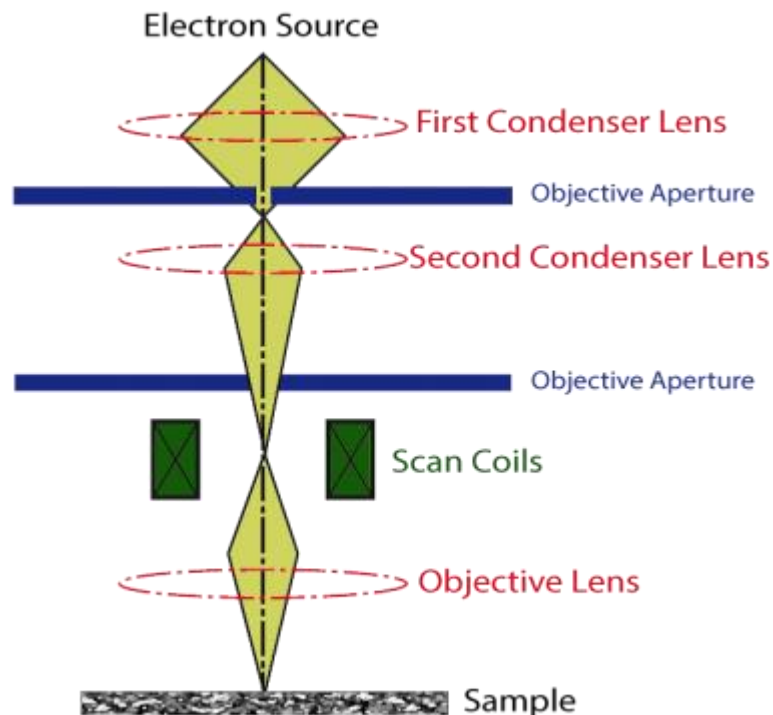


Figure 2.11 Schematic of components in a scanning electron microscope [129]

A scanning electron microscope consists of an electron source, several condenser lenses, objectives, and scan coils (Figure 2.11) [129]. The SEM operates as follows. First, a beam of electrons is emitted from an electron source. The electron beam travels through multiple condenser lenses and objectives to form an electron beam with a small spot size. Scan coils are used to control the position of the electron beam, allowing a lateral scan of the sample surface. Then, the objective lens is used to focus the electron beam on the sample surface. Electron detectors collect information from the surface and processed this information in a computer. The result is an image in black and white showing details of the sample surface on the order of nanometers.

Knoll [130] established the principle of scanning electron microscopy (SEM). In optical microscopy, white light is used, which has wavelengths ranging from 400 nm to 780nm. If light with 400 nm wavelength is used, the theoretical resolution would be 200 nm as resolution in microscopy is limited to approximately half the wavelength. To overcome this limit, electron beams are used which have much shorter wavelengths. The wavelength of electron beams can be calculated using the de Broglie relationship [131]:

$$\lambda = \frac{h}{p} \quad (2.5)$$

where λ is the wavelength of an electron, h is Planck's constant ($6.626 \times 10^{-34} \text{ J}\cdot\text{s}$), and p is the momentum of an electron. From classical physics, Equation 2.5 can be re-written as:

$$\lambda = \frac{h}{mv} \quad (2.6)$$

where m is the mass of an electron and v is the velocity. Since the kinetic energy of an electron is related to its velocity, Equation 2.6 can be re-written as [132]:

$$\text{KE} = q_e V = \frac{1}{2}mv^2 \rightarrow v = \sqrt{\frac{2q_e V}{m}} \quad (2.7)$$

$$\lambda = \frac{h}{\sqrt{2mq_e V}}$$

where q_e is the charge of an electron and V is the accelerating voltage of an electron beam. Since the mass of an electron is $9.1 \times 10^{-31} \text{ kg}$ and the charge of an electron is $1.6 \times 10^{-19} \text{ C}$, the wavelength of an electron can be obtained as shown in the following equation.

$$\lambda = \frac{6.62 \times 10^{-34}}{\sqrt{2 * 9.1 \times 10^{-31} * 1.6 \times 10^{-19} * V}} = \frac{12.25 \times 10^{-10}}{\sqrt{V}} \quad (2.8)$$

As the electron beam can reach 70% of the speed of light ($\sim 3.0 \times 10^8$ m/s), one must consider relativistic effects. Then, Equation 2.8 is modified to read:

$$\lambda = \frac{12.25 \times 10^{-10}}{\sqrt{V}} * \frac{1}{\sqrt{1 + \frac{q_e V}{2mc^2}}} \quad (2.9)$$

where c is the speed of light. If the accelerating voltage V is 5eV, then the calculated wavelength of the electron beam would be 0.55 nm, i.e., the theoretical resolution of the electron beam for the accelerating voltage of 5eV is 0.27 nm. Clearly, this value is much better than that of visible light. Figure 2.11 shows an optical microscopy image and an SEM image of a typical air bearing surface contaminated with hydrocarbon oil.

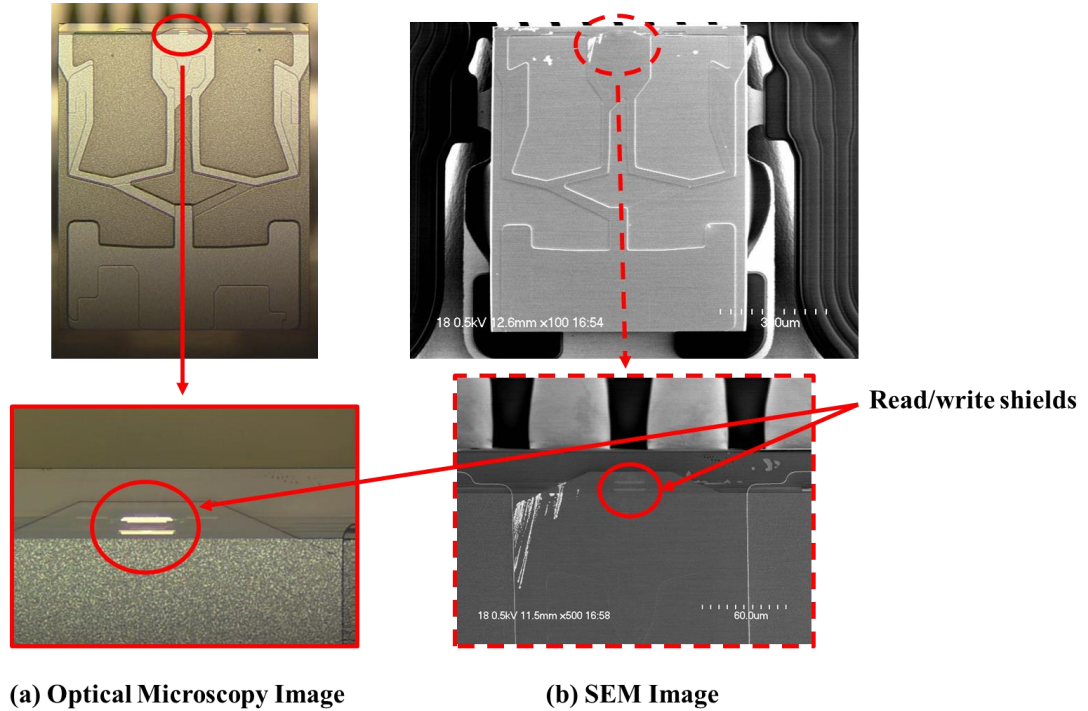


Figure 2.12 Images of an air bearing surface contaminated with hydrocarbon oil near the read/write element using (a) optical microscopy and (b) scanning electron microscopy [97].

The optical microscopy image (Figure 2.12(a)) shows only a small amount of contaminants and a generally clean surface otherwise. However, the scanning electron microscopy image (Figure 2.12(b)) shows that a thin layer of hydrocarbon is formed on the air bearing surface, and that contaminants are present in a number of places.

2.2.3 Atomic Force Microscopy (AFM)

Figure 2.13 shows the schematic of an atomic force microscope (AFM) [133] used to image surfaces on an atomistic scale.

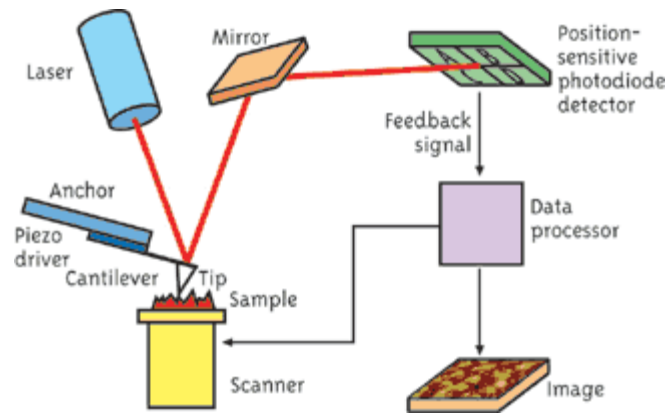


Figure 2.13 Schematic of atomic force microscopy [133]

An atomic force microscope consists of a laser, a piezoelectric positioning element, an AFM tip commonly made of silicon nitride, a mirror, a photodiode detector, and a data processor. In order to measure sample surface topography, a piezoelectric element positions an AFM tip close to the sample surface. The AFM tip is moved relative to the surface, changing its alignment depending on the surface topography. A laser is focused on the AFM tip during measurement. The laser beam is reflected from the tip surface. The reflected laser beam is directed to a position-sensitive photodiode detector using a mirror. The data processor compares the information from the reflected

beam to the reference tip position, allowing calculation of the image of the sample surface [133].

Three types of AFM are generally used, the *contact mode* AFM, the *non-contact mode* AFM and the *tapping mode* AFM. Figure 2.14 shows a schematic of the contact mode, non-contact mode and tapping mode AFM [134].

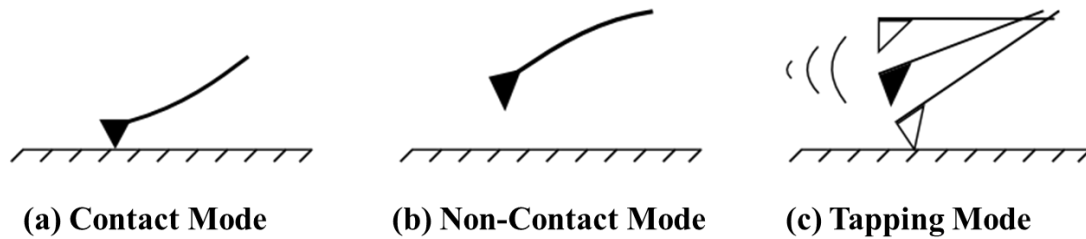


Figure 2.14 Schematic of (a) contact mode, (b) non-contact mode and (c) tapping mode of atomic force microscopy [134].

In the contact mode (Figure 2.14(a)), the AFM tip is in contact with the sample surface. The tip is “dragged” on the surface in the direction of the scan. The scan can be done with constant height or constant force. If the tip is controlled to have constant height, the surface topography is measured by looking at the cantilever deflection. Alternatively, the tip can be controlled to exert a constant force from the surface by using a feedback loop control. In this case, the vertical motion of the scanner is measured to capture the surface topography.

In the non-contact mode (Figure 2.14(b)), the cantilever beam “hovers” over the sample surface. Van der Waals forces between the sample surface and the tip are present. In this case, the atomic force microscope measures changes in amplitude, phase, and frequency of the cantilever oscillations due to interatomic forces. Since van der Waals

forces are strong only within a few nanometers, non-contact atomic force microscopy cannot accurately measure surfaces with sharp elevation changes.

In the tapping mode (Figure 2.14(c)), the cantilever beam is oscillated at the resonant frequency and “taps” on the sample surface during measurement. As the AFM tip taps the sample surface [135], the oscillation amplitude changes. Using a feedback loop control, the oscillation amplitude is adjusted back to the reference amplitude. During tapping of the sample surface, interatomic forces between the AFM tip and the sample surface are measured. Since the cantilever beam is oscillated at a high frequency in the tapping mode, the AFM tip can overcome adhesive force from the surface, unlike in contact mode and non-contact mode. Figure 2.15 shows an atomic force microscopy image of a crystallized hydrocarbon on the disk surface obtained in the tapping mode [97].

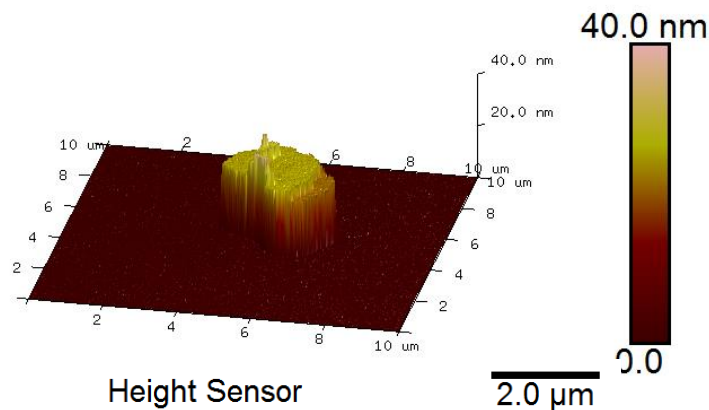


Figure 2.15 Atomic force microscopy image of a crystallized hydrocarbon on the disk surface [97]

The measurement shows that the hydrocarbon crystal has a height on the order of tens of nanometers and a diameter on the order of a few micrometers [97].

2.3 Experimental Techniques for Material

Characterization

For the investigation of lubricant transfer and hydrocarbon contamination at the head-disk interface, it is important to not only understand the surface properties but also to identify material composition. In this section, two techniques, energy dispersive X-ray spectroscopy and time-of-flight secondary ion mass spectrometry, will be discussed and their use in determining the chemical composition of contaminants. Both techniques are used in Chapter 7 of the dissertation.

2.3.1 Energy-Dispersive X-ray Spectroscopy

Energy-dispersive X-ray spectroscopy (also known as EDX, EDS, or XEDS) utilizes X-rays to analyze the chemical composition of a sample [136]. EDX can detect elements with atomic number larger than three and has a spatial resolution on the order of micrometers.

If a focused beam of electrons bombards a sample surface, the electrons of the beam interact with the surface atoms and emit two types of X-rays [137]: Bremsstrahlung and Characteristic X-rays. Bremsstrahlung X-rays are emitted from high-energy electrons that are decelerated as they interact with individual atoms [138]. As the freely moving electrons slow down, they lose kinetic energy, which is converted into photons. This is also known as braking X-ray or braking radiation (Bremsstrahlung X-ray). Characteristic X-rays, unlike Bremsstrahlung X-rays, are emitted when electrons move from the outer-shell to the inner shell of an atom in order to fill vacancy

[139]. These X-rays are collected by an energy-dispersive detector and analyzed to give the chemical composition of the sample surface. Figure 2.16 shows a schematic illustrating the working principle of an EDX [140].

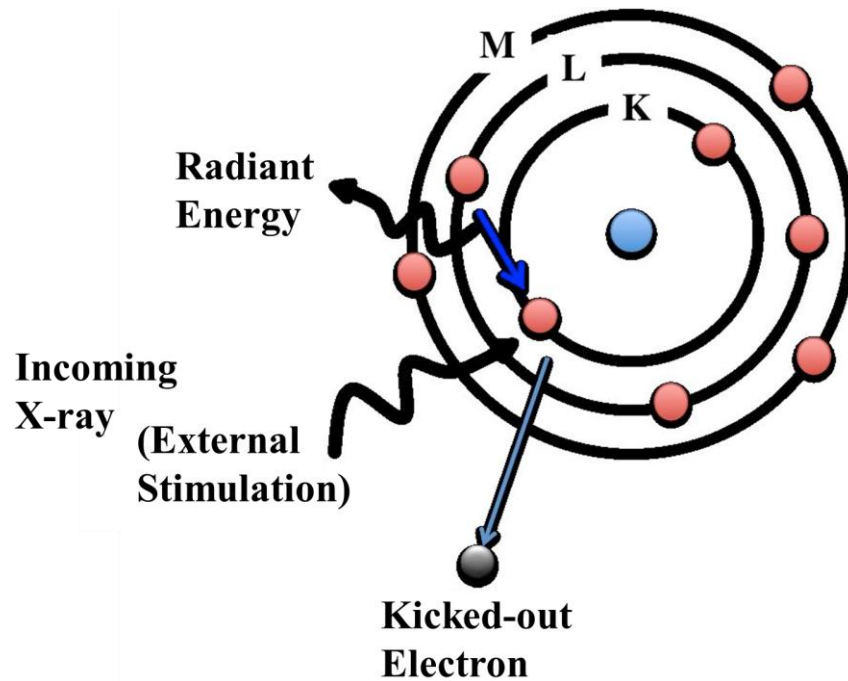


Figure 2.16 Schematic of the working principle behind EDX [140]

The incoming X-ray is shown as external stimulation in Figure 2.16. An excited electron leaves the orbiting atom. The electron is called a “kicked-out” electron. In order to fill the vacancy due to a kicked-out electron, an electron from the outer shell has to move to the inner shell. This motion emits radiant energy, or characteristic X-rays (Figure 2.16).

EDX can be used to analyze chemical components such as the compositions of contaminants on the air bearing surface.

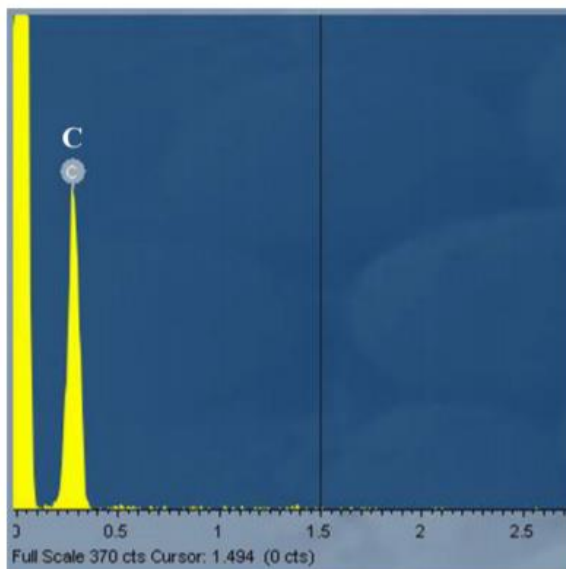


Figure 2.17 EDX analysis of an alkane crystal on the air bearing surface [97]

Figure 2.17 shows a typical EDX image of an alkane crystal on the air bearing surface [97]. EDX cannot detect hydrogen or helium, i.e., Figure 2.17 shows only a high carbon peak since alkane is composed only of hydrogen and carbon atoms.

2.3.2 Time-of-Flight Secondary Ion Mass Spectrometry

To analyze the chemical compositions of perfluoropolyether lubricants and hydrocarbon contamination, time-of-flight secondary ion mass spectrometry (ToF-SIMS) is useful. ToF-SIMS is a quasi-non-destructive tool that measures with mass resolution on the order atomic mass unit (amu) [141].

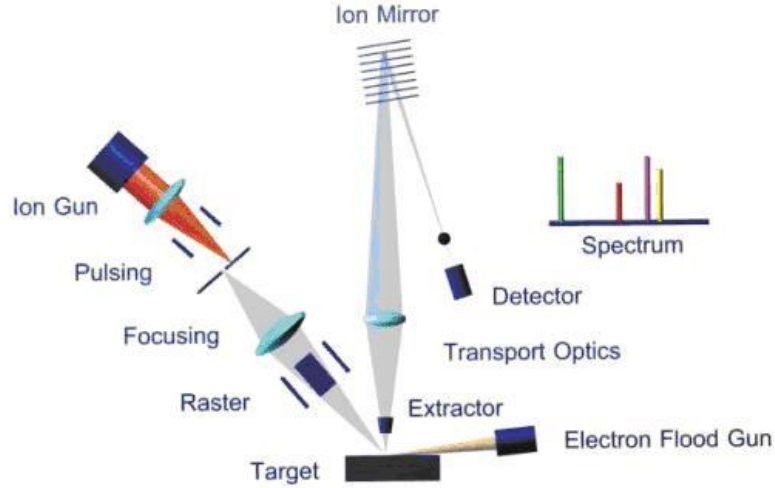


Figure 2.18 Schematic of time-of-flight secondary ion mass spectrometry [141]

Figure 2.18 shows the schematic of a time-of-flight secondary ion mass spectrometer, consisting of an ion gun, a focusing lens, an extractor, an ion mirror, an electron flood gun, and a detector [141]. ToF-SIMS focuses a beam of ions (typically cesium ion Cs^+ or gallium ion Ga^{3+}) using an ion gun on the sample surface. The ion beam is focused on the target sample surface using a focusing lens. An electron flood gun is used to neutralize charges on the sample surface throughout the measurement. Near the region where the ion beam is focused, dissociated (or secondary) ions are produced. These secondary ions are focused on an ion mirror and reflected to a detector. When the secondary ions are collected by the extractor, they are accelerated with a constant potential V on the order of 10^3 eV. This allows the ions to have the same kinetic energy as [142]:

$$KE = \frac{1}{2}mv^2 \quad (2.10)$$

where v is the velocity of the ion and m is the mass. If the path of flight has a length L , the relationship between the mass separation (m/z) and the time-of-flight is given by:

$$\frac{m}{z} = \frac{2Vt^2}{L^2} \quad (2.11)$$

where m/z is the mass separation, V is the accelerating potential, t is the time-of-flight, and L is the path length. Since all ions have the same kinetic energy, light ions arrive at the detector earlier than heavy ions. By obtaining this information, one can determine material composition of the sample surface.

The advantages of ToF-SIMS are that the technique measures elemental composition ranging from 0 amu to 10,000 amu, maps elements on the nanoscale, has a higher resolution than other techniques such as EDX and XPS, is quasi-non-destructive and can analyze both conductive and non-conductive surfaces [141-143]. The disadvantages of ToF-SIMS are that it is difficult to give quantitative measurements, that it has a limited optical path, and that it can cause the sample surface to accumulate charges by bombarding it with ions [141-143].

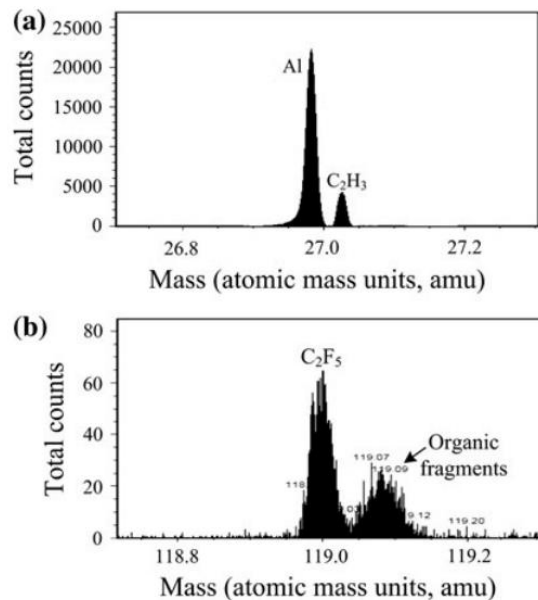


Figure 2.19 Typical ToF-SIMS spectrum showing (a) aluminum and (b) PFPE lubricant fragments and organic compounds [144]

Figure 2.19 shows typical results from ToF-SIMS [144]. ToF-SIMS was used on a slider surface to map clean and contaminated portions. Figure 2.19(a) shows aluminum ions indicating that the spectrum was generated on a clean part of the slider surface, while Figure 2.19(b) shows PFPE lubricant fragments and other organic compounds indicating that the spectrum was generated on a contaminated part of the slider surface.

Chapter 3

Basics of Molecular Dynamics

To analyze lubricant transfer and fragmentation, molecular dynamics is used. Molecular dynamics (MD) was first developed in the 1950s and 1960s in the field of theoretical physics [145-147]. Molecular dynamics utilizes classical Newtonian mechanics to model atoms and particle motion [148]. Maxwell and Boltzmann introduced statistical mechanics for simulating a large number of atoms in a defined volume [149]. Molecular dynamics is used mainly in the field of chemistry, material science, and biomedicine.

3.1 Molecular Mechanics

In order to model an atom accurately, Schrödinger's equation must be solved [150-151], i.e.,

$$H\Psi(r, t) = -i\hbar \frac{\partial \Psi(r, t)}{\partial t} \quad (3.1)$$

where $\Psi(r, t)$ is a wave function (quantum state of matter), r is the electronic position vector, t is the time, $\hbar$ is the reduced Planck's constant ($\hbar = \frac{h}{2\pi}$), and H is the Hamiltonian operator, which corresponds to the total energy of the system. Solving Schrödinger's equation, one can obtain an exact solution for a one-electron system (i.e., hydrogen) and

approximate solution for 3-body interactions or large systems containing up to 100 atoms (equivalent to 10^4 electrons) [152].

To simulate a large system of atoms and molecules, molecular mechanics has been developed. Molecular mechanics uses classical Newtonian mechanics to model interactions among atoms while ignoring the effects from electrons. This is based on the approximation by Born and Oppenheimer [153], i.e.,

$$\Psi_{\text{total}} = \Psi_{\text{electrons}} \times \Psi_{\text{nuclei}} \quad (3.2)$$

where the wave functions for the electrons and the nuclei can be treated as independent. This assumption is reasonable since electrons relax at a higher rate than nuclei, i.e., nuclei are much heavier than electrons. This allows the motion of nuclei to be described using classical Newtonian mechanics:

$$F = m \frac{d^2 r_a}{dt^2} \quad (3.2)$$

where F is the force acting on the nuclei, m is the mass of the nuclei, and r_a is the position vector of the nuclei. The force F can be obtained from empirical energy equations (force fields or potential functions) or quantum mechanical calculations [154-157]. The following equation shows the total energy associated with atoms and their interactions in a system [152]:

$$U(r^N) = \sum_i u^{(1)}(r_i) + \sum_i \sum_{j < i} u^{(2)}(r_i, r_j) + \sum_i \sum_{j < i} \sum_{k < j} u^{(3)}(r_i, r_j, r_k) + \dots \quad (3.3)$$

where U is the total energy, r is the atomic position vector, N is the total number of atoms in a system, and $u^{(1)}$, $u^{(2)}$, and $u^{(3)}$ is the energy associated with a single atom, a pair of atoms, and three atoms, respectively. In general, three and higher order

interaction terms are neglected for computational efficiency. In this case, Equation 3.3 can be modified as

$$U(\mathbf{r}^N) = \sum_i u^{(1)}(r_i) + \sum_i \sum_{j < i} u^{(2)}(r_i, r_j) \quad (3.4)$$

where the first term describes the energy associated with a single atom while the second term describes the energy associated with a pair of atoms.

Potential functions are the key to describing intramolecular and intermolecular interactions. Intramolecular interactions include all atomic interactions within a single molecule, while intermolecular interactions include all atomic interactions among different molecules.

3.1.1 Intramolecular Potential Functions

Intramolecular interactions involve *stretching*, *bending*, and *twisting* of bonds within a molecule. Figure 3.1 illustrates these three types of intramolecular interactions [152].

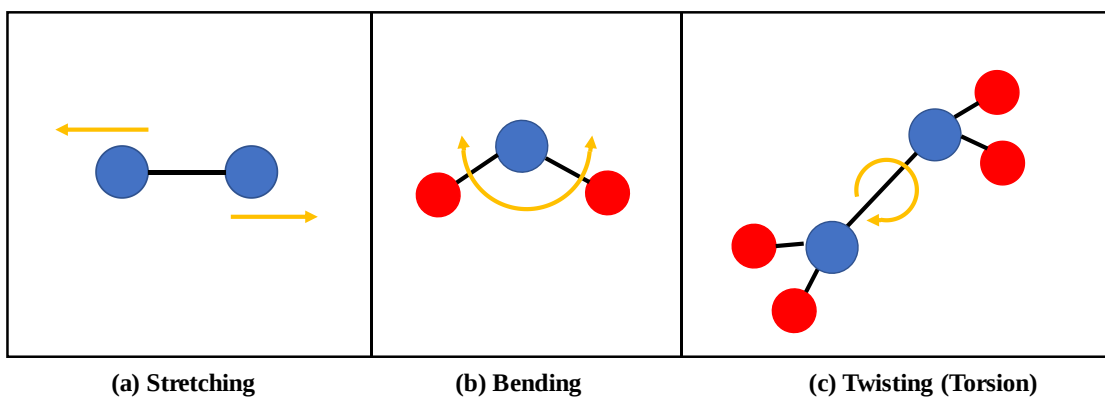


Figure 3.1 Schematic illustrating intramolecular interactions of (a) stretching, (b) bending, and (c) twisting (torsion)

Stretching Energy

Stretching energy, as the name suggests, corresponds to energy associated with stretching of a bond (Figure 3.1(a)). One way to model bond stretching mathematically is by using a linear harmonic potential function (Hooke's Law) [158]:

$$U(r_{12}) = \frac{1}{2} k(r_{12} - r_0)^2 \quad (3.5)$$

where U is the stretching energy, r_{12} is the bond length between two atoms, k is the spring constant obtained from either an experimental observation or quantum mechanical calculation, and r_0 is the equilibrium bond length. For long-chained polymers, instead of using Hooke's Law (Equation 3.5), the finitely extensible nonlinear elastic potential (FENE) function is used [159]:

$$U_{\text{FENE}} = \frac{1}{2} k_{\text{FENE}} r_0^2 \ln \left[1 - \left(\frac{r_{12}}{r_0} \right) \right] \quad (3.6)$$

where k_{FENE} is the spring constant for the FENE potential function. Neither of the two potential functions in Equation 3.5 and Equation 3.6 can approximate the effect of bond breakage. For the case of bond breakage, other potential functions have been introduced, as for instance, the Morse potential function [158]:

$$U_{\text{Morse}} = D \left(1 - e^{-\alpha(r_{12}-r_0)} \right)^2 \quad (3.7)$$

where D is the dissociation energy and α is the spring constant. When the energy U_{Morse} reaches the dissociation energy D , the bond between two atoms breaks, or dissociates.

For polymers, the so-called "quartic" potential function is used to simulate the FENE potential function when two atoms are bound and the Lennard-Jones potential function when unbound [160]:

$$U_{\text{quartic}} = k_q(r - R_c)^2(r - R_c - B_1)(r - R_c - B_2) + U_0 + 4\varepsilon \left[\left(\frac{\sigma}{r_{12}} \right)^{12} - \left(\frac{\sigma}{r_{12}} \right)^6 \right] \quad (3.8)$$

where k_q , B_1 , and B_2 are coefficients to simulate the FENE potential function. U_0 , σ , and ε are parameters to simulate interaction between two atoms after the bond breaks. When the bond length extends beyond the critical bond length R_c , the bond breaks.

Bending and Torsional Energy

Bending energy, as the name suggests, is associated with the bending of an angular bond (Figure 3.1(b)). One way to mathematically model bending is by using the angular harmonic potential function [158]:

$$U_{\text{Angle}} = \frac{1}{2} k_A (\theta - \theta_0)^2 \quad (3.9)$$

where k_A is the bending spring constant for the angular bond, θ is the bond angle between two atoms, and θ_0 is the equilibrium bond angle. Similar to the linear harmonic potential function (Equation 3.5), the angular spring constant k_A is obtained either from an experimental observation (e.g. Raman spectra) or from quantum mechanical calculations.

Torsional (dihedral) energy, as the name suggests, is associated with the twisting of a bond (Figure 3.1(c)). The simplest mathematical model for torsional energy is from the Fourier series of the potential energy associated with a dihedral bond [158]:

$$U_{\text{Torsion}} = \sum_{n=1} k_D (\cos(n\phi + \delta_n) + 1) \quad (3.10)$$

where k_D is the torsional spring constant, ϕ is the torsional angle, and δ_n is the phase shift. The potential function can capture different conformations of a molecule. For

example, ethane C_2H_6 ($n = 3$) has three stable conformations with the minimum energy [161].

For molecular dynamics simulation of alkane crystallization, the following torsional potential function will be used [162]:

$$U_{\text{Torsion}} = \frac{1}{2}k_1(1 - \cos(\phi)) + \frac{1}{2}k_2(1 - \cos(2\phi)) + \frac{1}{2}k_3(1 - \cos(3\phi)) \quad (3.11)$$

where k_1 , k_2 , and k_3 are torsional spring constants and ϕ is the torsional angle.

3.1.2 Intermolecular Potential Functions

Intermolecular interactions involve *van der Waals*, *electrostatic*, and *polarization* interactions between different molecules. Figure 3.2 illustrates the three types of intermolecular interactions [152].

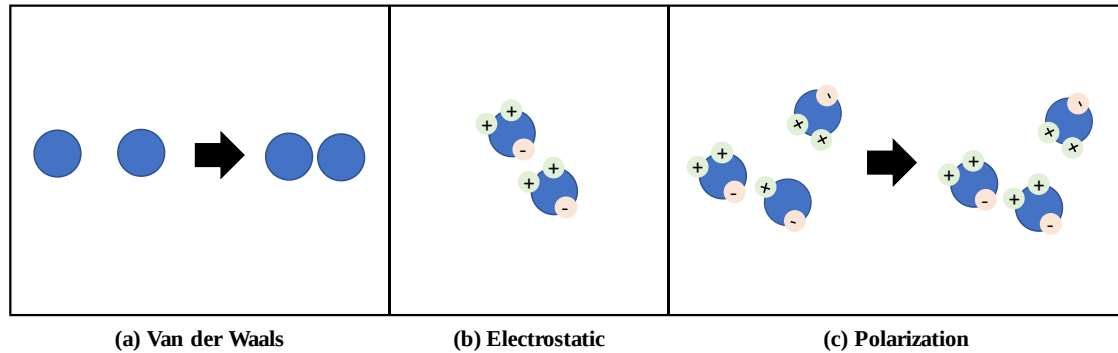


Figure 3.2 Schematic illustrating intermolecular interactions of (a) van der Waals, (b) electrostatic, and (c) polarization

Van der Waals

Van der Waals interactions describe weak interactions between atoms. The van der Waals force is also known as London or dispersion force. The following equation shows the mathematical model for the van der Waals interaction energy [158]:

$$U_{\text{vdw}} = -a \left(\frac{1}{r} \right)^6 \quad (3.12)$$

where a is the interaction coefficient and r is the distance between two atoms. Equation 3.12 only describes attraction between two atoms. It is known that when two atoms are very close to each other, they experience repulsion due to electron clouds coming into contact [163]. In order to simulate both attraction and repulsion, Lennard-Jones proposed the Lennard-Jones (LJ) potential function [164-165]:

$$U_{\text{LJ}} = \alpha \varepsilon \left[\left(\frac{\sigma}{r} \right)^n - \left(\frac{\sigma}{r} \right)^m \right], \quad \alpha = \frac{1}{n-m} \left(\frac{n^n}{m^m} \right)^{\frac{1}{n-m}} \quad (3.13)$$

where ε is the potential well-depth, σ is the diameter of an atom, and r is the distance between two atoms. In general, $n=12$ and $m=6$ are used for the LJ potential function to describe both attraction and repulsion. The values $n=12$ or $m=6$ do not have any physical meaning but are mathematical approximation of van der Waals forces. When $n=12$ and $m=6$ (12-6 LJ potential function), α is calculated to be 4. In order to increase computational efficiency, the LJ potential function is truncated, as shown in the following equation:

$$U_{\text{LJ}}^{\text{Truncated}} = 4\varepsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 - \left(\frac{\sigma}{r_c} \right)^{12} + \left(\frac{\sigma}{r_c} \right)^6 \right] \quad (3.14)$$

where r_c is the cut-off distance at which the LJ potential is assumed to be zero. Often, the cut-off distance r_c is chosen to be 2.5σ , where $U_{\text{LJ}}(r=2.5\sigma) = -0.0163\varepsilon$. Figure 3.3 shows different potential functions approximating the van der Waals attraction and repulsion. Figure 3.3(a) shows a comparison of Equation 3.12, Equation 3.13 and Equation 3.14. Clearly, Equation 3.12 cannot simulate repulsion between a pair of atoms.

Figure 3.3(b) and Figure 3.3(c) show that Equation 3.14 can closely simulate Equation 3.13.

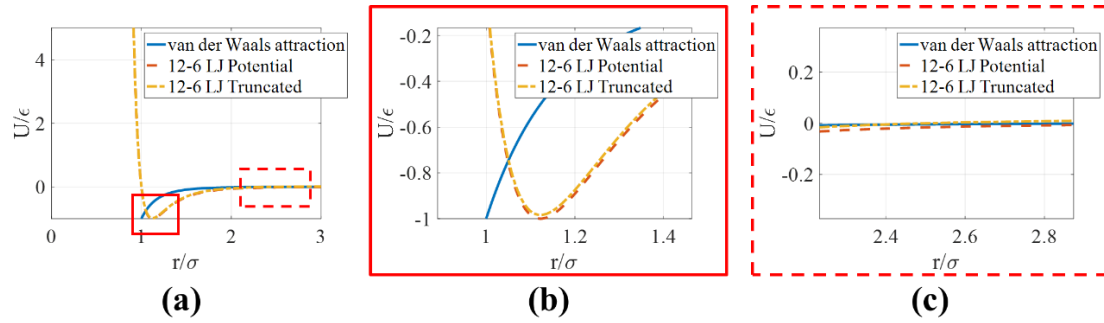


Figure 3.3 (a) Three potential functions approximating van der Waals attraction and repulsion. (b) Minimum energy for 12-6 LJ potential function and truncated 12-6 LJ potential function. (c) Comparison of three mathematical models at $r = 2.5\sigma$. All three plots are generated using MATLAB.

Electrostatic and Polarization Potential Functions

An electrostatic potential function describes interactions between atoms with electric charges. A simple mathematical model follows Coulomb's law as shown in the following equation [166]:

$$U_{\text{coulomb}} = \frac{q_1 q_2}{4\pi\epsilon_0 r} \quad (3.15)$$

where q_1 and q_2 are charges held by atom 1 and atom 2, respectively, $1/4\pi\epsilon_0$ is the Coulomb's constant and r is the distance between two charged atoms. For example, an electron has a charge of -1.602×10^{-19} C. The Coulomb potential function is long range.

For short-ranged polar attractive interactions, the so-called "EXP" potential function is used [167]:

$$U_{\text{EXP}} = -\epsilon^p \exp\left(-\frac{r - r_c}{d}\right) \quad (3.16)$$

where ε^p is the magnitude of the polar attraction and d is the decay length in the exponential function for short-ranged polar attraction. Figure 3.4 compares the 12-6 LJ potential function, the Coulomb potential function and the EXP potential function. Figure 3.4 shows that the Coulomb potential function is a long-ranged potential function since it does not reach 0 even if the distance between two atoms is far, i.e., $\frac{r}{\sigma} = 10$. In contrast, the 12-6 LJ potential function and the EXP potential function are short range potential function since both potential functions reach 0 around $\frac{r}{\sigma} = 2$ and $\frac{r}{\sigma} = 4$, respectively.

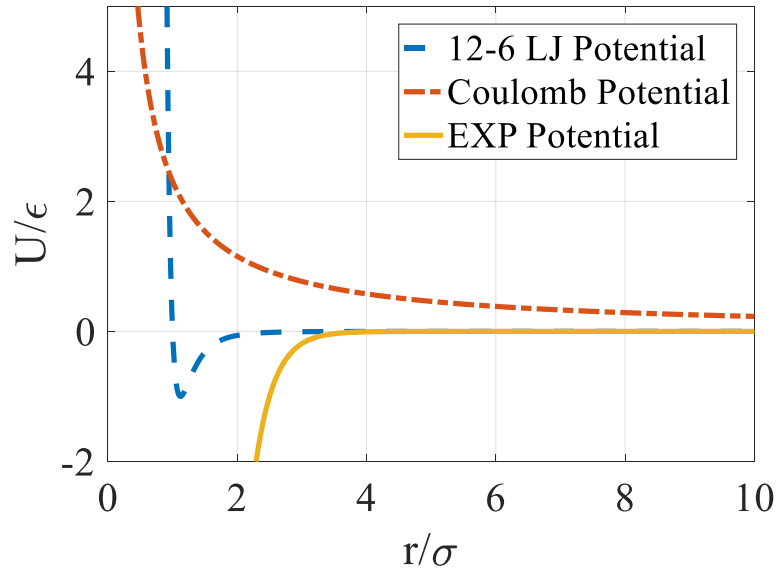


Figure 3.4 Comparison of the 12-6 LJ potential function, the Coulomb potential function and the EXP potential function. The plot was generated using MATLAB.

Polarization occurs when atoms experience charge redistribution due to other charged atoms or due to the presence of a strong electric field. Simulating polarization of atoms is an iterative process [152]. First, the electric fields around each charged atom need to be determined. Then, the adjusted charges for the atoms are calculated according

to their polarizability. Thereafter, the electric fields are re-calculated corresponding to the changes in charges. This process is repeated until numerical convergence is achieved.

Polarization is computationally expensive since the calculation must be repeated, even if a single molecule is moved from its previous position. The following electric potential of an atom at position k is shown in the following equation [168]:

$$V_k = \sum_{i \neq k} \frac{Q_i}{4\pi\epsilon_0 r_{ik}} + \sum_{j \neq k} \frac{r_{jk} \cdot \mu_j^{ind}}{4\pi\epsilon_0 r_{jk}^3} \quad (3.17)$$

where the first term is due to point-charge interactions and the second term is due to the induced dipole moments. Q_i is a point charge at position i , r_{jk} is the distance between the position i and k , and $1/4\pi\epsilon_0$ is Coulomb's constant. r_{jk} is the position between j and k and μ_j^{ind} is the induced dipole moment from the local electric field at position j , which can be written as the following equation [168]:

$$\mu_j^{ind} = \alpha_j E_j \quad (3.18)$$

where α_j is the point polarizability (ability to form dipoles) and E_j is the electric field at position j . The electric field due to all charges and dipoles can be described by the following mathematical model [168].

$$E_k = \sum_{i \neq k} \frac{Q_i r_{jk}}{4\pi\epsilon_0 r_{jk}^3} + \sum_{j \neq k} \frac{(3r_{jk}r_{jk} - Ir_{jk}^2)\mu_j^{ind}}{4\pi\epsilon_0 r_{jk}^5} \quad (3.19)$$

In MD simulations where all of the above intramolecular and intermolecular interactions are considered, the corresponding pair-wise energy can be divided into six superimposed energy terms as shown in Equation 3.20 [152]:

$$U_{Total} = (U_{stretch} + U_{bend} + U_{torsion}) + (U_{vdW} + U_{elect} + U_{polar}) \quad (3.20)$$

where the first three terms correspond to the intramolecular interactions, and the last three terms correspond to the intermolecular interactions.

3.2 Statistical Mechanics

Statistical mechanics provides the theoretical basis in which one can determine macroscopic properties of matter (e.g. thermodynamic properties) from statistical behaviors of atoms by using probability theory and the notion of “ensembles” [169]. In this section, a brief introduction to *ensembles* will be provided.

An *ensemble* is a “collection of all possible microstates of a thermodynamic system that are subject to a few constraints; each microstate is identical at macroscopic level but different at microscopic level” [169]. Figure. 3.5 illustrates an example of an ensemble.

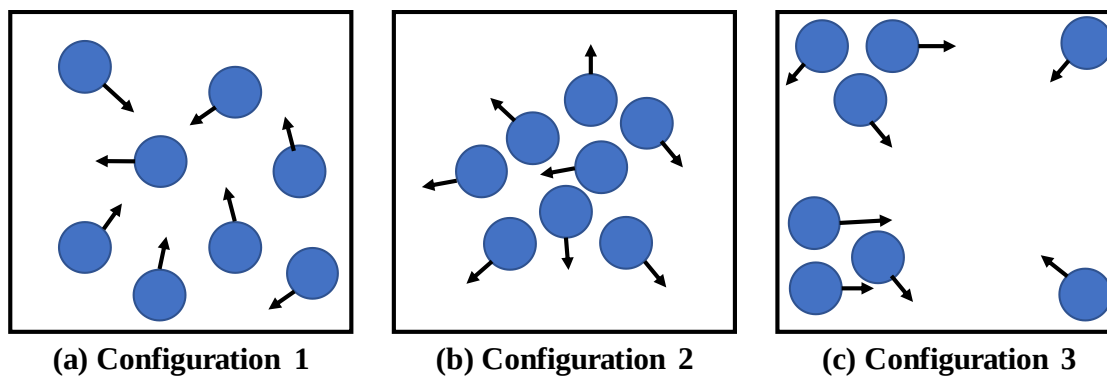


Figure 3.5 An example of an ensemble showing different configurations: (a) Configuration 1, (b) Configuration 2, and (c) Configuration 3

Assuming that within a set volume V at a constant temperature T , 8 atoms ($N=8$) are modeled. Figure 3.5 shows only three of many possible positions. Each configuration has its own specific information regarding atom positions and momenta.

In statistical mechanics, such configuration is called a “microstate” [169]. The following equation describes an average mechanical property for a particular ensemble:

$$\langle A \rangle = \frac{\sum_i A_i \rho_i}{\sum_i \rho_i} \quad (3.21)$$

where $\langle A \rangle$ is the ensemble average of the desired mechanical property (e.g., energy), A_i is the instantaneous value at the microstate i , and ρ_i is the probability in which the microstate i is likely to occur. There are two postulates when simulating an ensemble of atoms [169]:

- Postulate 1 involves the so-called “ergodic hypothesis.” The ergodic hypothesis states that the time-average value of A in Equation 3.20 equals the ensemble-average $\langle A \rangle$ [170].

$$\langle A \rangle = \frac{\sum_i A_i \rho_i}{\sum_i \rho_i} = \lim_{t \rightarrow \infty} \frac{1}{t} \sum_i A_i \Delta t_i \quad (3.22)$$

- Postulate 2 states that an ensemble must represent an isolated system of atoms.

3.2.1 Microcanonical Ensemble (NVE)

A microcanonical ensemble, also known as NVE ensemble, describes a situation in which the number of atoms N , the volume V , and the energy E are kept constant [170].

The probability P_i of a microstate configuration i is given as [169]:

$$P_i = 1/\Omega(N, V, E) \quad (3.23)$$

where $\Omega(N, V, E)$ is the partition function of the NVE ensemble. The partition function Ω is defined as [169]:

$$\Omega(N, V, E) = \frac{1}{h^{3N} N!} \int_{H(p^N, q^N)=E} dp^N dq^N \quad (3.24)$$

where N is the number of atoms, h is the Planck's constant, H is the Hamiltonian, and dp^N and dq^N refer to positions and momenta, respectively, of all atoms. Knowing the partition function of an NVE ensemble, the entropy of a system can be calculated using the following equation [169]:

$$S(N, V, E) = k_B \ln \Omega(N, V, E) \quad (3.25)$$

where S is the entropy and k_B is the Boltzmann constant. An NVE ensemble solves atomic motions without temperature control. To control temperature, many thermostat dynamics have been proposed. Here, the Langevin thermostat, which is one of the most widely used thermostats in conjunction with an NVE ensemble, will be briefly introduced.

The Langevin thermostat controls the temperature in an MD simulation by using a modified Newton's equation of motion [172-174]:

$$\dot{r}_i = \frac{p_i}{m_i}, \quad \dot{p}_i = F_i - \gamma_i p_i + f_i \quad (3.26)$$

where $\dot{r}_i$ is the velocity of atom i , p_i is the momentum, and m_i is the mass. $\dot{p}_i$ is the rate of change in the momentum, F_i is the force acting on the atom, γ_i is the friction coefficient, and f_i is the random force with the dispersion parameter σ_i , which is related to the friction coefficient by the following equation:

$$\sigma_i^2 = 2m_i\gamma_i k_B T / \Delta t \quad (3.27)$$

where k_B is the Boltzmann constant, T is the temperature, and Δt is the time step size.

3.2.2 Canonical Ensemble (NVT)

A canonical ensemble, also known as an NVT ensemble, describes a system for which the number of atoms N , the volume V , and the temperature T are kept constant

[175]. One must consider an NVT ensemble to be in an infinitely large bath with total energy E . Figure 3.6 illustrates this.

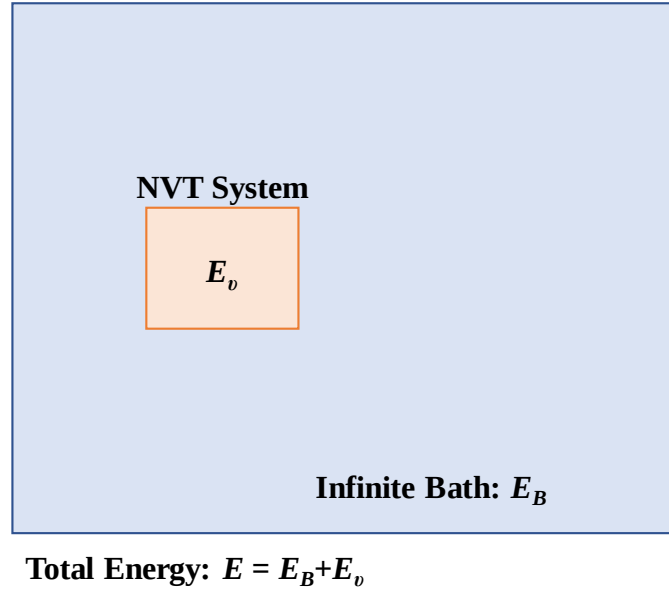


Figure 3.6 Schematic illustrating an NVT system in an infinitely large bath with the bath energy E_B and the system energy E_v

The probability of a microstate configuration with a specific energy E_v is shown below: [169]

$$P_v \propto e^{-\beta E_v} \quad (3.28)$$

where $\beta = \partial(\ln \Omega)/\partial E$, Ω is the partition function for the NVE ensemble (Equation 3.24) and E_v is the energy associated with the NVT system at a particular microstate.

The sum of all possible probabilities must equal 1:

$$\sum P_v = \sum C e^{-\beta E_v} = 1 \rightarrow C = \frac{1}{\sum_v \exp(-\beta E_v)} \quad (3.29)$$

where C is a constant. Then, Equation 3.29 can be modified to describe the probability of a microstate with energy E_v as following:

$$P_v = \frac{\exp(-\beta E_v)}{\sum_v \exp(\beta E_v)}, \quad Q = \sum_v e^{-\beta E_v} \quad (3.30)$$

where Q is the canonical partition function, which is defined by the following equation:

$$Q(N, V, T) = \frac{1}{h^{3N} N!} \int_{\Gamma} (e^{-\beta H(p^N, q^N)}) dp^N dq^N \quad (3.31)$$

where N is the number of atoms, h is the Planck's constant, H is the Hamiltonian, and dp^N and dq^N refer to positions and momenta, respectively, of all atoms. Knowing the canonical partition function, internal energy and pressure of an NVT ensemble can be calculated using the following equations [169]:

$$\langle E \rangle = \sum_v P_v E_v = \frac{\sum_v E_v \exp(-\beta E_v)}{Q} \quad (3.32)$$

$$\langle E \rangle = -\frac{1}{Q} \left(\frac{\partial Q}{\partial \beta} \right)_{N,V} = - \left(\frac{\partial (\ln Q)}{\partial \beta} \right)_{N,V} = k_B T^2 \left(\frac{\partial (\ln Q)}{\partial T} \right)_{N,V}, \quad \beta = \frac{1}{k_B T}$$

$$\langle \wp \rangle = \sum_v P_v \wp_v = \frac{\sum_v \wp_v \exp(-\beta E_v)}{Q} = \frac{\sum_v - \left(\frac{\partial E_v}{\partial V} \right)_N \exp(-\beta E_v)}{Q} \quad (3.33)$$

$$\langle \wp \rangle = k_B T \left(\frac{\partial (\ln Q)}{\partial V} \right)_{N,T}$$

where $\langle E \rangle$ is the internal energy and $\langle \wp \rangle$ is the pressure. Also, entropy S and the Helmholtz free energy A can be calculated using the canonical partition function Q .

$$U = \langle E \rangle = \sum_v P_v E_v$$

$$d\langle E \rangle = \sum_v E_v dP_v + \sum_v P_v dE_v \quad (3.34a)$$

$$d\langle E \rangle = -\beta^{-1} d \left(\sum_v P_v \ln P_v \right) - \langle \wp \rangle dV, \quad \beta = \frac{1}{k_B T}$$

By comparing the above equation to the first law of thermodynamics, the entropy S can be written as the following equation:

$$1^{st} \text{ Law of Thermodynamics: } dU = TdS - \wp dV \quad (3.34b)$$

$$\langle S \rangle = -k_B \left(\sum_v P_v \ln P_v \right)$$

Since the definition of the Helmholtz free energy is $A=U - TS$, it can be written as a function of the canonical partition function as shown below.

$$\langle A \rangle = \langle E \rangle + T \left(k_B \sum_v P_v \ln P_v \right) = -k_B T \ln Q \quad (3.35)$$

Then, Equation 3.34b can be modified as the following.

$$\langle S \rangle = \frac{\langle E \rangle}{T} + \frac{\langle A \rangle}{T} = k_B T \left(\frac{\partial (\ln Q)}{\partial T} \right)_{N,V} + k_B \ln Q \quad (3.36)$$

3.2.3 Other Ensembles

In addition to NVE and NVT ensembles, other ensembles exist, namely the isothermal-isobaric and grand canonical ensembles. The isothermal-isobaric ensemble, also known as an $N\wp T$ ensemble, describes a situation where the number of atoms N , the pressure $\wp$, and the temperature T are kept constant [176]. Since the volume is not kept constant, each microstate for an $N\wp T$ ensemble has a varying volume. The simulation “walls” are flexible (varying volume), impermeable (number of atoms cannot change), and heat conducting (temperature is controlled similar to NVT ensemble).

The grand canonical ensemble, also known as a μVT ensemble, describes a system for which the chemical potential (partial molar free energy) μ , volume V , and

temperature T are kept constant [177]. Chemical potential μ is the potential energy that is related to chemical reaction or phase transition. μ is defined as [169]:

$$\mu = \left(\frac{\partial A}{\partial N} \right)_{T,V} \quad (3.37)$$

where A is the Helmholtz free energy and N is the number of atoms. Since the number of atoms is not kept constant, each microstate for μVT ensemble has a varying number of atoms. The simulation “walls” are rigid (constant volume), permeable (atoms can enter or leave), and heat conducting (temperature is controlled similar to NVT ensemble). Figure 3.7 illustrates both $N\phi T$ and μVT ensembles.

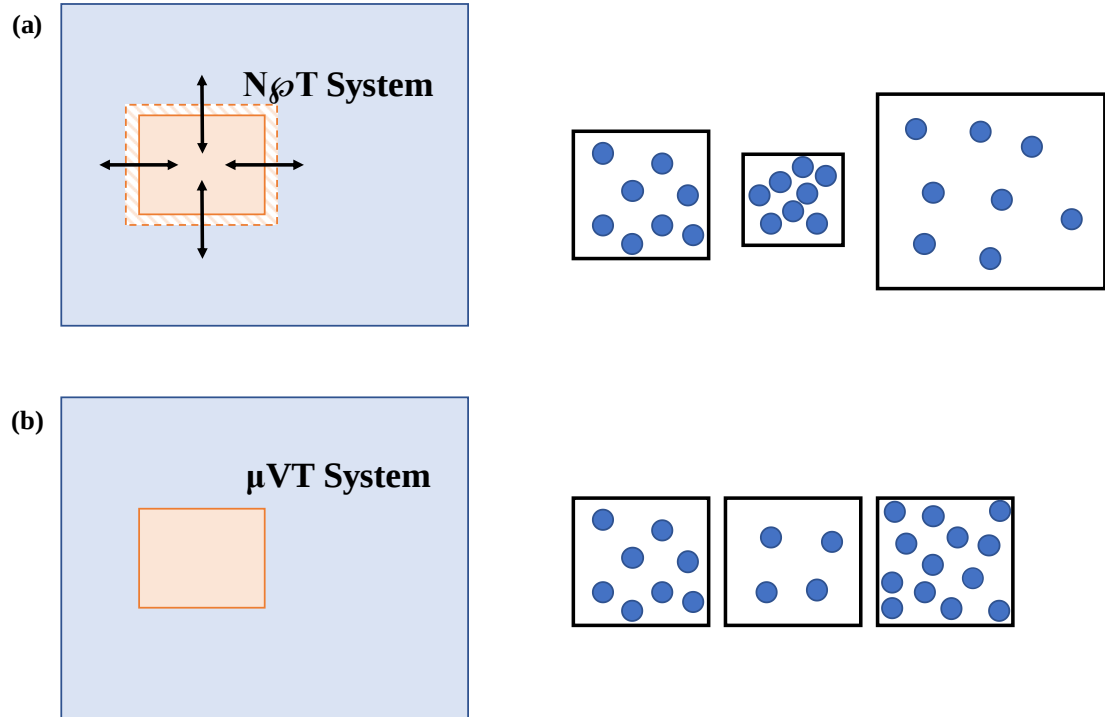


Figure 3.7 Schematic of (a) an $N\phi T$ ensemble and (b) a μVT ensemble

Table 3.1 summarizes all four ensembles discussed in this section.

Table 3.1 Ensembles and related equations: probability distribution, partition function, and bridge equation [169]

Name	Probability Distribution	Partition Function	Bridge Equation
Microcanonical (NVE)	$\frac{1}{\Omega}$	Ω	$\frac{S}{k_B} = \ln \Omega(N, V, E)$
Canonical (NVT)	$\frac{1}{Q} e^{-\beta E_i}$	$Q = \sum e^{-\beta E_i}$	$-\beta A = \ln Q(N, V, T)$
Isothermal-Isobaric (N ϕ T)	$\frac{1}{\Delta} e^{-\beta(E_i + \phi V_i)}$	$\Delta = \sum e^{-\beta(E_i + \phi V_i)}$	$-\beta G = \ln \Delta(N, \phi, T)$
Grand Canonical (μ VT)	$\frac{1}{\Xi} e^{-\beta(E_i + \mu N)}$	$\Xi = \sum e^{-\beta(E_i + \mu N)}$	$-\beta \phi V = \ln \Xi(\mu, V, T)$

3.3 Molecular Dynamics

Molecular dynamics (MD) studies the motion of atoms or molecules as a function of time, i.e., it is a computer simulation that solves Newton's equations of motion over time:

$$\ddot{x}_i(t) = \frac{F_i(t)}{m_i} \quad (3.38)$$

where $\ddot{x}_i(t)$ is the acceleration of an atom i at time t and $F_i(t)$ is the force acting on an atom i at time t . In this section, various numerical schemes for an MD simulation are introduced.

The simplest numerical scheme to simulate atomic motions is the first-order accurate Euler method [178]:

$$\begin{aligned} x(t + \Delta t) &= x(t) + v(t)\Delta t \\ v(t + \Delta t) &= v(t) + \dot{v}(t)\Delta t \end{aligned} \quad (3.39)$$

where x and v are position and velocity of an atom, respectively, and Δt is the time step size. The first-order Euler method is simple and requires little computational memory. However, due to its first-order accuracy and conditional stability criteria, only a small time step size can be used. For better accuracy and stability, the Verlet algorithm was introduced [179]:

$$x(t + \Delta t) = x(t) + \frac{1}{m}p(t)\Delta t + \frac{1}{2m}F(t)(\Delta t)^2 + \frac{1}{3!}\ddot{r}(t)(\Delta t)^3 + \vartheta((\Delta t)^4) \quad (3.40a)$$

$$x(t - \Delta t) = x(t) - \frac{1}{m}p(t)\Delta t + \frac{1}{2m}F(t)(\Delta t)^2 - \frac{1}{3!}\ddot{r}(t)(\Delta t)^3 + \vartheta((\Delta t)^4) \quad (3.40b)$$

where $p(t)$ is the momentum of an atom at time t . By combining and re-arranging Equations 3.38a and 3.38b, the following equation can be derived.

$$x(t + \Delta t) = 2x(t) - x(t - \Delta t) + \frac{1}{m}F(t)(\Delta t)^2 + \vartheta((\Delta t)^4) \quad (3.40c)$$

The Verlet algorithm provides better accuracy and numerical stability than the Euler method (Equation 3.38). However, the Verlet algorithm can possibly generate numerical errors due to the subtraction of large numbers (i.e. $x(t-\Delta t)$) and the addition of small numbers (i.e. Δt^2) [180]. Other numerical schemes such as the Verlet leap frog method [181] and velocity Verlet method [182] exist and are shown in the following equations, respectively:

Verlet Leap-Frog Method:

$$\begin{aligned} x(t + \Delta t) &= x(t) + v\left(t + \frac{1}{2}\Delta t\right)\Delta t \\ v\left(t + \frac{1}{2}\Delta t\right) &= v\left(t - \frac{1}{2}\Delta t\right) + \frac{1}{m}F(t)\Delta t \end{aligned} \quad (3.41)$$

Velocity Verlet Method:

$$x(t + \Delta t) = x(t) + v(t)\Delta t + \frac{1}{2m}F(t)(\Delta t)^2 \quad (3.42)$$

$$v(t + \Delta t) = v(t) + \frac{1}{2m} [F(t) + F(t + \Delta t)] \Delta t$$

Here, $F(t)$ is the force acting on atoms at time t . It is calculated by considering the potential functions discussed in the previous section of this chapter. The following relationship is used to calculate the force:

$$F = -\nabla_r U = -\left(\frac{\partial U}{\partial x} \hat{e}_x + \frac{\partial U}{\partial y} \hat{e}_y + \frac{\partial U}{\partial z} \hat{e}_z\right) \quad (3.43)$$

where U is the potential energy. For example, if two atoms are interacting “weakly” with each other, then the 12-6 LJ potential function (Equation 3.12) can be used to describe the interaction. The force acting on each atom can be written as:

$$\begin{aligned} F_{LJ}(r) &= \frac{\partial U}{\partial r} = \frac{\partial}{\partial r} \left(4\varepsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] \right) \\ &= \frac{48\varepsilon}{\sigma^2} \left[\left(\frac{\sigma}{r} \right)^{14} - \left(\frac{\sigma}{r} \right)^8 \right] r \end{aligned} \quad (3.44a)$$

$$\begin{aligned}
F_{LJ}(x, y, z) &= - \left(\frac{\partial U_{LJ}}{\partial x} \hat{e}_x + \frac{\partial U_{LJ}}{\partial y} \hat{e}_y + \frac{\partial U_{LJ}}{\partial z} \hat{e}_z \right) \\
&= - \frac{\partial U_{LJ}}{\partial r} \left(\frac{\partial r}{\partial x} \hat{e}_x + \frac{\partial r}{\partial y} \hat{e}_y + \frac{\partial r}{\partial z} \hat{e}_z \right), \quad r^2 = x^2 + y^2 + z^2 \\
&= - \frac{\partial U_{LJ}}{\partial r} \left(\frac{x}{r} \hat{e}_x + \frac{y}{r} \hat{e}_y + \frac{z}{r} \hat{e}_z \right) \tag{3.44b} \\
&= - \frac{F_{LJ}(r)}{r} (x \hat{e}_x + y \hat{e}_y + z \hat{e}_z) \\
&= - \frac{48\varepsilon}{\sigma^2} \left[\left(\frac{\sigma}{r} \right)^{14} - \left(\frac{\sigma}{r} \right)^8 \right] (x \hat{e}_x + y \hat{e}_y + z \hat{e}_z)
\end{aligned}$$

The above numerical methods provide efficient ways to compute atomic motions. However, for an MD model with a large number of atoms, a separate numerical scheme is required to minimize computation time by using a so-called “neighbor list.” A neighbor list is a numerical technique to establish a data structure for efficient MD simulations. In this section, a Verlet neighbor list will be introduced.

Since it is inefficient to compute interaction energy between far-separated atoms, only adjacent atoms are tabulated and considered for computation. Figure 3.8 illustrates a Verlet neighbor list.

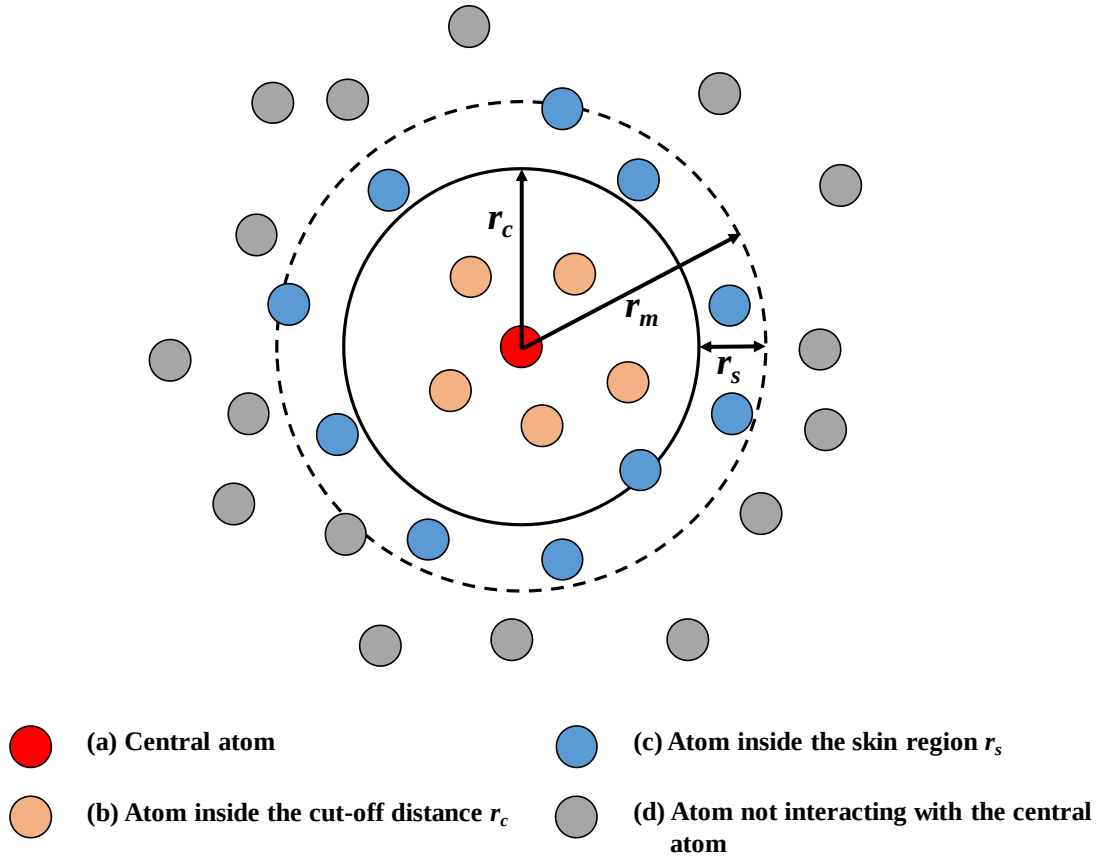


Figure 3.8 Schematic of a Verlet neighbor list with (a) the central atom, (b) atoms inside the cut-off distance r_c , (c) atoms inside the “skin region” r_s , and (d) atoms not interacting with the central atom

A Verlet neighbor list tabulates all atoms whose distances from the central atom are within r_m . The skin region r_s is determined by the following relationship [183-184]:

$$r_s = r_m - r_c > N_m v_{typ} \Delta t \quad (3.45)$$

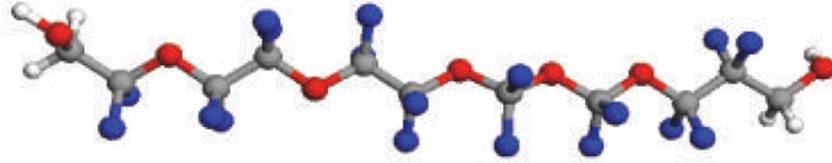
where r_m is the “neighboring” distance, r_c is the cut-off distance, N_m is the number of time steps before the list is updated, Δt is the time step size, and v_{typ} is the typical velocity of an atom, which is on the order of angstrom. In general, many of the interacting atoms remain near the central atom for a small period of time, typically 10 to 20 time steps. Thus, the neighbor list is updated every 10-20 times steps, i.e. $N_m = 10$ or 20.

3.4 Coarse-Grained Bead Spring Model

An MD simulation is a powerful tool that can simulate motions of particles or atoms at the atomistic scale. However, it would be computationally too expensive to model and simulate a continuum-scale model, such as the head-disk interface, using a classical MD simulation. Reduced order modeling (ROM) [185] is used in order to simulate models at a larger scale. In this section, the so-called “coarse-grained bead spring” (CG-BS) model will be discussed.

A CG-BS model is a molecular dynamics simulation modeling technique to reduce computation time for a complicated molecular system. The technique reduces, for example, a long chain of atoms into a short chain of pseudo-atoms where a pseudo-atom represents a group of atoms. This technique has been used to model proteins [186], lipids [187], other biomolecules [188], and lubricants [189]. The goal is to reduce the degrees of freedom to increase the computational speed while maintaining important physics considerations [185-189]. Figure 3.9 shows a schematic of constructing a CG-BS model of a PFPE hard disk lubricant molecule [189].

(a) Atomic Model of a PFPE Lubricant



(b) CG-BS Model of a PFPE Lubricant

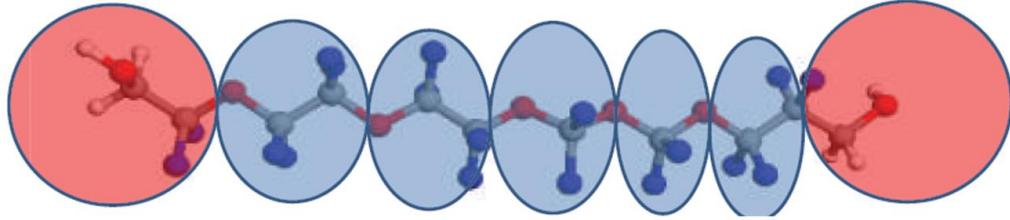


Figure 3.9 Schematic of (a) an atomic model of a PFPE lubricant and (b) a CG-BS model of a PFPE lubricant [189]

The atomistic model of a PFPE lubricant (Figure 3.9(a)) was modeled by Ref. [189] with the following intramolecular Hamiltonian:

$$h_a = \sum_i 0.5k_i^a(r_i - r_0)^2 + \sum_j 0.5k_j^a(\theta_j - \theta_0)^2 + \sum_{m,l} A_{m,l}P_{m,l} \quad (3.46)$$

where k_i^a , k_j^a , and $A_{m,l}$ are the bond, bending, and torsional coefficients, respectively. r_i and θ_j are the bond lengths and angles, respectively, while r_0 and θ_0 are the equilibrium bond lengths and angles, respectively. $P_{m,l}$ represents the Legendre polynomial. A CG-BS model of a PFPE lubricant (Figure 3.10(b)) was constructed by Ref. [189], describing the intramolecular interaction by considering only bond stretching:

$$h_m = \sum_i k_i^m(R_i - R_0)^2 \quad (3.47)$$

where k_i^m is the bond coefficient, R_i is the bond length, and R_0 is the equilibrium bond length. By fitting and comparing Equation 3.46 and 3.47 into Equation 3.28, the coefficients k_i^m and R_0 can be determined [190]. Noid et al. [190] state that “the CG model is consistent with the atomistic model in phase space if the equilibrium joint probability density of CG coordinates and momenta is equal to that implied by the atomistic probability density.”

For a Zdol 2000 lubricant molecule described in Chapter 1, we have constructed a CG-BS model with 10 beads. The intramolecular interactions are described by using the FENE (Equation 3.6) and the quartic (Equation 3.8) potential functions, while the intermolecular interactions are described by using the truncated 12-6 LJ (Equation 3.14) and EXP (Equation 3.16) potential functions. Figure 3.10 illustrates the coarse-grained bead spring model of a Zdol 2000 lubricant molecule [93].

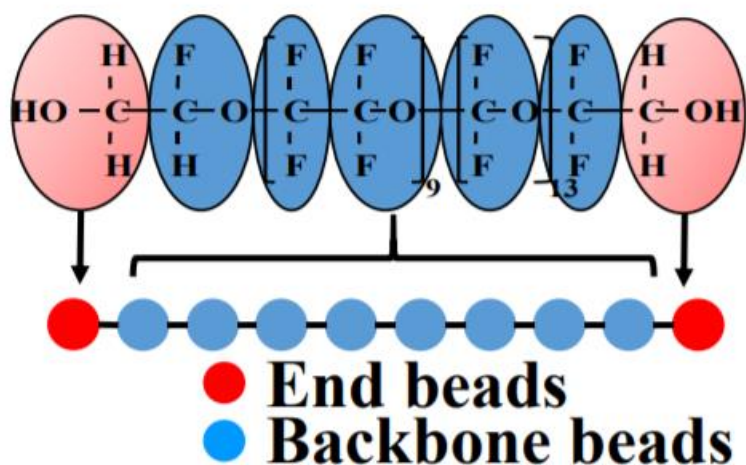


Figure 3.10 Schematic of the CG-BS model of a Zdol 2000 lubricant molecule [93]

3.5 Molecular Dynamics Simulation using

LAMMPS

In this dissertation, molecular dynamics simulations were performed using the *Large-scale Atomic/Molecular Massively Parallel Simulator* (LAMMPS) [191]. LAMMPS is written and maintained by the Sandia National Laboratory and readily available as an open-source software (<http://lammps.sandia.gov/>). This section will describe *LAMMPS* code to model a disk surface with perfluoropolyether lubricants.

In order to simulate a system of atoms or beads using molecular dynamics, the atomic positions must be “pre-processed.” Figure 3.11 shows a coarse-grained bead spring model of perfluoropolyether lubricants and diamond-like carbon overcoat constructed using MATLAB.

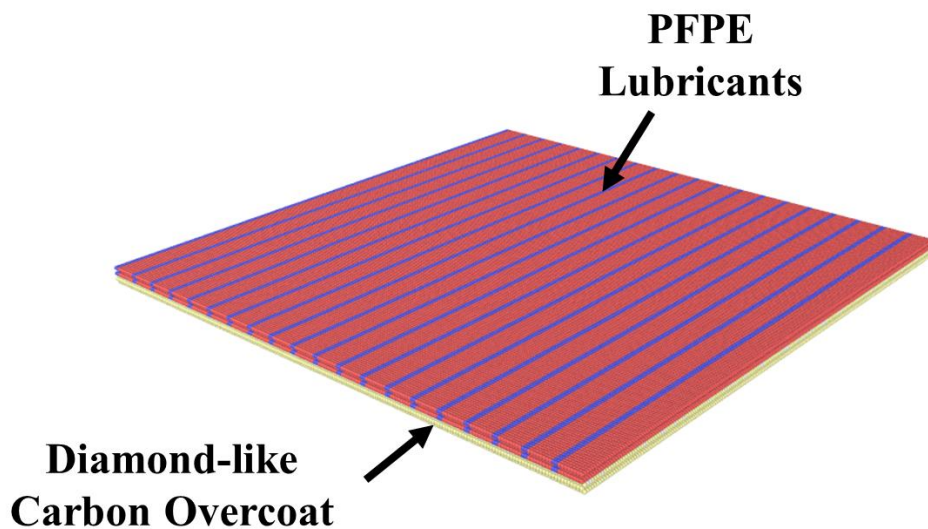


Figure 3.11 A disk surface consisting of a diamond-like carbon overcoat and a layer of perfluoropolyether lubricants.

The positions of all beads and their bond information are imported into LAMMPS. The following LAMMPS code imports the pre-processed model and defines the initial and boundary conditions.

```
read_data DiskSurf_200by200.data # Read the pre-processed data created
by MATLAB

units      lj      # Set the unit as LJ units
atom_style bond    # Only "bond" information will be considered
special_bonds fene  # FENE potential function will be used
boundary   p p s   # periodic in x, periodic in y, and shrink-wrap in z

# A variable "temp" is set to equal 1.0
variable   temp equal 1.0

# Group beads into different categories
# Type 1: PFPE backbone beads
# Type 2: PFPE functional end beads
# Type 3: DLC non-functional beads
# Type 4: DLC functional beads
group pfpe    type 1 2 # Create a group for PFPE layer
group endbead type 2    # Create a group for PFPE functional end groups
group DLCbead type 3 4  # Create a group for DLC layer
group DLCfunc type 4    # Create a group for DLC functional groups
```

After reading the model, the simulation unit is set to “LJ” unit, which is a dimensionless unit used in LAMMPS. We declare the “atom style” to be bond, i.e., the simulation considers only stretching intramolecular interactions using the finitely extensible non-linear elastic (FENE) potential function. Periodic boundary conditions are defined for x and y directions, respectively, while a so-called “shrink-wrapped” boundary condition is defined for the z direction. The shrink-wrapped boundary condition allows the simulation box to “encompass the atoms in that dimension, no matter how far they move” [191]. Then, the neighbor list for the

molecular dynamics simulation and the potential functions for molecular interactions are defined as shown in the following code.

```
# Define FENE potential function
bond_style fene
bond_coeff 1 30.0 1.5 1.0 1.0

# Define the LJ potential function
pair_style none
pair_style hybrid/overlay lj/cut 2.5 born 2.5
pair_coeff 1 1 lj/cut 1.0 1.0
pair_coeff 1 2 lj/cut 1.0 1.0
pair_coeff 3 3 lj/cut 0.0 0.0
pair_coeff 1 3 lj/cut 1.0 1.0
pair_coeff 2 2 lj/cut 1.0 1.0
pair_coeff 2 3 lj/cut 1.0 1.0
pair_coeff 4 4 lj/cut 0.0 0.0
pair_coeff 1 4 lj/cut 1.0 1.0
pair_coeff 2 4 lj/cut 1.0 1.0
pair_coeff 3 4 lj/cut 0.0 0.0

# Define the EXP potential function
pair_coeff 2 2 born -4.0 0.3 1.0 0.0 0.0
pair_coeff 2 4 born -4.0 0.3 1.165 0.0 0.0
```

In this code, the Lennard-Jones (LJ) potential function and the short-range attractive polar (EXP) potential function are defined for intermolecular interactions, while the finitely extensible non-linear elastic (FENE) potential function is defined to be used for intramolecular interactions among perfluoropolyether lubricants. Thereafter, an ensemble and temperature control algorithms are defined.

```

# Set an ensemble and equilibrate
# Use NVE Ensemble with Langevin thermostat control
fix      ensemble    all nve
fix temp_control  pfpe langevin 1.0 1.0 10.0 904297

# Set up an invisible, reflective wall to build a PFPE Lubricant Layer
fix eq_wall pdnve wall/reflect zhi 18.0 units box

# Run 500,000 time steps
run 500000

```

In this simulation, an NVE ensemble is used. This ensemble keeps the number of beads N , the volume V , and the energy E constant throughout the simulation. The temperature is controlled using the Langevin thermostat described in Equation 3.26 and Equation 3.27. 500,000 time steps are taken to equilibrate perfluoropolyether lubricants on the diamond-like carbon surface.

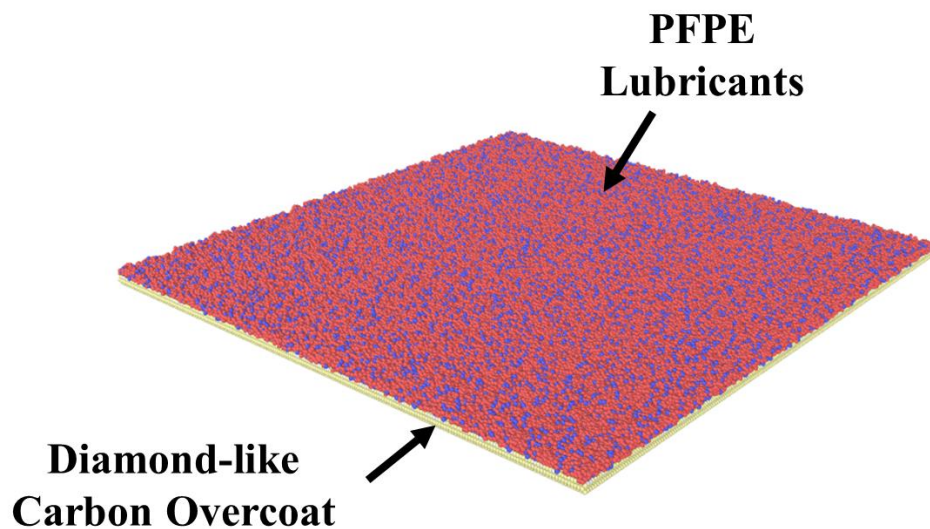


Figure 3.12 Molecular dynamics simulation of perfluoropolyether lubricants on the diamond-like carbon overcoat.

Figure 3.12 shows equilibrated perfluoropolyether lubricants that formed a layer on top of the diamond-like carbon overcoat.

Chapter 4

Hydrocarbon Contamination at the Head-Disk Interface

4.1 Introduction

In order to increase the areal density in hard disk drives, the flying height between the slider and the disk has decreased to the order of 1 nm. At this small spacing, lubricant migration as well as chemical and particle contamination of the head-disk interface has become of increasing concern. One of the contaminants in a hard disk drive is hydrocarbon oil, which is used to lubricate the suspension actuator pivot. Hydrocarbon-based bearing oil is known to cause contamination of the head-disk interface at elevated temperatures. In order to prevent hydrocarbon contamination, it is essential to understand the mechanism of hydrocarbon oil contamination of the head-disk interface.

For more than two decades, hydrocarbon oil contamination has been known as a potential problem and many efforts been undertaken in the past to solve the problems arising from hydrocarbon contamination [192-196]. Fowler et al. [98] visually observed the formation of hydrocarbon droplets on the slider surface. They hypothesized that these droplets play an important role in slider dynamics and the tribological performance of the head disk interface. Jesh and Segar [197] observed that outgassed contaminants

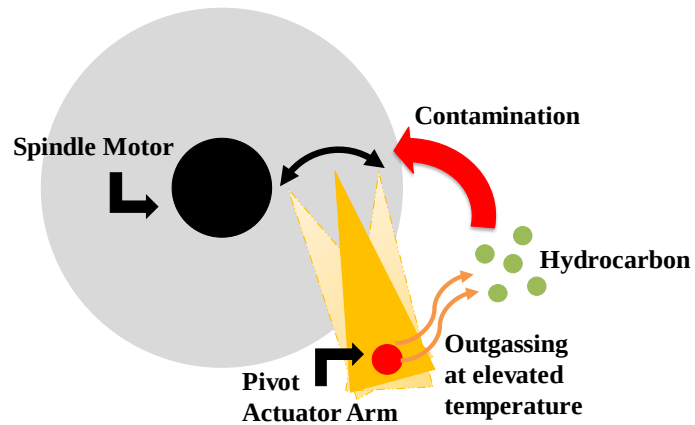
can affect the tribological performance of the head-disk interface in terms of stiction, wear resistance, hydrocarbon oil “smearing”, pole-tip corrosion and disk corrosion. Gao et al. [198] concluded that organic contaminants such as hydrocarbon oils can cause stiction between the flying head and the disk. For previous generations of contact-start-stop (CSS) hard disk drives, hydrocarbon oil contamination posed a severe problem in terms of stiction at the head-disk interface. Fowler and Geiss studied chemical contamination at the head-disk interface and observed that liquid droplets can accumulate on the slider surface [98]. Their experimental work indicated that the air bearing surface can become “flooded” with liquid contaminants during “parking” when the slider is lifted off from the disk surface. Fowler and Geiss [99] noted that the amount of airborne contaminants has decreased substantially over the last years due to improved cleanliness of hard disk drives. However, they observed that even a small amount of hydrocarbon oil can result in contamination of slider surfaces after long-time exposure. Lei and Gellman [222] investigated hydrocarbon oil contamination and its effect on PFPE lubricant interactions with the carbon overcoat. They concluded that the presence of hydrocarbon molecules weakens the interactions between disk lubricants and the carbon overcoat, leading to an increase in mobile lubricant. Da [223] studied degradation of CSS performance and failure of the head-disk interface in the presence of hydrocarbon contaminants. Akamatsu and Ohtani [100] investigated the adsorption behavior of siloxane and hydrocarbon at the head-disk interface. They observed that the desorption energy of hydrocarbon oil on the carbon-coated disk surface decreases if the surface is coated with PFPE lubricant. From this observation, they concluded that it may be possible to minimize contamination at the head-disk interface by surface treatment.

Raman et al. [102] stated that hydrocarbon oil used in hard disk drive components can contaminate the slider surface, adversely affecting the reliability of the head-disk interface. Sonoda [101] experimentally investigated the flying dynamics of sliders in the presence of airborne organic compounds. He speculated that the observed hydrocarbon droplets on the slider surface could accumulate in two ways: direct condensation of airborne hydrocarbon or transfer of deposited hydrocarbons from the disk surface. Kasai and Raman [103] concluded that the vapor pressure of hydrocarbons and ambient temperature affects the transfer behavior of hydrocarbon oil.

For a similar situation, Marchon et al. [200] studied numerically PFPE lubricant transfer from the disk to the slider and concluded that lubricant transfer and accumulation on the slider surface decrease exponentially with an increase in lubricant molecular weight. Guo et al., [201] investigated the tribo-chemistry of siloxanes in the absence of PFPE lubricant.

In this chapter, we investigate experimentally and numerically the mechanism of hydrocarbon contamination at the head-disk interface, in order to better understand the transfer mechanism of hydrocarbons from the disk to the slider surface, and to determine design parameters for future pivot actuator arm lubricants. Similar to [200], we assume that hydrocarbon contamination occurs in three steps. First, at elevated drive temperatures, hydrocarbon oil outgasses from the pivot actuator arm. Then, at lower temperatures, during shut-down of the drive, hydrocarbon oil condenses onto the disk surface. During subsequent flying of the slider at close spacing to the disk surface, the condensed hydrocarbon oil transfers from the disk to the slider surface, resulting in contamination of the air bearing surface. Figure 4.1 illustrates these steps schematically.

(a)



(b)

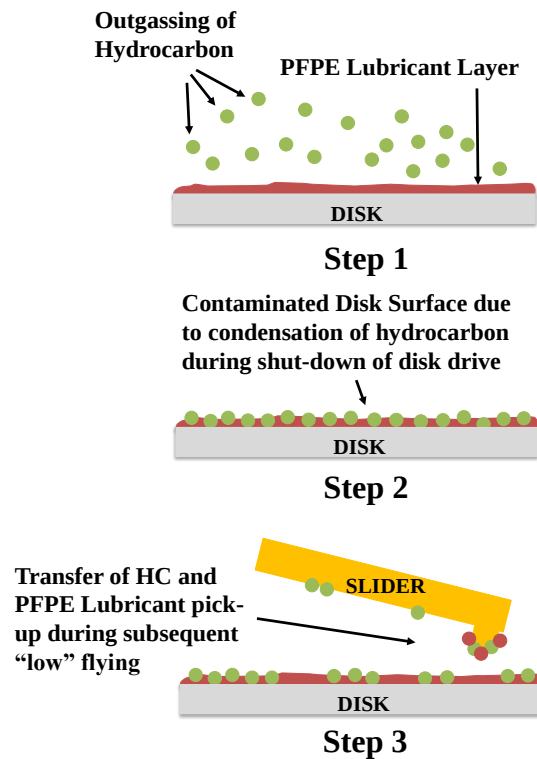


Figure 4.1 (a) Outgassing of hydrocarbon oil from the pivot actuator arm (b) Mechanism of hydrocarbon contamination at the head-disk interface

To investigate the three-step hypothesis of hydrocarbon contamination, we performed the following experiment. We first produced airborne hydrocarbon oil in a

thermal chamber by heating, and then contaminated a clean disk surface by condensing hydrocarbon oil during the “cool-down” process. Thereafter, the disk surface was analyzed using a commercially available optical surface analyzer (Candela 6100) and an atomic force microscope to study whether hydrocarbon contamination of the disk surface occurred. Finally, the contaminated disk was placed in a spin-stand tester (VENA) and a slider was flown at close spacing on the disk for a predetermined time and temperature. Then, the slider surface was analyzed using optical microscopy, scanning electron microscopy (SEM), and time-of-flight secondary ion mass spectrometry (ToF-SIMS), respectively.

We also modeled the motion of hydrocarbon oil and disk lubricant molecules using molecular dynamics simulation. We have used a so-called coarse-grained bead spring (CGBS) model with the Lennard-Jones (LJ) potential function, short-range polar attraction (EXP) potential function, and the finitely extensible nonlinear elastic (FENE) potential function.

4.2 Experimental Investigation

4.2.1 Hydrocarbon Contamination of Disk Surface

Experiment Procedure

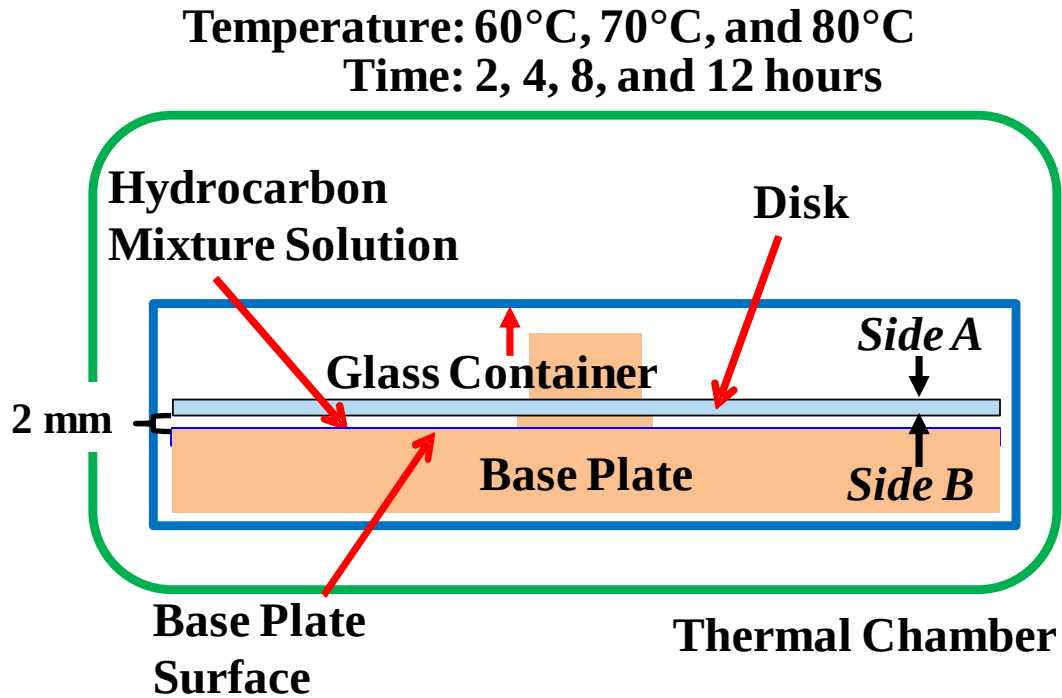


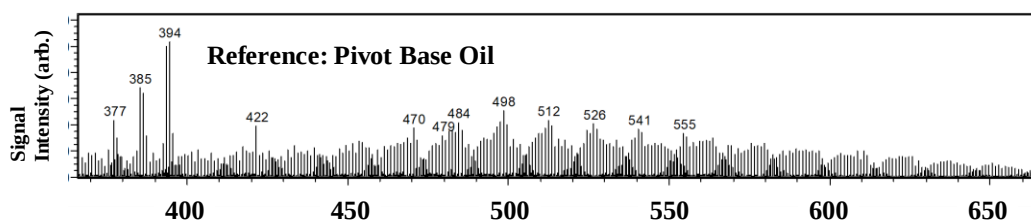
Figure 4.2 Schematic of hydrocarbon oil outgassing procedure (temperature: 60°C, 70 °C, 80 °C; time: 2 hours, 4 hours, 8 hours, 12 hours)

Hydrocarbon contamination may take months or years before it leads to failure of a hard disk drive [101]. In order to accelerate hydrocarbon contamination, the following experiment was performed. First, a mixture of a typical pivot base oil and four linear hydrocarbons (tetracosane: $C_{24}H_{50}$, octacosane: $C_{28}H_{58}$, dotriacontane: $C_{32}H_{66}$, and hexatriacontane: $C_{36}H_{74}$) was prepared at a ratio of 6:1:1:1:1. The pivot base oil is a mixture of mineral oils and poly-alpha olefins. Table 4.1 shows the physical data of the four hydrocarbons used in this study. The four linear hydrocarbon molecules were used as "signature" molecules to investigate the effect of molecular weight on hydrocarbon contamination. Then, a mixture of pivot oil and four linear hydrocarbons was applied on the top surface of the base plate (Figure 4.2), and a disk was positioned

approximately two mm above the base plate surface. The base plate and a spacing of 2 mm were chosen to allow uniform oil distribution on the disk surface. Thereafter, a glass container and aluminum foil were used to prevent external contaminants from getting on to the disk surface. Finally, the enclosure was placed in a thermal chamber and exposed to heat at a given temperature and time. The temperature ranged from 60°C to 80°C and time ranged from 2 hours to 12 hours. The condensation process is most likely driven thermodynamically due to chemically inert nature of hydrocarbon molecules. In other words, the adsorption of hydrocarbon on the disks surface may be described as physisorption rather than chemisorption. The temperature and time values were chosen to emulate the in-drive operating condition as closely as possible while accelerating the disk contamination process at the same time. During this step, the hydrocarbon mixture evaporates, and condenses on the disk, preferentially on *Side B*, the side closer to the base plate surface (Figure 4.2). After this step, the disk surface was investigated using an optical surface analyzer (OSA – Candela 6100) and an atomic force microscope (AFM).

Table 4.1 Physical data of hydrocarbons used [203-204]

Name	Formula	Density (g/mL)	MP** (°C)	MW [‡] (g/mol)	T _C [†] (K)	P _C ^{††} (MPa)
Tetracosane	C ₂₄ H ₅₀	0.799	52.0	338.65	811.1	1.051
Octacosane	C ₂₈ H ₅₈	0.807	64.5	394.77	844.0	0.954
Dotriacontane	C ₃₂ H ₆₆	0.812	69.0	450.88	872.0	0.889
Hexatriacontane	C ₃₆ H ₇₄	0.814	74.0 ~ 76.0	506.99	896.0	0.845
Pivot base oil*	C ₁₂ ~ C ₆₀	0.850	n/a	n/a	n/a	n/a



[‡] MP: melting point

^{‡‡} MW: molecular weight

[†] T_C: critical temperature

^{††} P_C: critical pressure

An optical surface analyzer (Candela 6100) and its proprietary software was used to recognize and count the number of scatter sites. After condensing, linear hydrocarbons form a crystal structure on the disk surface [205-206], the optical surface analyzer identifies the hydrocarbon crystals as “scatter sites” and maps them as shown in Figure 4.3(b). By counting the number of scatter sites, one can estimate the amount of hydrocarbon oil mixture condensed on the disk surface.

In order to eliminate contamination from other sources, the glass container and the base plate were washed thoroughly with methylene chloride (CH₂Cl₂) and isopropanol (C₃H₈O).

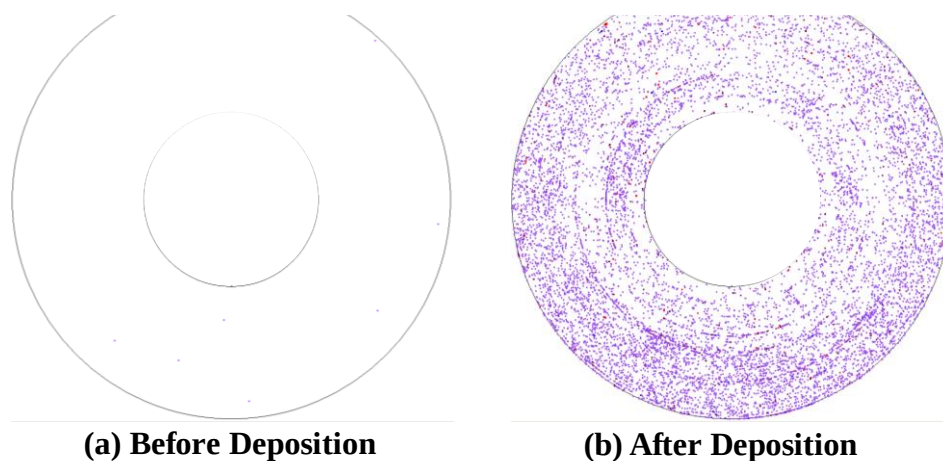


Figure 4.3 Disk surface (Side B) analyzed using an optical surface analyzer (a) before and (b) after hydrocarbon contamination. The disk was baked at 80°C for 12 hours in the presence of hydrocarbon oil mixture.

Figure 4.3 shows a clean, unused disk (Figure 4.3(a)) and a contaminated disk (Figure 4.3(b)). It is apparent from Figure 4.3(b) that hydrocarbon contamination is present over the whole disk surface. The results of Figure 4.3(b) are representative for the way hydrocarbon contamination occurs and should be interpreted as qualitative results, rather than quantitative results. The important point that should be emphasized is that the experimental procedure employed allows acceleration of head-disk interface contamination studies, i.e., instead of having to wait years for results, the chosen approach reduces the experimental time period from years to hours. Clearly, exposing a disk to a hydrocarbon oil mixture at elevated temperature causes contamination of the disk surface.

Disk Heat Exposure Experiment Results

In order to understand the effect of temperature and time on the number of scatter sites observed on the disk surface, we repeated the experiments for different temperature and time.

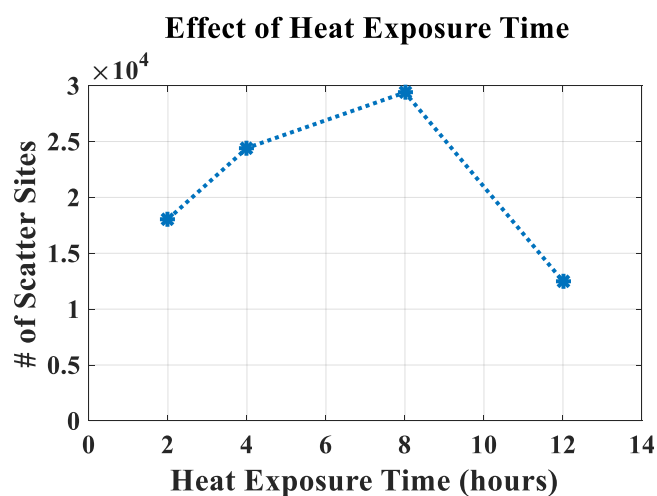


Figure 4.4 Effect of heat exposure time on the number of scatter sites at 80°C

Figure 4.4 shows the effect of time of heat exposure on the number of measured scatter sites on the disk surface. The results indicate that the number of contaminant sites increases initially with an increase in heat exposure time, but decreases after long exposure time. More testing would be required to be able to report the standard deviation for this data and to understand the reasons for this behavior.

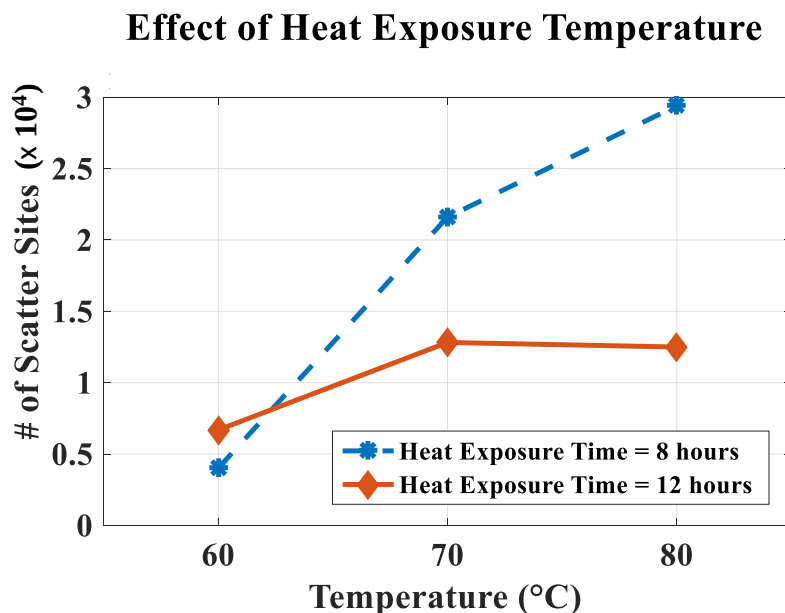


Figure 4.5 Optical surface analysis measurements of disk surface with hydrocarbon oil mixture condensed at 60°C, 70°C, and 80°C for 8 hrs. and 12 hrs.

In order to investigate hydrocarbon contamination of a disk surface in more detail, we repeated the previous experiments by keeping the temperature at 60°C, 70°C, and 80°C constant for 8 hours or 12 hours, respectively. Figure 4.5 shows the effect of temperature and heat exposure time on the total number of scatter sites. We observe that the total number of scatter sites increases with an increase in temperature for a heat exposure time of 8 hours. However, the number of scatter sites is smaller after 12 hours than after eight hours, as shown by the solid line in Figure 4.5 and the data point shown in Figure 4.4.

Although the decrease in the number of scatter sites with time is surprising, “zoomed-in” OSA images shown in Figure 4.6 for 8 and 12 hours are in qualitative agreement with Figure 4.4 and show that the data is not an artifact of the OSA measurement.

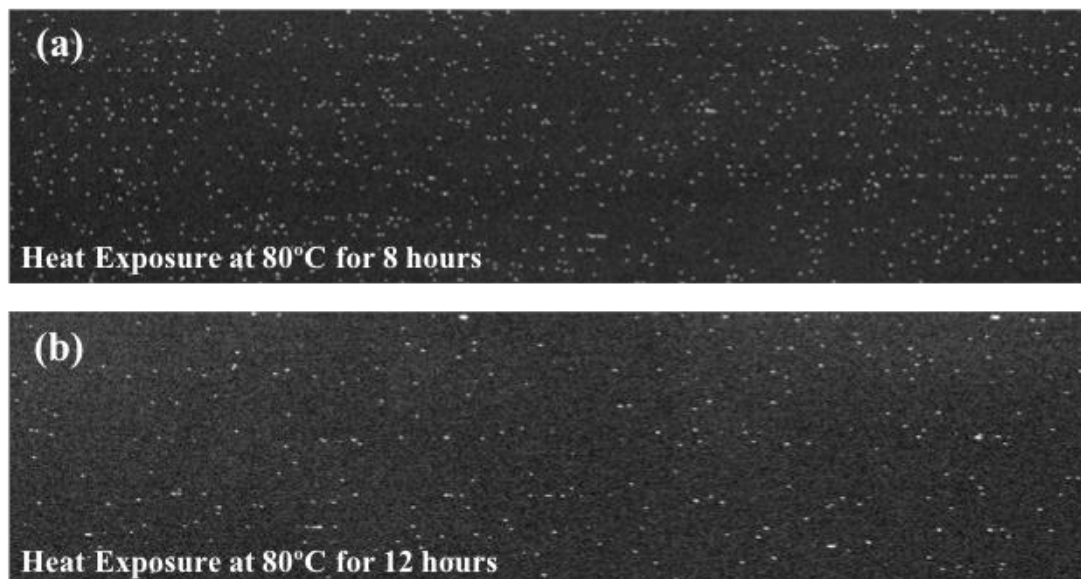


Figure 4.6 OSA images of a disk exposed to heat at 80°C for (a) 8 hours and (b) 12 hours

We hypothesize that the decrease in the number of scatter sites is related to the type of pivot base oil used, which is a mixture of mineral oils and poly-alpha olefins. Linear alkanes are packed together very tightly, forming a crystalline structure through Van der Waals attraction. However, pivot base oil inhibits crystallization of linear alkanes, resulting in a reduction of scatter sites as shown in Figure 4.4. Further experimental results are needed to investigate this hypothesis in more detail.

To analyze the morphology of the adsorbed contaminants on the disk surface, we used atomic force microscopy. From the AFM measurements, two types of contaminants were observed: crystal-like contaminants and droplet-like contaminants. Repeated AFM scans did not change the morphology of contaminants.

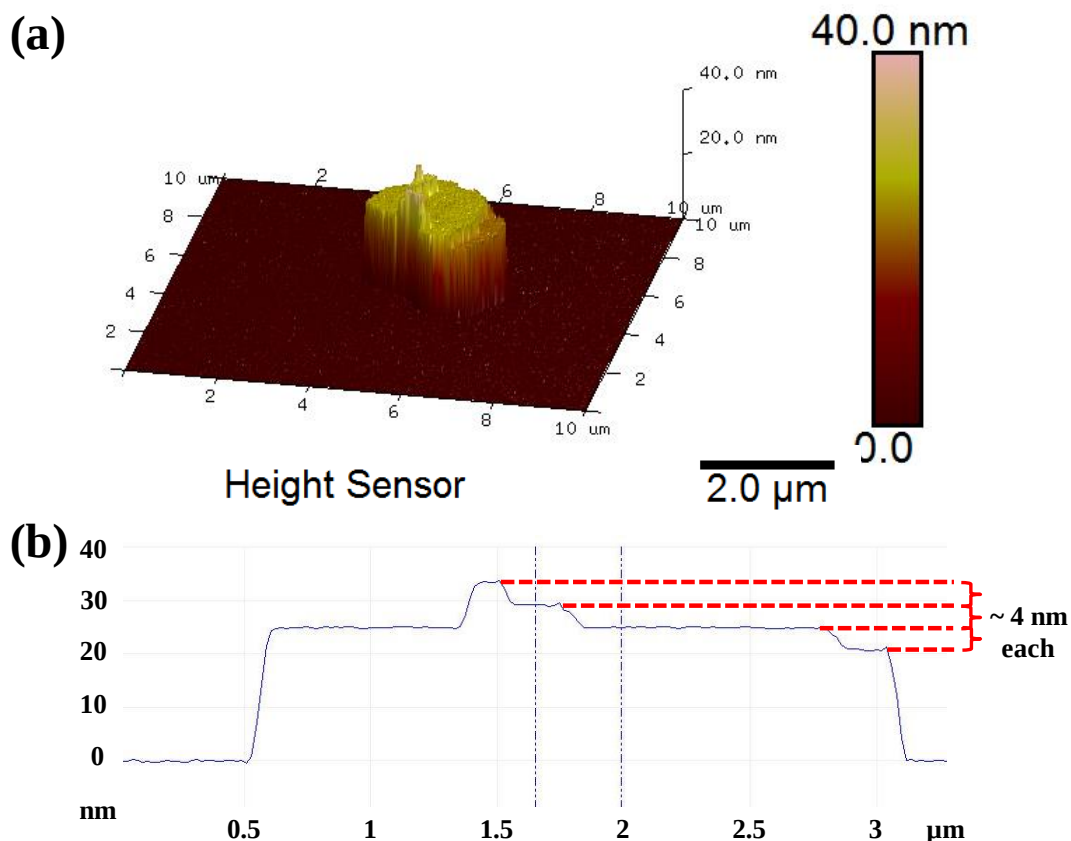


Figure 4.7 AFM scan on a disk after heat exposure for 8 hours at 60°C (a) 3D image and (b) cross-section of contaminant

Figure 4.7 shows AFM results for typical contaminants found on a disk surface. We observe a terrace-like crystal structure with walls nearly perpendicular to the disk surface. A number of researchers [205-206] have studied the characteristics of thin hydrocarbon films and concluded that they are thermodynamically stable in the state of perpendicular orientation. From these studies as well as our own AFM measurements, we can conclude that these solid-like contaminants on the disk surface are straight-chain hydrocarbons oriented vertically. As shown in Figure 4.7(b), the average stack height is observed to be approximately 4 nm. For comparison, the extended chain length of C_{24}

is 2.9 nm and the length of C_{36} is 4.4 nm. It is therefore justifiable to conclude that the observed crystals are likely crystallized linear hydrocarbons.

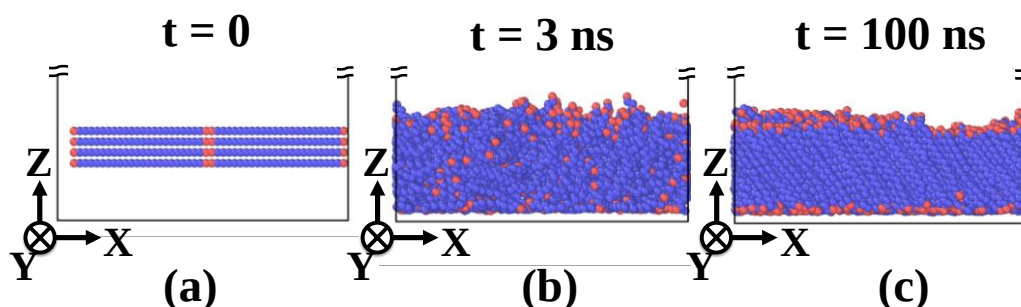


Figure 4.8 Crystallization of $C_{24}H_{50}$ (tetracosane) using molecular dynamics simulation.

To investigate whether the linear hydrocarbon chains in the used mixture could form a crystalline structure at room temperature, we used molecular dynamics simulation and employed the so-called “united atom model (UAM).”

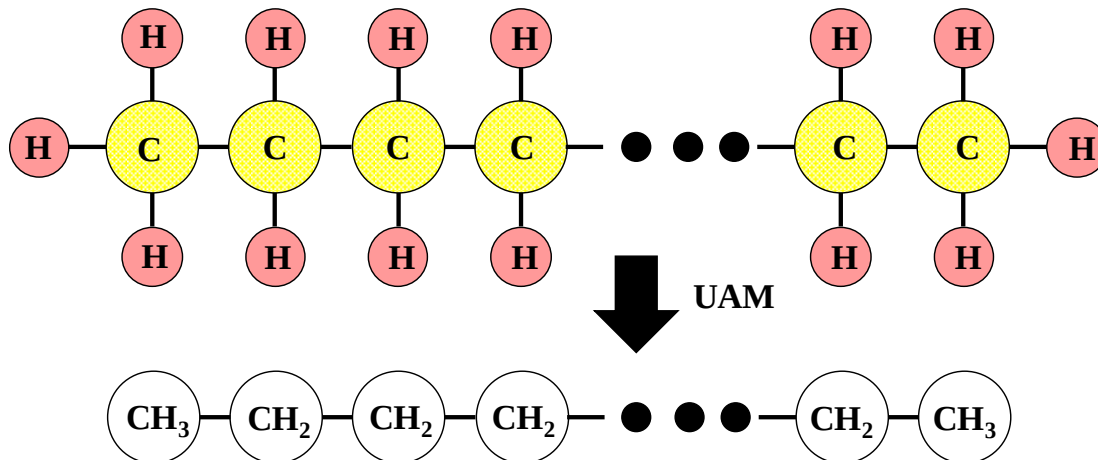


Figure 4.9 Schematic of “United Atom Model” of a linear hydrocarbon chain

As shown in Figure 4.9, the UAM approach models CH_2 and CH_3 as beads in order to reduce computational cost while accurately reproducing thermodynamic properties of linear hydrocarbon chains [214]. Using the *Large-scale Atomic/Molecular*

Massively Parallel Simulator (LAMMPS) [191] and appropriate potential functions and corresponding parameters [162, 191, 214-218], we were able to simulate the crystallization of linear hydrocarbon chains.

For non-bonded interactions, we used the Lennard-Jones potential function given by Equation 3.13:

$$U_{\text{LJ}} = 4\varepsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right], \quad r < r_c \quad (3.13)$$

where ε is 0.112 kcal/mol, $\sigma = 4.5\text{\AA}$, and $r_c = 12\text{\AA}$. The bond interaction was described as linear harmonic potential function given by Equation 3.5:

$$U_{\text{Bond}} = K_L(r - r_o)^2 \quad (3.5)$$

where $K_L = 350 \text{ kcal/mol } \text{\AA}^2$ and $r_o = 1.53\text{\AA}$. The angular bond interaction for linear hydrocarbon chains was simulated by the following potential function (Equation 3.9):

$$U_{\text{Angle}} = K_\theta(\theta - \theta_o)^2 \quad (3.9)$$

where $K_\theta = 60 \text{ kcal/mol rad}^2$ and $\theta_o = 109.5^\circ$, or 1.91 rads. The dihedral bond interaction for the molecules was given by Equation 3.11:

$$U_{\text{Dihedral}} = \frac{1}{2}k_1(1 - \cos\varphi) + \frac{1}{2}k_2(1 - \cos2\varphi) + \frac{1}{2}k_3(1 - \cos3\varphi) \quad (3.11)$$

where $k_1 = 1.6 \text{ kcal/mol}$, $k_2 = 0.867 \text{ kcal/mol}$, and $k_3 = 3.24 \text{ kcal/mol}$. Lastly, for the wall-atom interaction was modeled using the following potential function:

$$U_{\text{Wall-Atom}} = 2\pi\varepsilon_w \left[\frac{2}{5} \left(\frac{\sigma_w}{z} \right)^{10} - \left(\frac{\sigma}{z} \right)^4 - \frac{\sqrt{2}\sigma^3}{3(z + (0.61/\sqrt{2})\sigma)^3} \right], \quad z < z_c \quad (4.1)$$

where $\varepsilon_w = 1.0 \text{ kcal/mol}$, $\sigma_w = 3.8\text{\AA}$, and $z_c = 9.5\text{\AA}$.

The linear hydrocarbon chains were first positioned as shown in Figure 4.8(a). Then, we imported the position data and applied the above potential functions in

LAMMPS [184]. The MD simulation was first carried out in the canonical (NVT) ensemble with a time step size $\Delta t = 2$ fs. An NVT ensemble is a thermo-statistical system in which the number of atoms (N), the volume of the simulation box (V), and the temperature (T) are kept constant. With the NVT ensemble, we randomly distributed the linear hydrocarbon chains for 100,000 time steps (Figure 4.8(b)). The system was then equilibrated at 450K for a total of 600,000 time steps. Thereafter, we used the microcanonical ensemble (NVE) and the Langevin thermostat to quench the equilibrated system of linear hydrocarbon chains to 290K for 1,000,000 time steps, at a cooling rate of $1.5 \times 10^{11} \text{ K/s}$. The system was then equilibrated at 300K for 50,000,000 time steps in order to grow crystals of linear hydrocarbon chains as shown in Figure 4.8(c).

The simulation results showed that the height of single-stack C_{24} crystals is approximately 3 nm, confirming the experimental observations. Using the same molecular dynamics approach, we also investigated C_{36} hydrocarbons and found that the predicted crystal height is about 4 nm. Clearly, that the growth of contaminants observed from molecular dynamics studies is consistent with the presence of linear hydrocarbon chains in the hydrocarbon oil mixture.

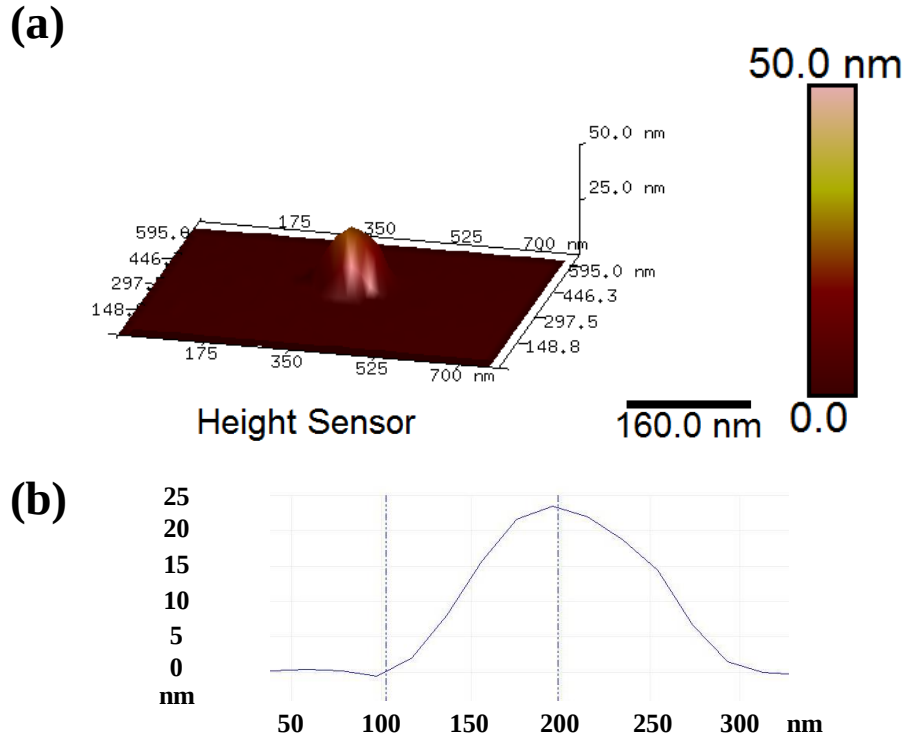


Figure 4.10 Droplet-like contaminant: (a) 3D image and (b) cross-section of typical droplet observed

AFM results also showed droplet-like contaminants on the disk surface as in Figure 4.10. The contact angle, calculated from measured profile data, was about 53° . In order to verify that the droplet-like contaminants are hydrocarbon oil mixture, additional investigations were carried out using contact angle measurements.

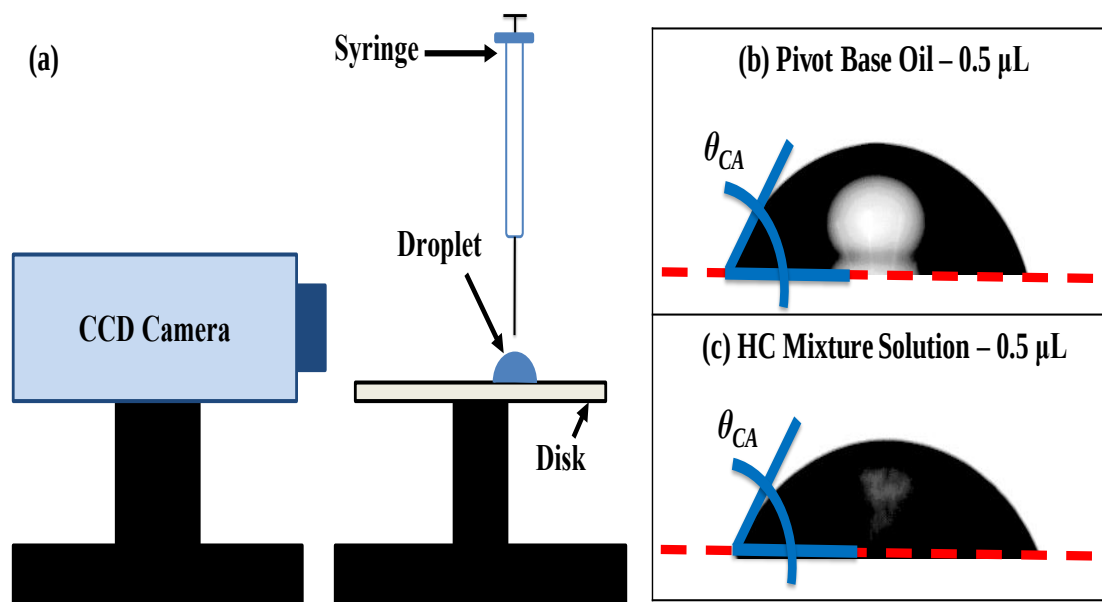


Figure 4.11 (a) Schematic of contact angle measurement. Contact angle measurements on 0.5 μL droplets of (b) pivot base oil, and (c) pivot base oil mixed with four linear hydrocarbons. Dashed line represents the disk surface.

Figure 4.11(a) shows the schematic of the experimental setup for contact angle measurement. Images of droplets were captured within 20 seconds to eliminate errors due to droplet spreading [207]. Figure 4.11(b) and (c) show droplet images of HC oil droplets of 0.5 μL volume at room temperature of 23°C.

Image analysis was performed using open-source image processing software (*ImageJ*) [208]. Pivot base oil has a contact angle of 65°, while hydrocarbon oil mixture has a contact angle of 55°, within 2° of the AFM measurements. The dispensed droplets were much larger in volume compared to those studied with atomic force microscopy. However, investigation by Taylor et al. [209] have shown that contact angle measurements are independent of the volume used. Thus, the contact angle analysis

supports our conjecture that the droplet-like contaminants observed on the disk surface are indeed hydrocarbon oil mixture.

4.2.2 Slider Surface Contamination

Experiment Procedure

After studying the adsorption characteristics of the hydrocarbon oil mixture on a disk surface, an experimental procedure was developed to contaminate slider surfaces. This procedure consisted of placing a contaminated disk in a spin-stand tester (VENA-VS90), flying a slider at very close spacing, and setting appropriate environmental condition for hydrocarbon contaminants and lubricant transfer to occur at the head-disk interface. Figure 4.12 shows the experimental setup involving the spin-stand tester.

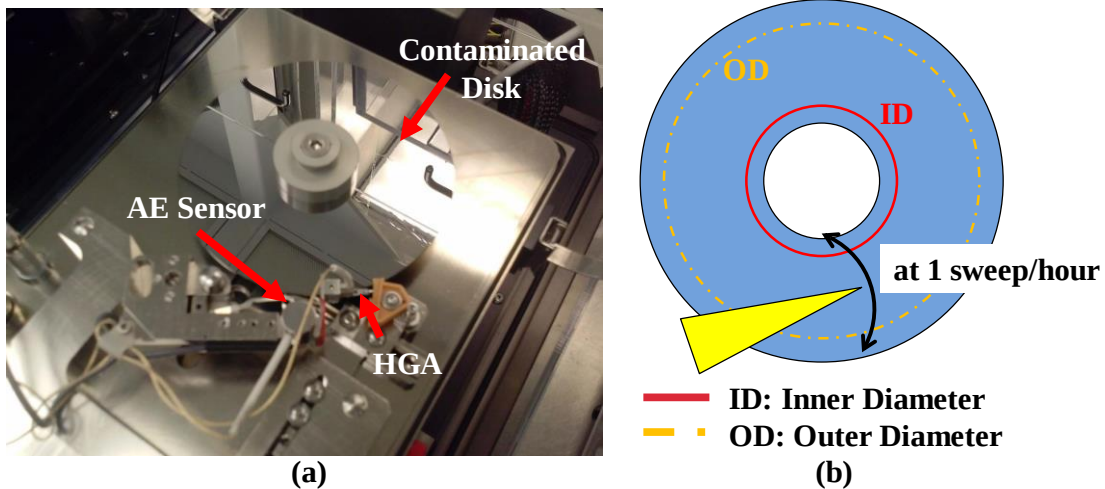


Figure 4.12 (a) Spin-stand tester (VENA-VS90). (b) Schematic of “sweep test” using the spin-stand tester

A contaminated disk was placed on the spindle as shown in Figure 4.12(a). Then, a “down-facing”, clean head-gimbal assembly (HGA) was attached to the spin-stand tester. In order to minimize head-disk interface contamination from external

contaminants, the spin-stand tester was located in a cleanroom class 100 environment. After mounting the disk and the HGA, we used an environmental chamber (VENA-VC10) to isolate the tester from its surroundings. An environmental controller was utilized to control temperature inside the chamber. The temperature was equilibrated at the desired value for 1 hour before conducting any experiment. This process was followed in order to be certain that the temperature at the head-disk interface would be close to the desired temperature. Then, the disk was rotated at a rotational speed of 7,200 rpm. Thereafter, the HGA was controlled to sweep the disk surface from the inner diameter (ID or 22 mm) to the outer diameter (OD or 41 mm), and vice versa, at a rate of one sweep per hour, as shown in Figure 4.12 (b). The rate of “one sweep per hour” is much slower than sweep speeds encountered typically during normal hard disk drive operations. This slow sweep speed was used intentionally in order to accelerate the contamination transfer process from the disk to the slider surface. In a “sweep test”, “one” sweep was defined as the slider traveling from ID to OD, or OD to ID. Sweep tests lasted for 4 or 12 hours in an effort to increase the transfer of hydrocarbon oil onto the slider surface. Details of the sweep testing and the disk surface exposure conditions presented in this paper are shown in Table 4.2.

Table 4.2 Sweep Test Conditions

Test #	Disk Exposure Temp.	Disk Exposure Time	Chamber Temp.	Duration	Nominal FH*	TFC** On/Off (B.O. [‡])
1	80°C	8 hrs.	50°C	4 hrs.	10 nm	On (10 mW)
2	80°C	12 hrs.	60°C	4 hrs.	10 nm	On (5 mW)
3	60°C	12 hrs.	60°C	4 hrs.	10 nm	Off (N/A)
4	80°C	8 hrs.	60°C	4 hrs.	10 nm	On (10 mW)
5	80°C	2 hrs.	50°C	4 hrs.	10 nm	On (10 mW)
6	80°C	8 hrs.	60°C	12 hrs.	10 nm	Off (N/A)

* FH: flying height

**TFC: thermal flying height control

‡ B.O.: “back-off” power

After completion of the sweep tests, all sliders were analyzed using optical microscopy, scanning electron microscopy (SEM), and time-of-flight secondary ion mass spectrometry (ToF-SIMS), respectively.

Sweep Test Results

Optical microscopy was used to determine whether visible contamination was present [101, 103]. Figure 4.13 shows optical images of a typical slider surface after a sweep test of 4 hours at 50°C. Prior to sweep testing, the disk was exposed to hydrocarbon contamination for 8 hours at 80°C.

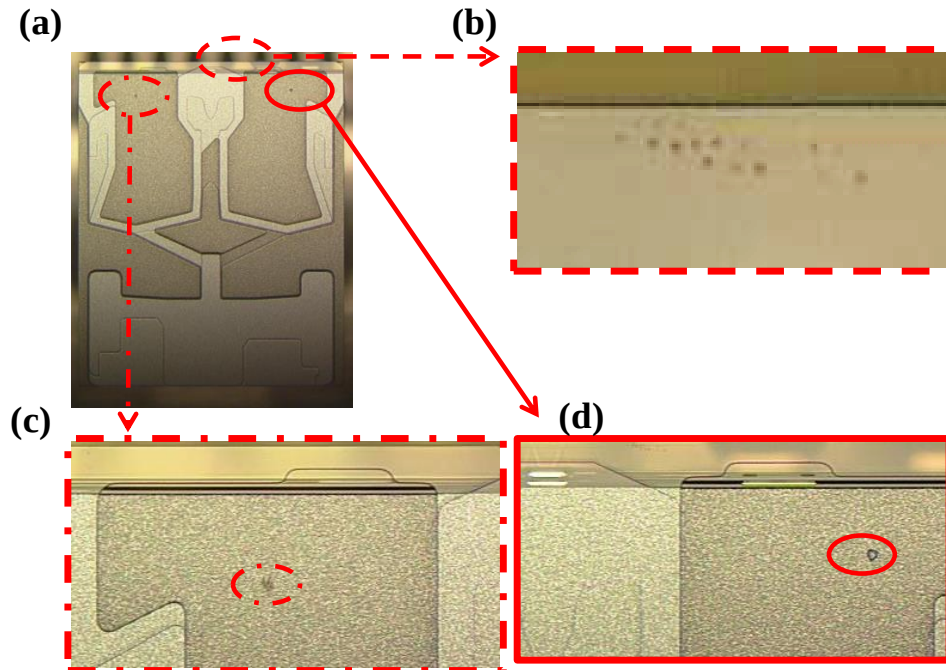


Figure 4.13 Slider surface after sweeping over a contaminated disk surface at a temperature of 50°C for 4 hours. (a) Contaminated air bearing surface. (b) Droplets formed at the trailing edge. (c) and (d) Contaminants in the air bearing cavities. Prior to the sweep test, the disk surface was exposed to hydrocarbon contaminants for 8 hours at 80°C

A clean and unused slider shows typically no signs of contamination under an optical microscope using 200x magnification. On the other hand, the slider shown in Figure 4.13 clearly shows signs of contamination on the shallow step at the trailing edge near the read/write shields, as well as on the cavities on the slider near the trailing edge. This contamination result is similar to results reported in Ref. [101] and Ref. [103]. The largest contamination sites are indicated with circles in Figure 4.13.

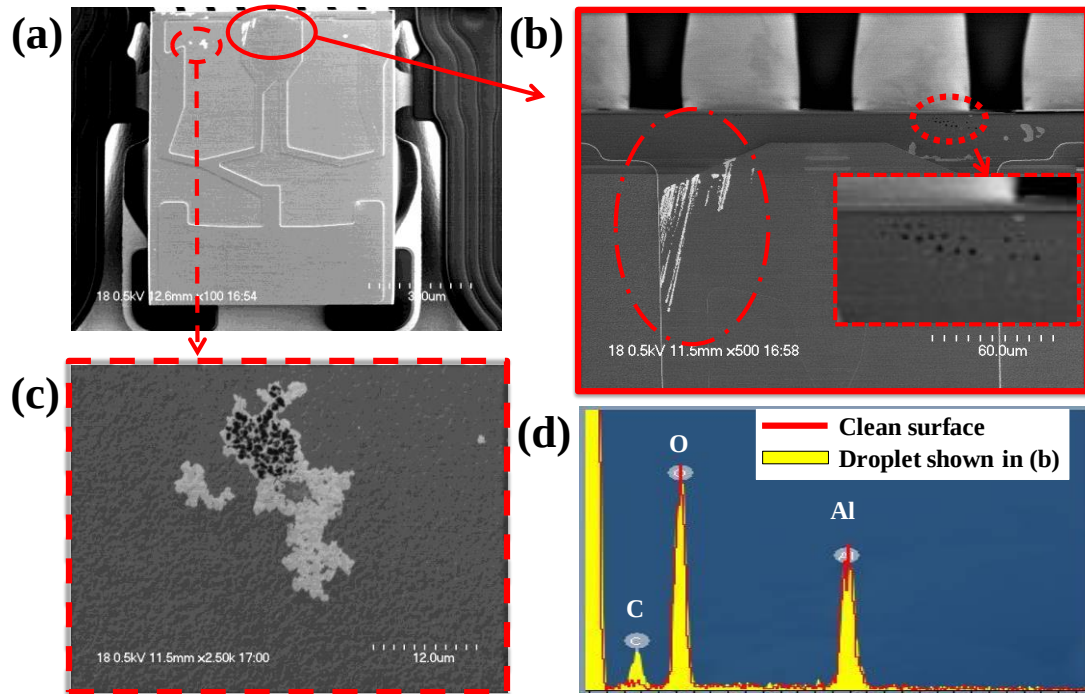


Figure 4.14 SEM analysis of the slider surface shown in Figure 4.13. (a) SEM image of the entire air bearing surface, (b) Signs of “smearing” and droplet formation near the pole-tip region, (c) Crystallized hydrocarbon in the air bearing cavity, (d) EDX analysis of droplets shown in (b)

For the same head, SEM images showed more contaminants at low accelerating voltage of 0.5kV than could be seen using optical microscopy (Figure 4.13). During the sweep test, thermal flying height control (TFC) was applied. Three types of contaminants were observed with scanning electron microscopy. Figure 4.14(b) shows “smear-like” deposits. In addition, droplets on the shallow step at the trailing edge were detected with the SEM. Finally, as shown in Figure 4.14(c), contaminants with dendritic morphology were observed in the cavity of the air bearing surface, suggesting crystallization of linear hydrocarbon chains. In order to verify that the transferred contaminants were indeed hydrocarbon oil mixture, energy-dispersive X-ray spectroscopy (EDX/EDS) was used on one typical droplet. Figure 4.14(d) shows typical

EDX results in line format, indicating two peaks for alumina (Al_2O_3). Results from EDX analysis of a droplet are shown in Figure 4.14(d). In addition to peaks for oxygen and aluminum, a carbon peak can be seen. Since fluorine was not detected, the droplet was likely a hydrocarbon oil mixture, rather than PFPE lubricant.

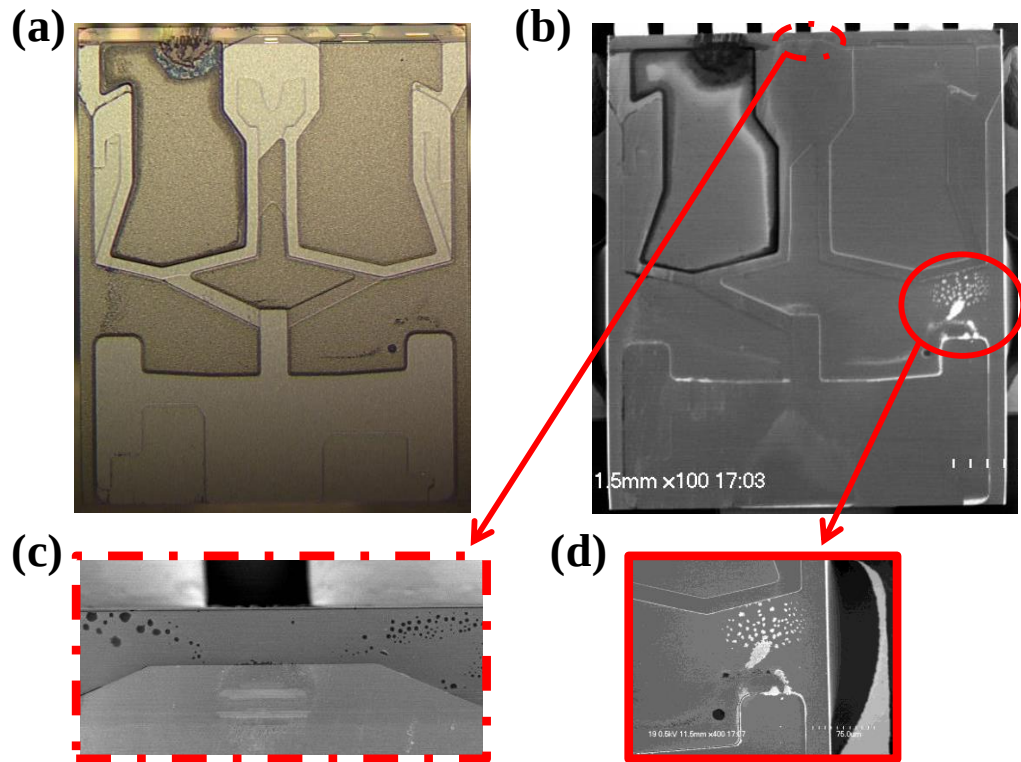


Figure 4.15 Slider surface after sweep testing at 60°C for 4 hours. (a) Optical microscope image of the slider air bearing surface. (b) SEM image of the slider air bearing surface. (c) Droplet on the trailing edge near the pole tip region. (d) Crystallized hydrocarbon in the air bearing cavity near the leading edge. Prior to sweep testing, the disk surface was exposed to a hydrocarbon oil mixture for 12 hours at 80°C

In order to avoid slider contact with hydrocarbon crystals on the disk surface, the temperature of the spin-stand chamber was raised to 60°C. This temperature was chosen after a series of experiments were conducted in which we observed that heads were flying most stably at the environment temperature of 60°C compared to lower

temperatures. Figure 4.15 shows a slider surface after sweep testing over a contaminated disk for 4 hours at 60°C. The disk was exposed to a hydrocarbon oil mixture for 12 hours at 80°C. The thermal flying height control function of the slider was activated during the experiment. Figure 4.15(a) shows microscope images of a contaminated slider surface. The left cavity near the trailing edge is “flooded” with an oil-like substance. Figure 4.15(b) shows an SEM image of the air bearing surface. Again, heavy contamination can be observed near the trailing edge cavity, similar to the topical image in Figure 4.15(a). Focusing on the pole-tip region (Figure 4.15(c)), we observe many droplets near the trailing edge. Figure 4.15(d) shows the cavity near the leading edge of the air bearing surface, indicating droplets and contaminants of “dendritic” morphology. EDX was used to analyze these crystals.

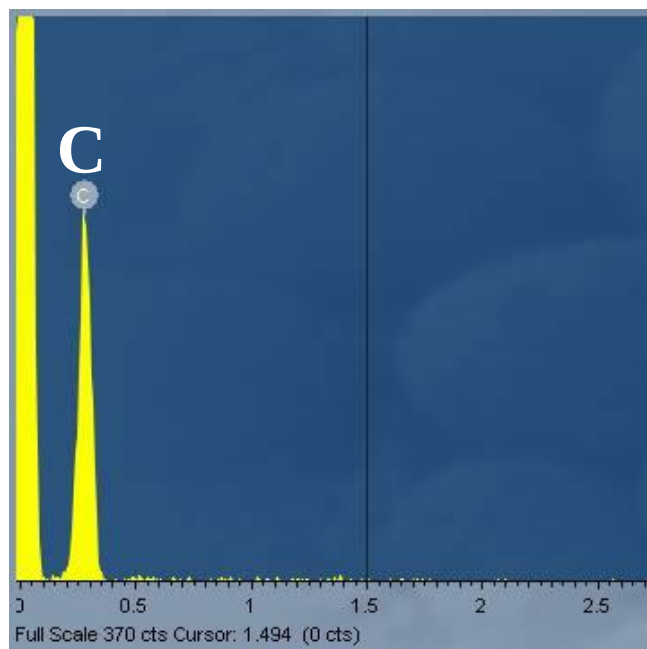


Figure 4.16 EDX analysis of the crystals shown in Figure 4.15(d)

As shown in Figure 4.16, EDX analysis of the leading edge cavities showed a high carbon peak. This indicates that the contaminants on the slider surface are likely to be hydrocarbon oil mixtures.

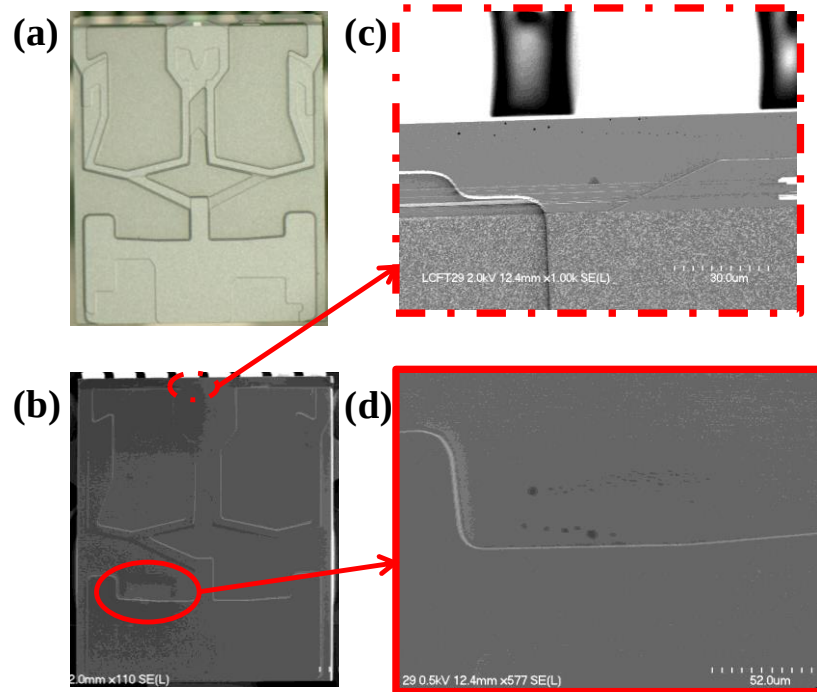


Figure 4.17 Slider surface after sweep testing for 4 hours at 60°C. (a) Optical microscope image of the slider surface. (b) SEM image of the entire air bearing surface. (c) Droplets formed on the trailing edge near the pole-tip region. (d) Droplets formed in the air bearing cavity near the leading edge. Prior to sweep testing, the disk surface was exposed to a hydrocarbon oil mixture for 12 hours at 60°C

Figure 4.17 shows microscope and SEM images after sweep testing for 4 hours at 60°C. The disk surface was exposed to a hydrocarbon oil mixture for 12 hours at 60°C. The thermal flying height control was not used in this test, i.e., the slider was flying at 10 to 12 nm. Using optical microscopy, we did not observe any signs of hydrocarbon contamination (Figure 4.17(a)). However, when the slider was subjected to low voltage SEM analysis, hydrocarbon oil droplets were observed on the trailing edge and the air bearing cavity near the leading edge.

Thus, optical microscopy and SEM results showed that transfer of hydrocarbon molecules can occur at the head-disk interface in the absence of head-disk contact. In order to determine the chemical composition of the contaminants, three sliders were selected for ToF-SIMS analysis after sweep testing. The results from the ToF-SIMS analysis are shown in Figure 4.18.

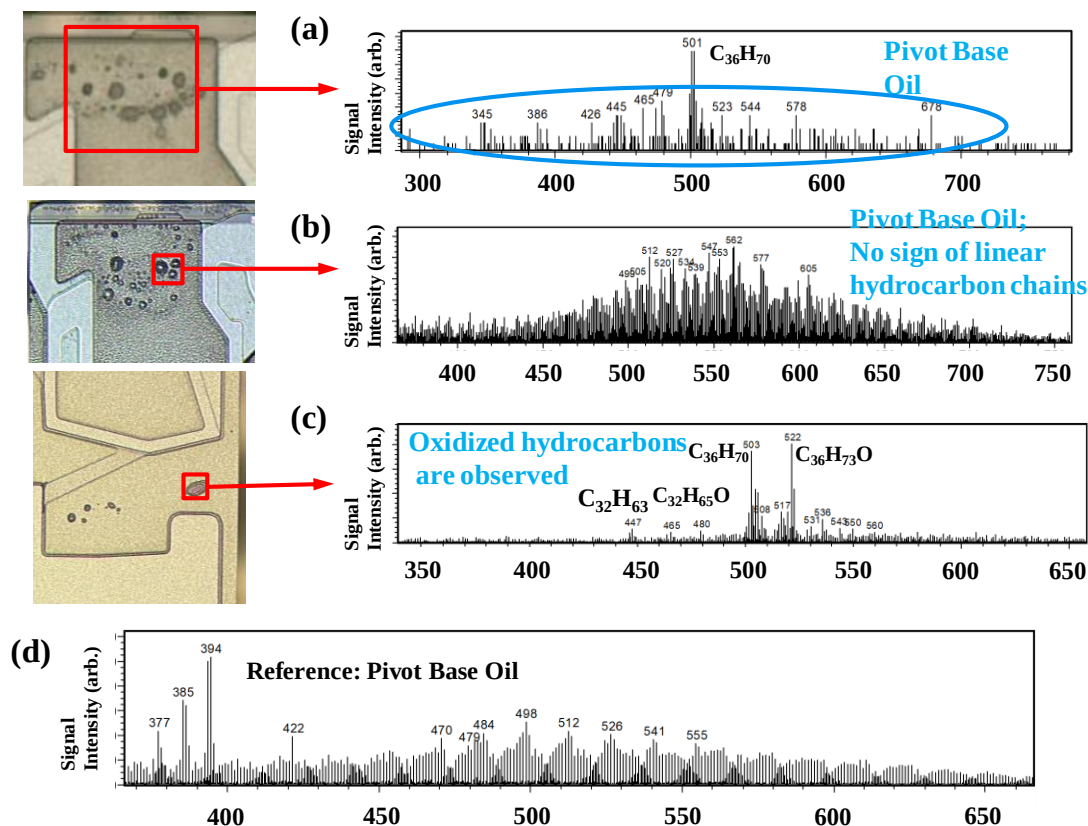


Figure 4.18 ToF-SIMS results of contaminants on different slider surfaces of the same air bearing design (a) Slider 1, (b) Slider 2, (c) Slider 3, and (d) reference ToF-SIMS result of pivot base oil

Figure 4.18 shows three sliders of the same air bearing design and their corresponding time-of-flight secondary ion mass spectrometry (ToF-SIMS) results after sweep testing. The reference spectrum of the pivot base oil is also shown.

In this experiment, a mixture of pivot base oil and four straight-chain hydrocarbons was used to contaminate the disk surface. Subsequently, the contaminants were transferred to the slider surface during sweep testing. ToF-SIMS was used to determine which type of hydrocarbon molecules were transferred to the slider surface. On *Slider 1*, Figure 4.18(a), hydrocarbon molecules and pivot base oil molecules were observed. Hydrocarbon chains of C_{24} , C_{28} , and C_{32} were absent, even though they were present in the contaminant solution that was prepared for the experiment. *Slider 2* showed no sign of linear hydrocarbon contaminants, only pivot base oil, as shown in Figure 4.18(b). Comparing Figure 4.18(a) and Figure 4.18(b) with the pivot base oil reference spectrum in Figure 4.18(d), we conclude that the observed droplets were pivot base oil. *Slider 3* in Figure 4.18(c) showed oxidized hydrocarbon molecules. Similar to Figure 6.18(a), C_{24} and C_{28} were not present on the third slider surface. The ToF-SIMS results verified that the deposited pivot base oil and straight-chain hydrocarbon chains transferred from the disk to the slider surface.

Sweep testing showed strong evidence that the proposed three-step hydrocarbon transfer mechanism hypothesis is a viable hypothesis. The optical microscope results as well as the SEM and ToF-SIMS results showed that the contaminants observed on the slider surface were indeed mixtures of pivot base oil and linear hydrocarbon oil exposed to the disk surface. We could not detect any signs of C_{24} or C_{28} . As shown in Figure 4.18, the ToF-SIMS detected C_{32} and C_{36} only. The absence of light hydrocarbon molecules is interesting and may be explained by the following. Hydrocarbon molecules first transfer onto the disk surface. However, those with low molecular weight, namely C_{24} and C_{28} , evaporate or outgas from the disk surface since they are highly volatile, i.e.,

hydrocarbons with lower molecular weight are prone to transfer at a higher rate than those with heavier molecular weight. This is evidenced by the vapor pressure [210-211] and the desorption energy barrier [212-213] of hydrocarbons.

Chirico et al. measured vapor pressure of n-decane ($C_{10}H_{22}$), n-eicosane ($C_{20}H_{42}$), and n-octacosane ($C_{28}H_{58}$) [210]. They observed that at constant temperature, n-octacosane has the lowest vapor pressure. Also, Morgan and Kobayashi [211] performed direct vapor pressure measurements of hydrocarbons ranging from n-decane to n-octacosane, and observed that heavier hydrocarbons have lower vapor pressure than light hydrocarbons. Expressed differently, heavier hydrocarbon molecules evaporate at a lower rate than lower weight ones. Desorption behavior of hydrocarbons is another important factor to explain our results. Gellman and Paserba [212-213] studied the desorption of hydrocarbons from graphite surface. They observed that the desorption energy barrier can be approximated by

$$\Delta E_{\text{des}} = -29 + 42N^{0.5} \quad (4.2)$$

where ΔE_{des} is the desorption energy barrier in kJ/mole and N is the chain length of the hydrocarbon used. Hydrocarbons with longer chain lengths have a higher desorption energy barrier, i.e., more energy is required to separate C_{60} from a graphite surface than C_{10} .

In summary, the experimental work in this section successfully illustrated that airborne hydrocarbon molecules can transfer from the disk surface to the slider surface without actual head-disk contact present.

4.3 Numerical Investigation

4.3.1 Molecular Dynamics Modeling

Molecular dynamics modeling is a time-consuming and complicated numerical procedure [146]. Most accurate results are obtained, in general, if all calculations are performed at the atomic level. However, computation times for atomic level calculations are generally very long. Thus, in order to reduce computational time while still simulating the main physical characteristics of the transfer process, we implemented a so-called “coarse-grained bead spring” (CGBS) model which “lumps” a number of individual atoms into a “bead”. This reduces the complexity of the numerical calculations.

A serious limitation that arises in molecular dynamics simulations is the difference in scaling between the actual head-disk interface and the modeled head-disk interface. The footprint of a typical air bearing surface is $800\text{ }\mu\text{m} \times 700\text{ }\mu\text{m}$. The time scale of interest is on the order of hours, months, or even years. However, typical molecular dynamics can only simulate a length scale on the order of nanometers, and calculation times are not longer than a few nanoseconds.

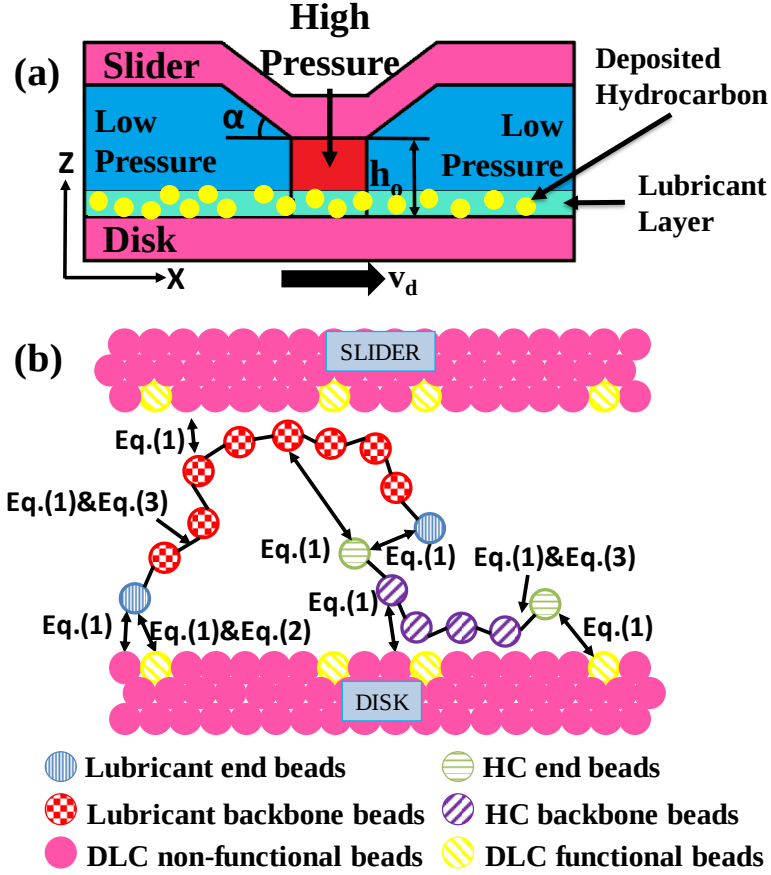


Figure 4.19(a) Schematic of the simulation for a typical air bearing step and (b) coarse-grained bead spring model of disk, slider, lubricant, and hydrocarbon molecules, in which intermolecular and intramolecular interactions are modeled using Eq.(1)-LJ, Eq.(2)-EXP, and Eq.(3)-FENE potential functions

In Figure 4.19(a), a schematic of the head-disk interface model used in references [93, 228] is shown. This model was modified and used in the present paper to study hydrocarbon contamination at the head-disk interface. Similar to the model in [93, 228], we assume that the disk has a perfectly flat diamond-like carbon overcoat. A lubricant layer is assumed to be deposited on the carbon overcoat. The slider surface was modeled to show a typical air bearing feature, consisting of a step with a converging and diverging air bearing channel defined by the convergence angle α . Also, low and

high pressure regions are assumed to be present as shown in Figure 4.19(a). Linear hydrocarbons were introduced as contaminants to the head-disk interface in addition to Zdol 2000 PFPE lubricant molecules. In our simulation, each Zdol 2000 perfluoropolyether (PFPE) molecule was modeled with two “end beads” and eight “backbone beads” in order to characterize the interactions between the hydroxyl (-OH) groups, i.e., the “end beads” of the lubricant molecule and the functional groups on the disk or the slider surface. In addition, linear hydrocarbon chains were approximated by one hydrocarbon bead to represent four methyl (-C₄H₈-) groups. The hydrocarbon end beads are indicated in different color and pattern in order to represent heavier molecular weight of -C₄H₁₀. Unlike PFPE lubricant end beads, hydrocarbon end beads are not functional.

Figure 4.19(b) shows a schematic of intra- and inter-molecular interactions for the disk, the slider, the PFPE lubricant, and the hydrocarbon molecules using the Lennard-Jones potential function, the short-range attractive polar potential function, and the finitely extensible nonlinear elastic potential function. To describe the Van der Waals forces among the molecules, the truncated 12-6 Lennard-Jones potential function (Equation 3.14) was used, i.e.,

$$U_{LJ}^{Truncated} = 4\varepsilon_{LJ} \left[\left(\frac{\sigma_{LJ}}{r} \right)^{12} - \left(\frac{\sigma_{LJ}}{r} \right)^6 - \left(\frac{\sigma_{LJ}}{r_c} \right)^{12} + \left(\frac{\sigma_{LJ}}{r_c} \right)^6 \right] \quad (3.14)$$

where σ_{LJ} is the bead diameter (reduced LJ unit of length), r is the distance between two beads, r_c is the cutoff distance, and ε_{LJ} is the potential well-depth of the 12-6 Lennard-Jones potential function (reduced LJ unit of energy). In addition, the short range attractive polar (EXP) potential function (Equation 3.16) was used to describe the

interaction energy between the hydroxyl groups of the Zdol 2000 molecules and the functional groups on the diamond-like carbon surface [167]:

$$U_{\text{EXP}} = -\varepsilon^p \exp\left(-\frac{r - r_c}{d}\right) \quad (3.16)$$

where d is the characteristic length between two neighboring beads for short-range polar interactions. Lastly, the intramolecular interaction between two beads was described by a nonlinear harmonic oscillator. Here, a so-called finitely extensible nonlinear elastic (FENE) potential function (Equation 3.6) was used [159].

$$U_{\text{FENE}} = \frac{1}{2} k_{\text{FENE}} R_0^2 \ln \left[1 - \left(\frac{r_{12}}{R_0} \right)^2 \right] \quad (3.6)$$

where R_0 is the maximum extent of the nonlinear “spring” and k is the “spring” constant [90]. Also, for computational convenience, the simulations were performed in dimensionless units where σ is the non-dimensional unit of length, τ the non-dimensional unit of time, and ε the non-dimensional unit of energy.

Using the simulation parameters as used by Deng et al. [228] and Seo et al. [93], we have simulated the hydrocarbon and lubricant transfer process as a function of (a) temperature T , (b) minimum spacing between head and disk $H_{\min}$, and (c) hydrocarbon chain length. In this simulation study, the bead diameter σ is assumed to be 0.7 nm and the mass of a PFPE lubricant bead is 0.2 kg/mol , and the disk velocity is $2.5 \sigma/\tau$. Due to limitation of our coarse-grained bead spring model, we can only provide approximate values for ε and τ . Energy ε is on the order of 10^{-21} J and time τ on the order of 100 ps . From this, we estimated the disk velocity of $2.5 \sigma/\tau$ to be on the order of 10 m/s . Also, for all simulations in this paper, the ratio of functional to non-functional DLC beads was kept constant at 5% for both the disk and the slider surface.

In this simulation, we assumed that the lubricant layer is already contaminated with hydrocarbon molecules. Similar to our previous studies, the molecular dynamics simulation was divided into two parts [93, 228]. First, the simulation was run using the so-called “canonical (NVT) ensemble” with a cutoff distance r_c of $2^{1/6}$ in order to randomly deposit perfluoropolyether lubricant and hydrocarbon molecules on the disk surface [93, 228]. An NVT ensemble is a statistical ensemble in which probability distribution of states depends on the number of particles (N), the volume of the simulated system (V), and the absolute temperature (T) of the system. In our simulations, a temperature of $1 \text{ } \epsilon/k_B$ was assumed, where k_B is the Boltzmann constant. Lastly, a time step size of 0.005τ was chosen. A total number of 140,000 simulation steps was taken for the first part of the simulation. After establishing the distribution of hydrocarbon and lubricant molecules on the disk surface, the slider was brought to a desired spacing H_{min} . Then, the simulations were performed using the parameters listed in Table 1, assuming a “microcanonical (NVE) ensemble” with a cutoff distance r_c of 2.5σ [93, 228]. An NVE ensemble is a statistical ensemble in which the probability distribution of states depends on the number of particles (N), the volume of the simulated system (V), and the energy (E) of the system. In this part of the simulation, the time step size was decreased to 0.0005τ . The calculation was carried out using the *Large-scale Atomic/Molecular Massively Parallel Simulator* (LAMMPS) code [191]. After a total of 1,640,000 simulation time steps corresponding to a simulation time of 820τ , the results were post-processed using MATLAB.

Table 4.3 Parameters for the molecular dynamics simulation model

Symbol	Name	Value (Reduced LJ unit)
T	Temperature	1.0, 1.2, 1.4, 1.6, 1.8 [ϵ/k_b]
H_{min}	Minimum spacing	7, 10, 30, 100, 145 [σ]
V_d	Disk velocity	2.5 [σ/τ]
ΔP	Pressure difference	1.0 [ϵ/σ^3]
t	Simulation time	820 [τ]
N_{PFPE}	Number of PFPE Beads	23,000 (2,300 chains)
N_{HC}	Number of Hydrocarbon Beads	7,200 (1,200 chains of C₂₄)

In this study, we have used a total of 23,000 PFPE lubricant beads and 7,200 hydrocarbon beads. The number of beads was chosen to allow a direct comparison with our lubricant transfer simulation models in Ref [93] and Ref [228]. Also, a large number of hydrocarbon beads was chosen in order to “accelerate” hydrocarbon transfer in our molecular dynamics simulation. All numerical calculation started with the same number of lubricant and hydrocarbon molecules.

4.3.2 Simulation Results

Figures 4.20-25 show molecular dynamics simulation results for both disk lubricant transfer and hydrocarbon transfer from the disk to the slider surface as a function of temperature T , minimum spacing H_{min} , disk velocity V_d , and hydrocarbon chain length, respectively. A schematic model of the molecular dynamics simulation at

time $t = 0$, $t = 445\tau$, and $t = 490\tau$ is shown in Figure 4.20(a), (b), and (c), respectively, for a minimum spacing of 10σ .

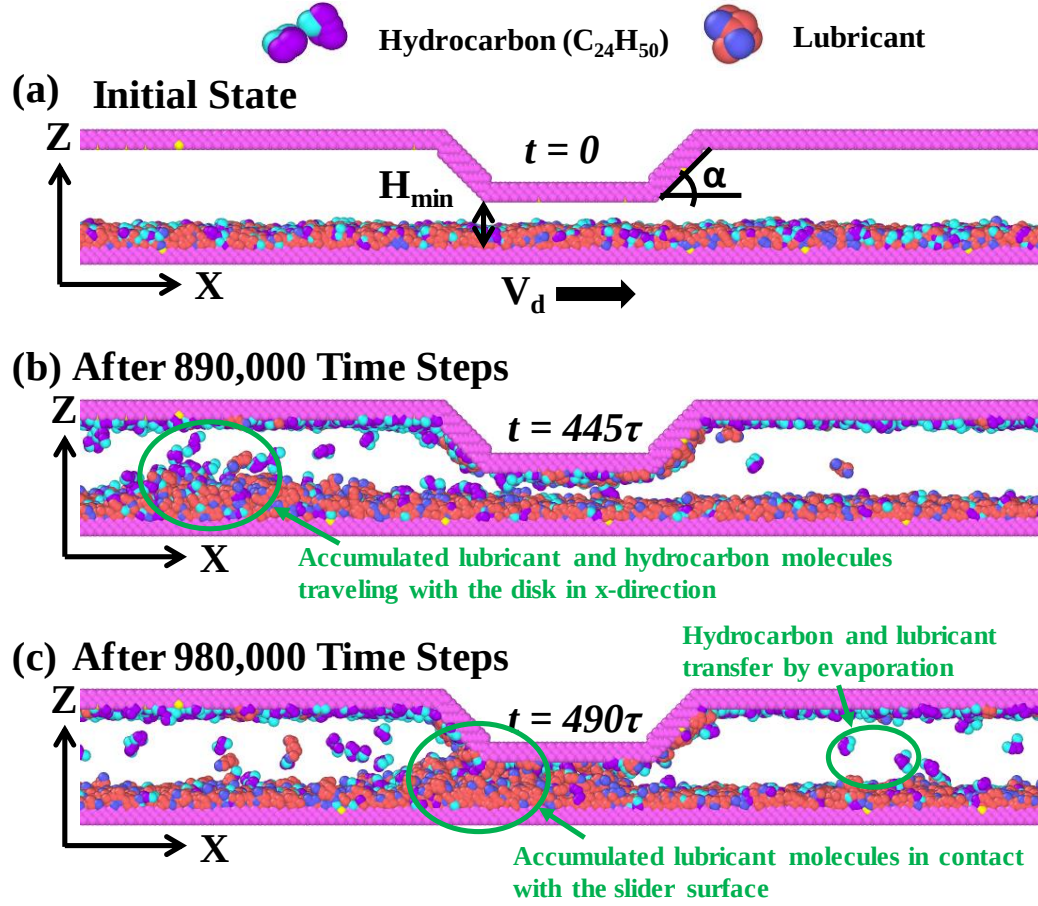


Figure 4.20 Molecular dynamics simulation with parameters $T = 1.6\epsilon/k_B$, $V_d = 2.5\sigma/\tau$, $H_{\min} = 10\sigma$, and $\alpha = 45^\circ$ for C_{24} contamination at (a) $t = 0$, (b) $t = 445\tau$, and (c) $t = 490\tau$

In Figure 4.20(a), the initial state of the molecular dynamics simulation is shown for a minimum spacing of 10σ and a temperature T of $1.6\epsilon/k_B$, while Figure 4.20(b) and (c) show the distribution of hydrocarbon and lubricant molecules on the disk and slider surface after $t = 445\tau$ and 490τ , respectively. We observe that for both $t = 445\tau$ and 490τ hydrocarbon molecules are present in the open space between the slider and the disk. At elevated temperature, molecules vibrate more rapidly and at larger amplitude than at

low temperature. When supplied with enough energy, a molecule may break away from its neighbors. In the simulations, we observe that hydrocarbon molecules break away from their neighbors and travel the open space between the slider and the disk, i.e., hydrocarbon transfer occurs by evaporation from the disk to the slider surface.

It is apparent from the schematic in Figure 4.20(b) and (c) that accumulated lubricant molecules are large enough to make contact in the narrow section of the head-disk interface, i.e., transfer of lubricant molecules occurs predominantly by mechanical transfer. This behavior is similar to that reported previously in molecular dynamics lubricant transfer simulations by Deng et al. and Seo et al. [93, 228].

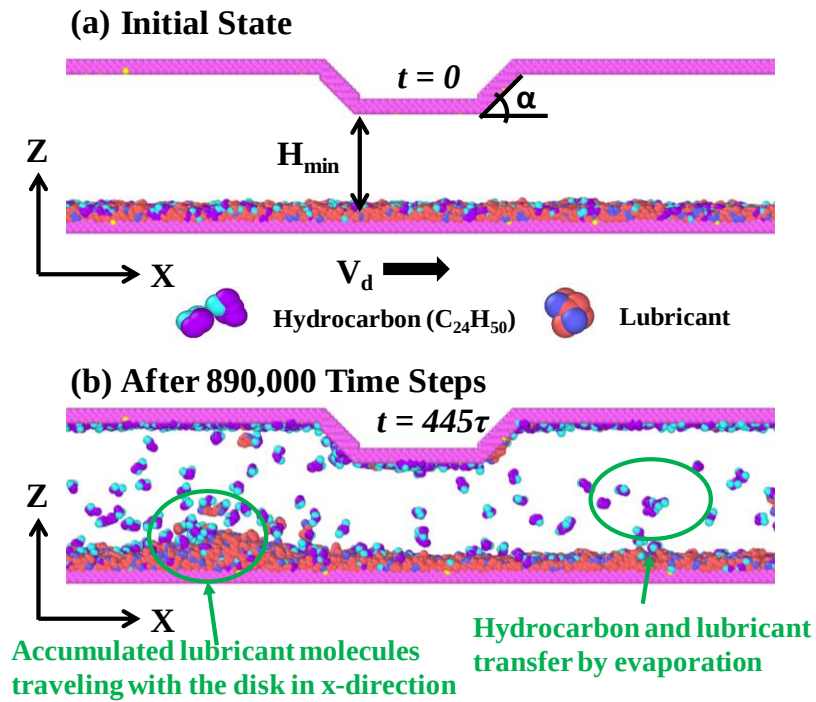


Figure 4.21 Schematic of the molecular dynamics simulation with parameters of $T = 1.6\epsilon/k_B$, $V_d = 2.5\sigma/\tau$, $H_{\min} = 30\sigma$, and $\alpha = 45^\circ$ for C_{24} contamination at (a) $t = 0$ and (b) $t = 445\tau$

In Figure 4.21(a), the simulation model is shown for a minimum spacing of 30σ at time $t = 0$, while in Figure 4.21 (b) the results are shown for the same spacing but at a time of $t = 445\tau$. We observe that at the given conditions (temperature $T = 1.6\epsilon/k_B$ and minimum spacing $H_{\min} = 30\sigma$), both hydrocarbon and lubricant molecules are present in the gap between slider and disk. Thus, for these conditions, transfer occurs by evaporation since oil molecules first transfer from the disk surface into the open space between slider and disk, and then become adsorbed onto the slider surface. For large values of $H_{\min}$, the lubricant accumulation shown in Figure 4.21 (b) does not grow large enough to make contact with the slider surface. Both lubricant and hydrocarbon molecules transfer from the disk to the slider surface without direct contact. This phenomenon is observed if the minimum spacing $H_{\min}$ is 30σ or larger.

MD Simulations with C24 Hydrocarbon Contamination

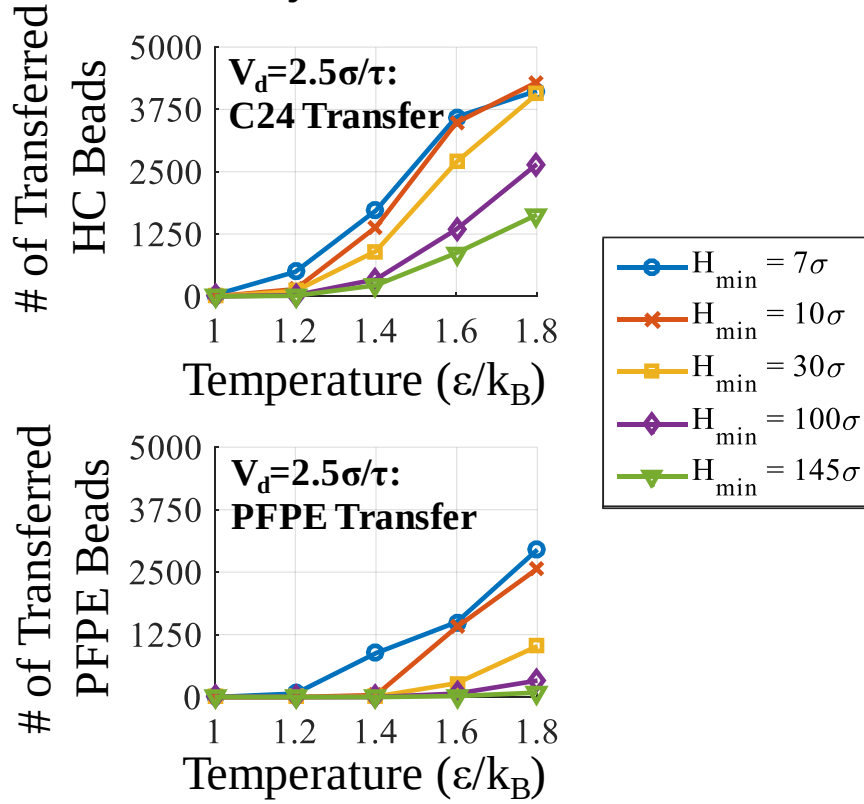


Figure 4.22 Molecular dynamics simulation of C₂₄ transfer and the effect of C₂₄ on lubricant transfer at the V_d of $2.5 \sigma/\tau$.

Figure 4.22 shows transfer of C₂₄ hydrocarbon and PFPE lubricant as a function of temperature for a minimum head-disk spacing of 7σ , 10σ , 30σ , 100σ , and 145σ , respectively, and a disk velocity of $2.5 \sigma/\tau$. We observe that transfer of both C₂₄ and PFPE lubricant increases with an increase in temperature T and a decrease in minimum spacing $H_{\min}$. Using the estimated value of ϵ , we find that the reduced temperature range from $1.0 \epsilon/k_B$ to $1.8 \epsilon/k_B$ corresponds to an actual temperature range from approximately room temperature to 250°C .

MD Simulations with C_{36} Hydrocarbon Contamination

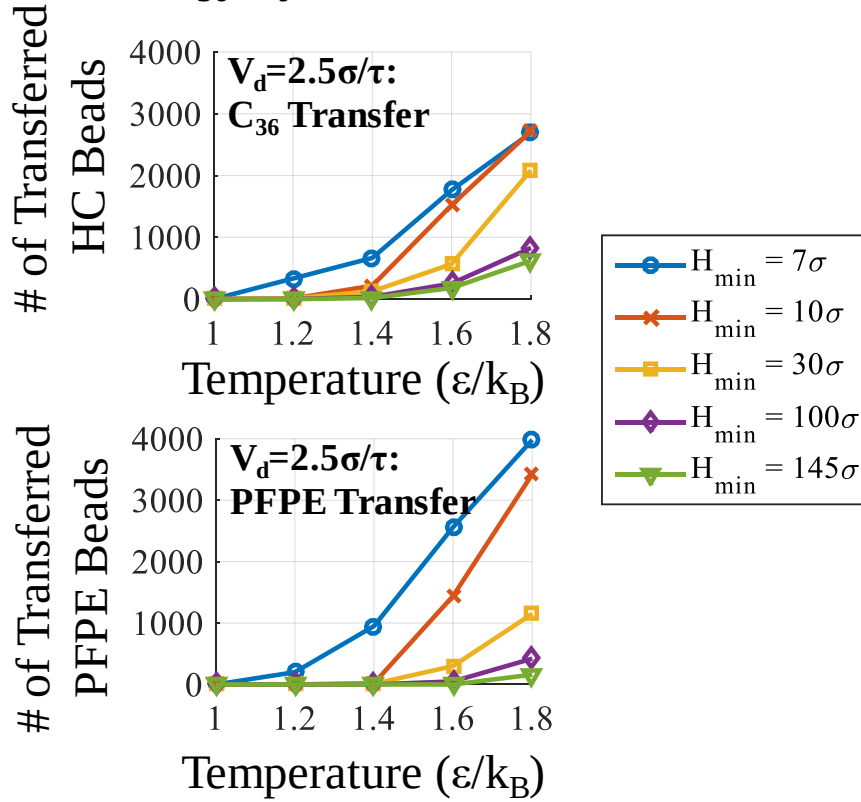


Figure 4.23 Molecular dynamics simulation of C_{36} transfer and the effect of C_{36} on lubricant transfer at the V_d of $2.5 \sigma/\tau$

In Figure 4.23 simulation results are shown for lubricant transfer in the presence of C_{36} contamination. We observe that both hydrocarbon and lubricant transfer increase as a function of temperature. On the other hand, transfer of both lubricant and hydrocarbon molecules decreases as the minimum spacing increases. These trends are similar to those found for the previously reported molecular dynamics simulations of PFPE contaminated with C_{24} molecules.

In addition to C_{24} and C_{36} transfer, we also simulated hydrocarbon contamination with C_{28} and C_{32} . The results for lubricant and hydrocarbon transfer

showed similar trends as for C_{24} and C_{36} transfer (Figures 4.22 and 4.23), i.e., hydrocarbon molecule transfer occurs predominantly by a process that is similar to evaporation, while lubricant molecule transfer occurs by a mechanical process, especially at small minimum spacing as shown in Figure 4.21. However, the simulation results do not provide a strong correlation between hydrocarbon chain length and lubricant transfer. In order to study this relationship in more detail, we performed a so-called “long time” simulation with 15.64 million time steps, corresponding to a non-dimensional simulation time of $7,820\tau$. This simulation time is approximately ten times larger than the simulation time shown in Figures 4.22 and 4.23.

MD Simulations ‘Long Time ($t = 7,820\tau$)’ Transfer of Hydrocarbon Molecules

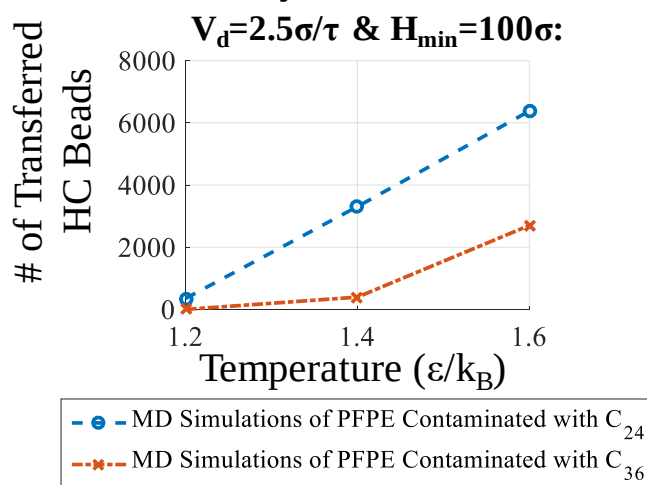


Figure 4.24 “Long time” ($t = 7,820\tau$) simulation results showing hydrocarbon transfer in which the PFPE layer was contaminated with C_{24} and C_{36} , receptively. Simulations were performed at $T = 1.2 \epsilon/k_B$, $1.4 \epsilon/k_B$, and $1.6 \epsilon/k_B$, respectively, at $H_{\min} = 100 \sigma$ and $V_d = 2.5 \sigma/\tau$.

Figure 4.24 shows that the transfer of hydrocarbon molecules increases with an increase in temperature, similar to Figures 4.22 and 4.23. Due to the lower molecular weight, more C_{24} hydrocarbon molecules are transferred than C_{36} molecules for the

same conditions. Clearly, less energy is required to transfer lighter molecules from the disk to the slider surface.

MD Simulations ‘Long Time ($t = 7,820\tau$)’ Transfer of PFPE Lubricant Molecules

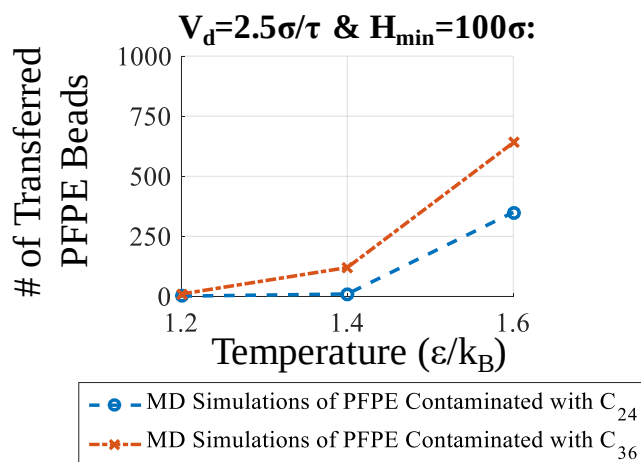


Figure 4.25 “Long time” ($t = 7,820\tau$) simulation results showing PFPE lubricant transfer in which the PFPE layer was contaminated with C_{24} and C_{36} , receptively. Simulations were performed at $T = 1.2 \epsilon/k_B$, $1.4 \epsilon/k_B$, and $1.6 \epsilon/k_B$, respectively, at $H_{\min} = 100 \sigma$ and $V_d = 2.5 \sigma/\tau$.

Figure 4.25 shows transfer of PFPE lubricant molecules in which the head-disk interface was contaminated with C_{24} and C_{36} , respectively. We observe that lubricant transfer increases as a function of molecular weight of the added hydrocarbon chains. Thus, the molecular weight of hydrocarbon contaminants affects not only hydrocarbon transfer (Figure 4.24), but also lubricant transfer at the head-disk interface (Figure 4.25). We believe that this phenomenon is a consequence of the availability of functional carbon sites on the disk surface. Heavier hydrocarbons have higher desorption energy when adsorbed on to the carbon overcoat, as was reported by Weaver et al [167]. Thus, fewer functional carbon sites are available on the disk surface for bonding of lubricant

molecules in the presence of hydrocarbon contaminants, resulting in an increase in lubricant transfer as shown in Figure 4.25.

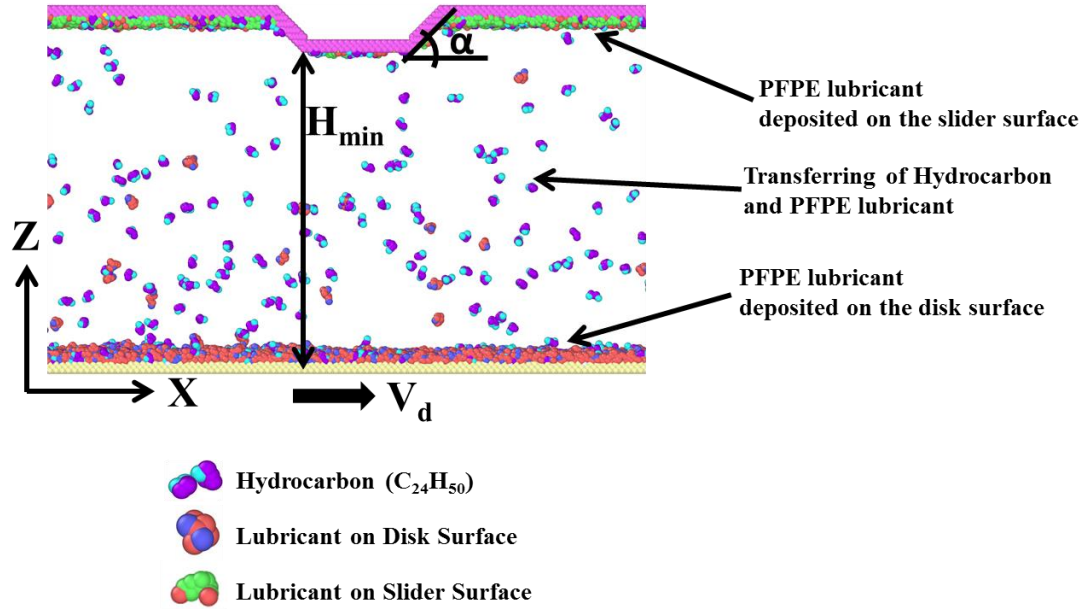


Figure 4.26 Schematic of molecular dynamics simulation with parameters of $T = 1.6\epsilon/k_B$, $V_d = 2.5\sigma/\tau$, $H_{\min} = 100\sigma$, and $\alpha = 45^\circ$ for C_{24} contaminations. A monolayer of PFPE lubricant was deposited on the slider surface prior to the molecular dynamics simulation

In Figure 4.26, we show a molecular dynamics simulation for C_{24} contamination for the case that a monolayer of PFPE lubricant is present on the slider surface prior to the beginning of the simulation. This situation is an interesting one since a PFPE monolayer is generally formed on a slider surface, especially after “electrical testing” of the head elements. In the simulation model, the PFPE lubricant molecules deposited on the disk and the slider surfaces are assumed to have the same chemical composition. The simulations were performed at a disk velocity of $2.5\sigma/\tau$, a minimum spacing $H_{\min}$ of 100σ , and a simulation time t of $7,820\tau$. The temperatures T were $1.2 \epsilon/k_B$, $1.4 \epsilon/k_B$, and $1.6 \epsilon/k_B$, respectively. The simulation results are presented in Figures 4.27 and 4.28.

MD Simulations with PFPE Lubricant on the Slider Surface and C₂₄ Contaminants

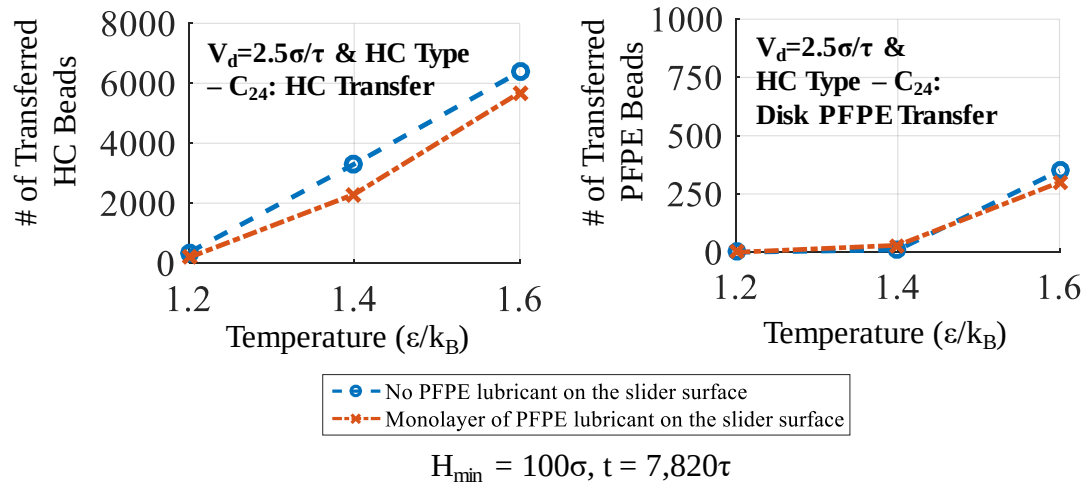


Figure 4.27 Molecular dynamics simulation after depositing a monolayer of PFPE on the slider surface prior to simulating lubricant and hydrocarbon transfer. Simulations were performed at $H_{min}=100\sigma$, $t=7,820\tau$, and $V_d = 2.5\sigma/\tau$ with C₂₄ hydrocarbon contaminants

From Figure 4.27, we observe a small decrease in the transfer of C₂₄ hydrocarbon and disk lubricant molecules in the presence of a monolayer of PFPE lubricant molecules on the slider surface. This result is to be expected since adsorption sites for C₂₄ hydrocarbon and disk lubricant molecules decrease in the presence of a thin layer of lubricant on the slider.

MD Simulations with PFPE Lubricant on the Slider Surface and C₃₆ Contaminants

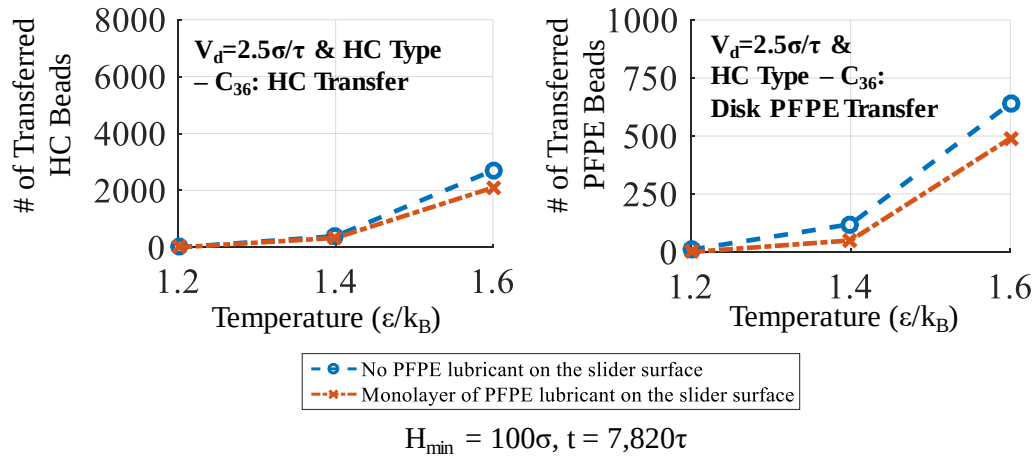


Figure 4.28 Molecular dynamics simulation after depositing a monolayer of PFPE on the slider surface prior to simulating lubricant and hydrocarbon transfer. Simulations are run at $H_{\min}=100\sigma$, $t=7,820\tau$, and $V_d = 2.5\sigma/\tau$ with C₃₆ hydrocarbon contaminants

In Figure 4.28 we observe the same trend as in Figure 4.27, i.e., the transfer of both C₃₆ and disk lubricant molecules decreases in the presence of PFPE lubricant monolayer on the slider surface due to fewer activation sites on the slider surface. Also, compared to the results shown in Figure 4.27, C₃₆ hydrocarbon transfer is decreased substantially compared to C₂₄ while disk lubricant transfer is increased due to the higher desorption energy of C₃₆ molecules.

4.3.3 Discussion

Molecular dynamics simulations were performed for hydrocarbon and lubricant transfer at the head-disk interface in order to investigate the role of lubricants and hydrocarbons on the tribology of the head-disk interface. Despite the scale differences in length and time between the real head-disk interface and our simulation model, we

observe that the simulation results are in good agreement with our expectations as to how hydrocarbon and PFPE lubricant molecules would behave.

The simulation results indicate that hydrocarbon transfer occurs mainly by evaporation. At low temperature, there is insufficient energy for hydrocarbon molecules to separate from their neighbors. However, at elevated temperature, more energy is available and some hydrocarbon molecules to break away and travel the open space between the disk and the slider surface. As can be seen in Figures 4.22 and 4.23, hydrocarbon transfer occurs even if the minimum spacing is large and corresponds to a value at which very little lubricant transfer occurs. This suggests that lubricant molecules transfer from the disk to the slider surface by contact, i.e., by ‘mechanical transfer’ [93, 228]. As the volume of the accumulated lubricant on the disk grows over time (Figure 4.20), van der Waals interactions between the lubricant molecules and the slider surface increase, leading to lubricant transfer from the disk to the slider surface. Therefore, as the spacing increases, the van der Waals interactions decay, resulting in a decrease in lubricant transfer.

Another interesting phenomenon observed in our molecular dynamics simulations is related to the effect of molecular weight of hydrocarbon contaminants on PFPE lubricant transfer. It is apparent that more energy is required to transfer heavier molecules, as seen in Figure 4.24. In Figure 4.25, we observe that lubricant transfer increases with an increase in hydrocarbon molecular weight. Lei and Gellman [222] concluded that hydrocarbon contaminants weaken interactions between disk lubricant and carbon overcoat on the disk surface. This relates to the difference in desorption energy of hydrocarbon chains on the disk surface. Desorption energy is the energy

required for a molecule to be released from the binding surface. Weaver et al. [167] presented desorption energies for short linear hydrocarbon chains on gold, platinum and copper. Their data indicate that the desorption energy increases with an increase in molecular weight. Sexton and Hughes [159] investigated hydrocarbon molecules and determined that the desorption energy increases for C₅ (pentane) to C₁₀ (decane) hydrocarbons with an increase of each methylene (-CH₂-) unit. Considering the findings of Sexton and Hughes, we can hypothesize that increasingly more lubricant molecules are displaced by hydrocarbon contaminants if the molecular weight of the contaminants increases, i.e., more hydrocarbon contaminants are adsorbed on the carbon overcoat surface. Thus, more mobile lubricant molecules are present which increases lubricant transfer as shown in Figure 4.25.

One last point should be emphasized concerning lubricant transfer in the presence of a monolayer of PFPE, as shown in Figure 4.25. This point is that the amount of both hydrocarbon and disk lubricant transfer was observed to decrease in comparison to simulation results when no lubricant layer was present on the slider. Tyndall et al. [225] reported that hydroxyl groups in Zdol PFPE lubricant molecules bond with the carbon overcoat adsorption sites when forming the first layer on the surface. Thus, if additional lubricant molecules are to be deposited, there is a decrease in the number of active adsorption sites on the slider surface, leading to a decrease in transfer of hydrocarbon and disk lubricant molecules.

Finally, we would like to emphasize that molecular dynamics simulations correspond to a time scale on the order of nanoseconds, which is orders of magnitude shorter than the life time of operation of a hard disk. We believe that molecular

dynamics simulations can determine qualitatively trends but not quantitative values for any of the simulated parameters, and, in particular, for the reduction of contaminants on the slider surface due to deposition of a PFPE monolayer.

4.4 Summary and Conclusion

From the experimental results, we observe:

- 1) The amount of condensed hydrocarbon oil mixture increases initially as a function of heat exposure time (2 hours to 8 hours). After long heat exposure time (12 hours) a decrease in the amount of deposited hydrocarbons was observed. We verified that this is not an artifact from the optical surface analyzer. Further investigations are needed in order to clarify the reasons for the observed reduction in the number of scatter sites on the disk surface.
- 2) The base plate and the disk were placed in the thermal chamber in order to transfer hydrocarbon oil mixtures from the base plate surface to the disk surface. An increase in condensed hydrocarbon contaminants was observed as a function of chamber temperature.
- 3) AFM analysis showed crystallized hydrocarbons and droplet-like contaminants present on the disk surface. Using molecular dynamics simulation and contact angle analysis, we have verified that these contaminants originate from the hydrocarbon mixture.
- 4) Transferred hydrocarbon molecules were found not only near the pole tip protrusion region, but also in the air bearing cavities where large head-disk spacing is present.

- 5) ToF-SIMS results identified the contaminants to be pivot base oils and straight-chain hydrocarbons. However, no sign of C_{24} (tetracosane) or C_{28} (octacosane) was detected on the slider surfaces, only C_{32} (dotriacontane) and C_{36} (hexatricosane).
- 6) The characteristics of hydrocarbon contamination were found to be similar to those reported by Ref. [101-103]. In particular, droplets were found on the trailing edge as well as in the cavities on the sliders. The experiment showed that once the disk surface is heavily contaminated with hydrocarbons, organic compounds can easily transfer to the slider surface, showing a similar contamination behavior as reported in Ref. [101, 103, 201-202]. This process is influenced significantly by temperature and time.

From the simulation research, we conclude:

- 1) Both hydrocarbon and PFPE lubricant transfer increases with an increase in temperature and a decrease in minimum spacing.
- 2) Hydrocarbon transfer occurs predominantly by evaporation, as indicated in Figures 4.20 and 4.21, while PFPE lubricant transfer occurs by contact between accumulated PFPE lubricants and the slider surface at small minimum spacing. This is similar to results observed by Deng et al. and Seo et al. [93, 228].
- 3) With an increase in hydrocarbon chain length, hydrocarbon transfer decreases.
- 4) With an increase in hydrocarbon chain length, PFPE lubricant transfer increases.

- 5) If a monolayer of PFPE lubricant is present on the slider surface, transfer of both hydrocarbon and disk lubricant molecules decreases in comparison to a clean slider.
- 6) In order to avoid hydrocarbon contamination on the slider surface, it is advisable to limit the use of light-weight hydrocarbon oil molecules because of their high volatility and probability to outgas and contaminate the head-disk interface. Clearly, heavy molecular-weight hydrocarbons are much less volatile and would not escape the spindle motor or actuator arm pivot.

From both the numerical work and the experimental work, we can conclude that in order to prevent hydrocarbon contamination at the head-disk interface, it is essential to use hydrocarbon oil with “good” lubrication properties, such as high viscosity, in addition to having low thermal volatility. we speculate that there are two possible types of “good pivot actuator arm oils”. The first type consists of organic compounds with low molecular weight and high volatility. This type of oil would easily evaporate from an adsorbed surface at elevated temperature and would be captured by the recirculation filter once entered the air stream. The second type is oil with high molecular weight and low volatility. This type of oil would not outgas from the pivot actuator arm even at elevated drive temperatures. However, the problem is excessive friction, and therefore, high energy consumption in the pivot actuator arm.

4.5 Acknowledgement

Chapter 4, in part is a reprint of the material as it appears in "Simulation of hydrocarbon oil contamination at the head–disk interface using molecular dynamics," Seo, Young Woo, Andrey Ovcharenko, and Frank E. Talke, *Tribology Letters* 61, no. 3 (2016): 28. The dissertation author was the primary investigator and author of this paper.

Chapter 4, in part is a reprint of the material as it appears in "Experimental Investigation of Hydrocarbon Contamination at the Head–Disk Interface." *Tribology Letters* 65, no. 2 (2017): 54. The dissertation author was the primary investigator and author of this paper.

Chapter 5

Lubricant Transfer and Fragmentation at Head-Disk Interface

5.1 Introduction

The reduction in flying height between head and disk has increased the likelihood of intermittent head-disk contacts and lubricant transfer from the disk to the head. Lubricant transfer can occur even in the absence of head-disk contacts, affecting the flying characteristics of the heads and the possibility of catastrophic failure [92].

Lubricant transfer has been addressed in various publications. Deoras and Talke [226] experimentally investigated lubricant transfer and concluded that lubricant thickness and slider skew angle are important parameters for lubricant depletion on the disk surface. Canchi and Bogy [227] observed lubricant transfer in the absence of actual head-disk contact. Ma and Liu [91] suggested that lubricant transfer depends on molecular weight, lubricant thickness, and bonding ratio. Pan et al. [228] developed a molecular dynamics model for lubricant transfer and concluded that lubricant transfer increases with local pressure change and lubricant bonding ratio. Seo et al. [93] applied

Pan's model [228] to finite width air bearings, and observed that lubricant transfer is a function of local pressure change and disk velocity. They also observed that lubricant transfer depends on air bearing convergence angle, functional beads on the disk surface, minimum head-disk spacing, and mass of backbone-beads.

Chen et al. [229] performed drag tests and observed that high mechanical stress can lead to lubricant fragmentation. Bogy and Bhatia [230] also observed fragmentation of perfluoropolyether lubricant in a tribo-chamber during drag testing of a head against a disk coated with Zdol. Zhao et al. [231] concluded that the mechanism of lubricant fragmentation is related to low-energy electron emission from rubbing surfaces and mechanical shear stress. Similarly, Tao and Bhushan [232] observed lubricant fragmentation as a consequence of mechanical chain scission and tribo-electrical effects. They also noted that relative humidity can affect lubricant fragmentation. Nath and Wong [233] used molecular dynamics to study the effect of temperature on lubricant fragmentation and observed that lubricant fragmentation increases with temperature. Pan et al. [234] used molecular dynamics to study the effect of lubricant fragments on lubricant transfer by assuming a fixed number of lubricant fragments at the start of the simulation. This assumption is equivalent to assuming that dynamic effects are negligible.

In this study, we simulate lubricant transfer and lubricant fragmentation using molecular dynamics assuming that the number of lubricant fragments is variable. This assumption is equivalent to postulating that dynamic effects are important. Throughout the simulation, we investigate lubricant transfer and lubricant fragmentation as a function of temperature T , local pressure change ΔP , and disk velocity V_{disk} .

5.2 Molecular Dynamics Simulation Model

To speed up the numerical calculations, we use the so-called “coarse-grained bead spring” approach [93, 228]. This approach groups a number of atoms into a “bead”, rather than treating each atom at an atomistic level [189]. For instance, a perfluoropolyether chain of Zola 2000 is modeled as a molecule of ten beads: two functional end beads and eight backbone beads [93].

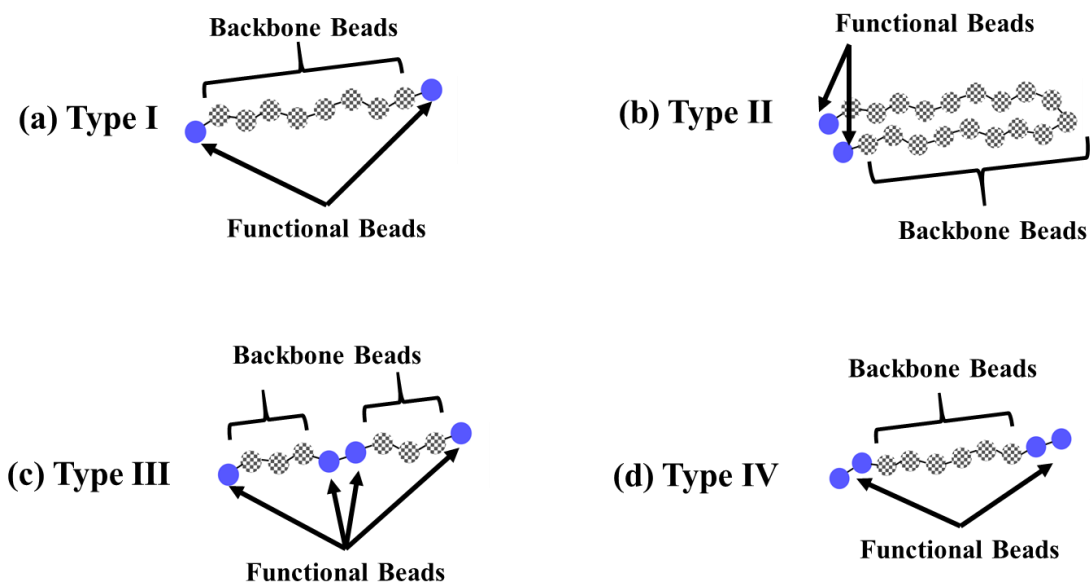


Figure 5.1 Four different types of lubricant molecules used in the present molecular dynamics simulation.

Figure 5.1 shows four different types of lubricant molecules used in this study. Type I (Figure 5.1(a)) consists of two functional end beads and eight backbone beads [93, 228]. Type II (Figure 5.1(b)) is a molecule that is twice as long as Type I and has two functional end beads and eighteen backbone beads. Type III lubricant (Figure 5.1(c)) has two functional end beads, two functional center beads, and six non-functional backbone beads [189]. Lastly, Type IV lubricants (Figure 5.1(d)) consist of four

functional end beads and six backbone beads. Comparing lubricant Type I, III and IV, we observe that each molecule has the same number of beads. However, Type III and IV lubricants have twice the number of functional beads than Type I lubricant. Due to the increased number of functional groups for Type III and IV lubricants, polar interactions between the individual chains are more likely to occur. In our simulation, a total of 23,000 lubricant beads are modeled, regardless of the type of lubricant used.

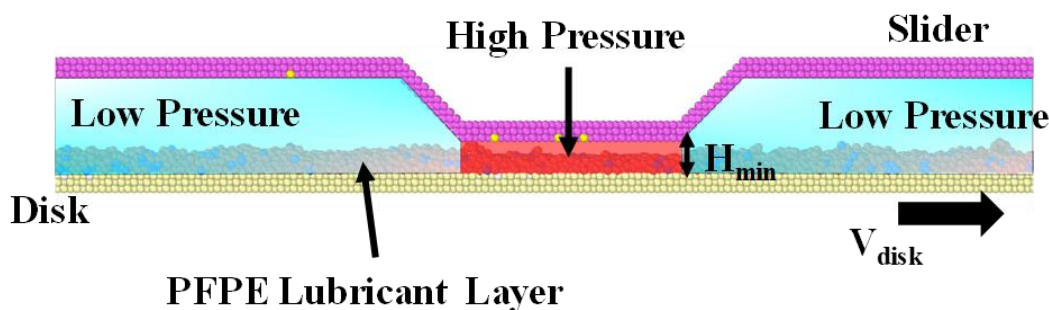


Figure 5.2 Schematic of simplified head-disk interface.

Figure 5.2 shows a simplified model of the head-disk interface [93], consisting of low pressure regions at the inlet and outlet of the bearing, and one high pressure region in the center of the bearing to represent the typical pressure distribution under an air bearing surface. The disk velocity V_{disk} and the minimum spacing H_{min} between the head and the disk were chosen to correspond to the actual disk velocity and the minimum flying height found in typical present-day hard disk drives.

Similar to Ref. [93], bead interactions were described using the following potential functions. The 12-6 LJ potential function was used to describe van der Waals forces among the beads [228]. Polar attractions between functional beads were described using the EXP potential function [167]. Bonds among PFPE lubricant beads

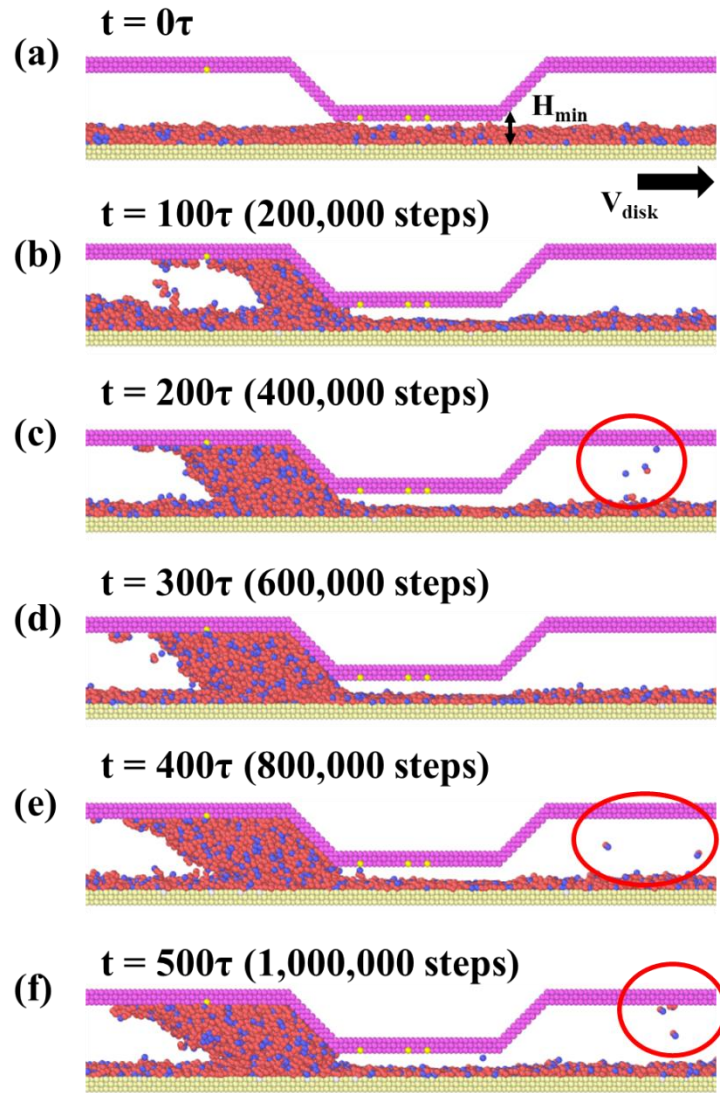
were modeled using the FENE potential function [159]. In addition, the quartic potential function was used to describe bond breaking [160, 235]. In this study, the molecular dynamics simulations were performed using *LAMMPS* [191].

Similar to Ref. [93], the simulation was divided into two steps. First, a canonical ensemble (NVT) was assumed. For this system, 140,000 time steps with a step size of 0.005τ were performed. In the second step of the simulation, we assumed a micro-canonical ensemble (NVE). The Langevin dynamics were used to control the temperature during the simulation [191]. A total of 1,640,000 time steps with a step size of 0.0005τ were performed to simulate lubricant transfer and lubricant fragmentation at the head-disk interface. After this, the head and the disk were separated from each other to a distance of 40σ for post-processing to count the number of transferred lubricant beads and the number of fragmented lubricant chains. Throughout the calculations, we used the LJ units ($\sigma = 0.7$ nm, $\tau \sim 100$ ps, and $\varepsilon \sim 10^{-21}$ J) [191].

5.3 Results and Discussion

Figure 5.3 gives simulation results for lubricant transfer and lubricant fragmentation versus time for a local pressure change of $\Delta P = 5\varepsilon/\sigma^3$ between the inlet and the center of the bearing, a disk velocity $V_{\text{disk}} = 2.5\sigma/\tau$, a minimum spacing between the head and the disk of $H_{\text{min}} = 5\sigma$, and a temperature $T = 1.2\varepsilon/k_B$, where k_B is the Boltzmann constant. Figure 5.3(a) shows the initial state with a thin layer of Type I lubricants on the bottom surface. At $t = 100\tau$ (Figure 5.3(b)), we observe that lubricant molecules accumulate at the converging side of the interface where the pressure changes from low pressure to high pressure (*left* interface of low-to-high pressure region). A

lubricant bridge is formed between the head and disk surface, similar to the lubricant bridge found by Pan et al. [228] and Seo et al. [93]. The accumulation of lubricant at the converging step increases with time (Figure 5.3(b), (c), (d)) and covers the entire converging region after 1,000,000 steps ($t = 500\tau$). In addition to lubricant accumulation, lubricant fragments are formed, as shown by the dots in the highlighted circles on the right-hand side of Figure 5.3 (see Figure 5.3(c), (e), and (f)). The number of lubricant fragments in the diverging section of the head is much smaller than the number of adhering lubricant molecules in the converging section.



$$\Delta P = 5\epsilon/\sigma^3, V_{\text{disk}} = 2.5\sigma/\tau, H_{\text{min}} = 5\sigma, T = 1.2\epsilon/k_B$$

Figure 5.3 Molecular dynamics simulation results at different times: (a) $t = 0 \tau$, (b) $t = 100 \tau$, (c) $t = 200 \tau$, (d) $t = 300 \tau$, (e) $t = 400 \tau$, and (f) $t = 500 \tau$.

5.3.1 Lubricant Transfer

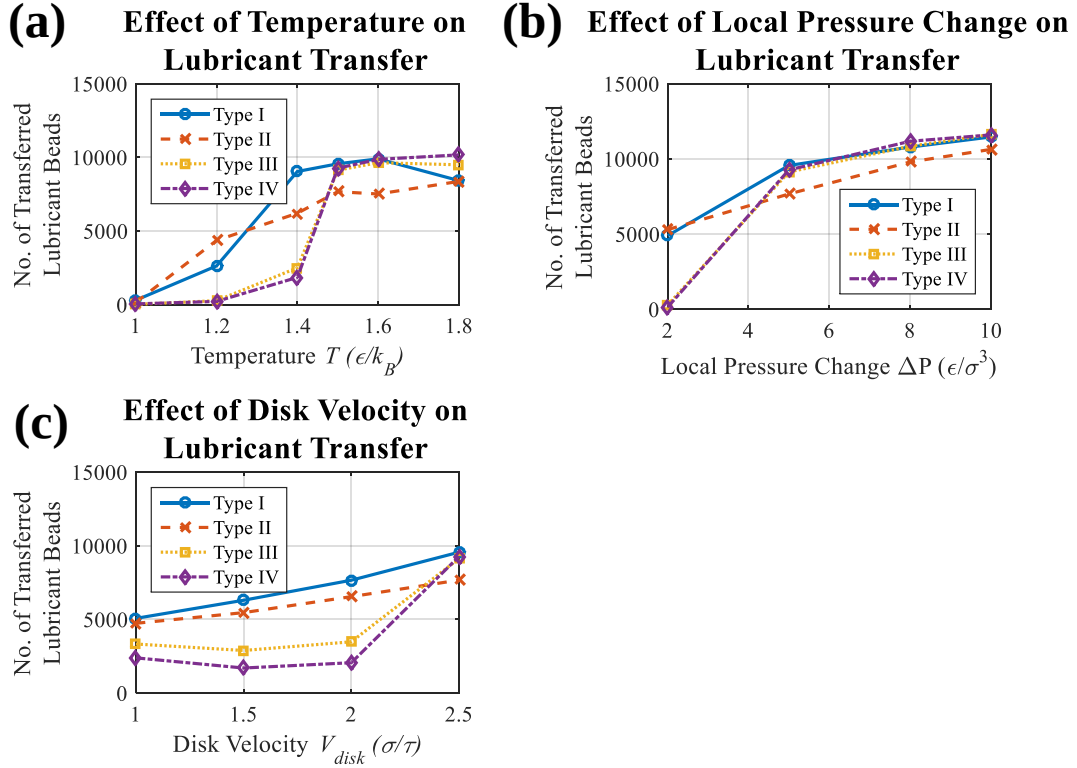


Figure 5.4 Molecular dynamics simulation of lubricant transfer versus (a) temperature, (b) local pressure change, and (c) disk velocity.

Figure 5.4 shows molecular dynamics results of lubricant transfer for all four types of lubricants as a function of temperature (Figure 5.4(a)), local pressure change (Figure 5.4(b)), and disk velocity (Figure 5.4(c)). We observe that lubricant transfer increases for all four types with an increase in temperature (Figure 5.4(a)), local pressure change (Figure 5.4(b)) and disk velocity (Figure 5.4(c)). For Type I lubricants, we observe a slight reduction in lubricant transfer at a temperature of $1.8\epsilon/k_B$. At low temperature, only a few lubricant molecules are seen to transfer to the head for Type I, Type III, and Type IV lubricants, while at high temperature lubricant transfer increases

sharply before leveling off at values of T exceeding $1.4\epsilon/k_B$. Also, at low temperature and low disk velocity, the amount of Type III and IV transferred lubricant molecules is much smaller than that of Type I and II (Figure 5.4(a) and (c)). This result is related to the fact that Type I and II lubricants have two functional beads, while Type III and IV lubricants have four functional beads (see Figure 5.1 for details), i.e., Type III and IV lubricants have stronger bonds with the disk surface than Type I and Type II. Comparing our numerical study with those of others [93, 199, and 228], we conclude that our simulations show similar results, i.e., lubricant transfer is reduced with an increase in bond strength of PFPE lubricants on the disk surface. Guo et al. [237], Sonoda et al. [238] and Shirakawa et al. [239] stated that multidentate lubricants with multiple functional beads throughout the lubricant chain and multifunctional lubricants with multiple functional end groups have strong bonding to the disk surface. Similarly, we observe that Type III (multidentate) lubricants and Type IV (multifunctional) lubricants show stronger bonding to the disk surface than Type I and II lubricants.

Type III lubricants have two functional end beads and two functional center beads, while Type IV lubricants have four functional end beads (Figure 5.1). Despite these differences, the simulation results were similar for Type III and IV lubricants, suggesting that the location of functional beads (center or end) is of minor importance.

5.3.2 Lubricant Fragmentation

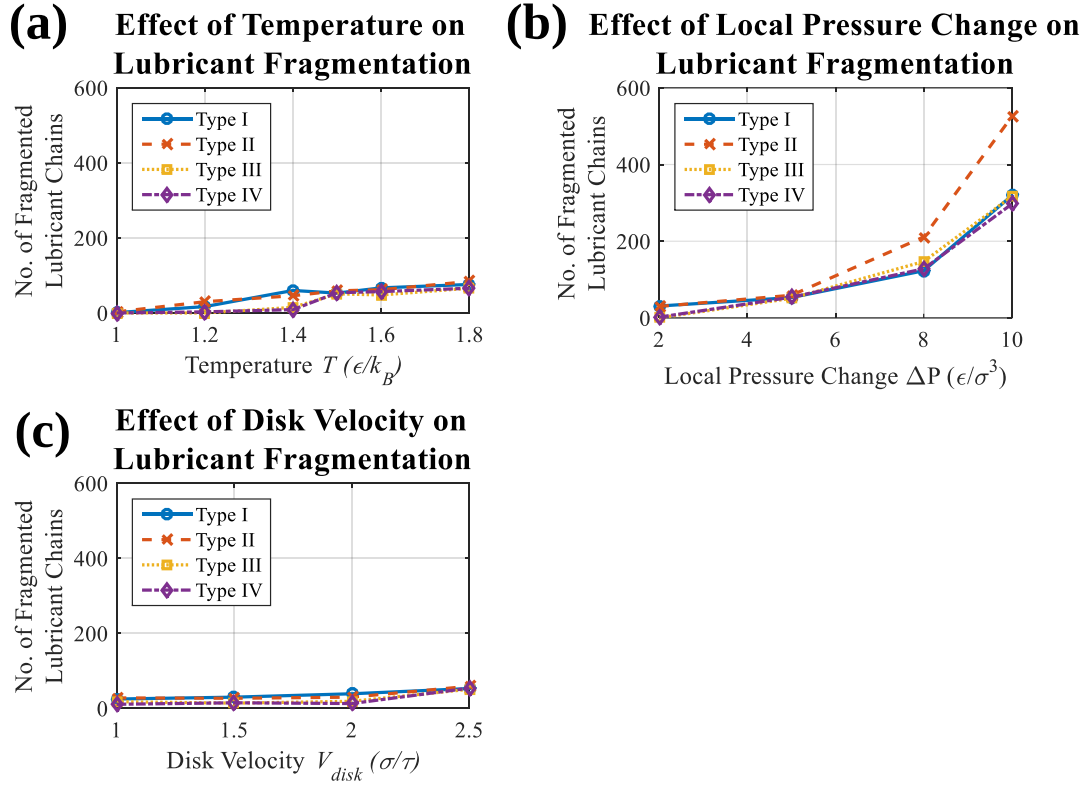


Figure 5.5 Molecular dynamics simulation of lubricant fragmentation versus (a) temperature, (b) local pressure change and (c) disk velocity.

Figure 5.5 shows lubricant fragmentation results for all four types of lubricant molecules investigated versus temperature, local pressure change, and disk velocity. We note that for all four types, lubricant fragmentation increases with an increase in temperature (Figure 5.5(a)), local pressure change (Figure 5.5(b)), and disk velocity (Figure 5.5(c)). Clearly, lubricant fragmentation is most affected by local pressure change. We also observe that the number of fragmented lubricant chains is largest for Type II (Figure 5.5(b)). This is a consequence of the fact that lubricant chains of Type II are twice as long as Type I with only two functional end-beads, i.e., this type of

lubricant is prone to fragmentation because of its large chain length. However, this does not imply that the amount of transferred Type II lubricants is larger than that of other lubricant types. In fact, as can be seen in Figure 5.4(b), the number of transferred Type II lubricant beads is smaller than that of other lubricant types at a local pressure change of $\Delta P = 5\epsilon/\sigma^3$, $8\epsilon/\sigma^3$ and $10\epsilon/\sigma^3$, respectively. Pan et al. [234] concluded that lubricant fragmentation is one of the reasons for lubricant transfer. In our study, we observe that lubricant transfer from the disk to the head appears to be caused mainly by the formation of a lubricant bridge as shown in Figure 5.3.

Lubricant fragmentation is most significantly affected by local pressure change as shown in Figure 5.5(b). Since shear stress at the wall is related to local pressure change ΔP , it is apparent that lubricant fragmentation is a function of the shear stress. The pressure gradient and the shear stress in an air bearing at high Knudsen numbers are related by [240-241]:

$$\tau_w|_{disk} = -\rho\lambda \sqrt{\frac{RT_0}{2\pi}} \frac{U}{2\lambda + h} - \frac{h}{2} \frac{dp}{dx} \quad (5.1)$$

where dp/dx is the air bearing pressure gradient, ρ is the density of air, λ is the mean free path of air molecules, R is the specific gas constant, T_0 is the ambient temperature, U is the disk velocity, and h is the spacing between the head and the disk. Equation 5.1 shows that the shear stress depends both on the disk velocity U and the pressure gradient dp/dx .

Wei et al. [242] reported that shear stress can cause lubricant fragmentation by stretching the intramolecular bond until it breaks. In our molecular dynamics simulation, the mechanism for bond breakage is simulated in which the intramolecular bond breaks

when the bond length is extended beyond the cutoff distance. Assuming that the local pressure change ΔP in our molecular dynamics simulation corresponds to the pressure gradient dp/dx of the air bearing surface, it follows that the shear stress on the disk surface is related to the local pressure change ΔP . With an increase in local pressure change, the shear stress increases, and an increase in shear stress leads to an increase in lubricant fragmentation.

Equation 5.1 shows that shear stress in an air bearing depends on the pressure gradient and the disk velocity. Our simulation results, on the other hand, showed that disk velocity V_d has a smaller effect on lubricant fragmentation (Figure 5.5(c)) than the local pressure change ΔP . We believe that this can be explained by the fact that the range of disk velocities investigated was smaller in comparison to the range of local pressure change, i.e., velocity V_d was investigated from $1.0\sigma/\tau$ to $2.5\sigma/\tau$ ($\frac{\max}{\min} = 2.5$) while ΔP was investigated from $2\varepsilon/\sigma^3$ to $10\varepsilon/\sigma^3$ ($\frac{\max}{\min} = 5.0$). Clearly, an increase in disk velocity beyond $2.5\sigma/\tau$ would increase the shear stress effect, resulting in lubricant fragmentation due to disk velocity comparable to lubricant fragmentation due to local pressure change.

5.4 Summary

Molecular dynamics simulation was carried out to study lubricant transfer and lubricant fragmentation for four different lubricant types. We conclude that

1. Lubricant transfer is a function of temperature, local pressure change and disk velocity.

2. Fewer lubricant beads are transferred at low temperature for Type III (two functional end beads and two functional center beads) and Type IV (four functional end beads) lubricants compared to Type I or Type II lubricants.
3. Type II lubricant chains fragment more easily with high local pressure change than other lubricant types.
4. Lubricant fragmentation is most significantly affected by local pressure change.

5.5 Acknowledgement

Chapter 5, in part is a reprint of the material as it appears in "Molecular Dynamics Simulation of Lubricant Transfer at the Head-Disk Interface Considering Lubricant Fragmentation," Seo, Young Woo, Andreas Rosenkranz, and Frank E. Talke, *In Preparation for Publication*. The dissertation author was the primary investigator and author of this paper.

Chapter 6

Lubricant Depletion under Pulsed Laser Irradiation

6.1 Introduction

In order to increase the areal density of hard disk drives, heat assisted magnetic recording is being investigated as an alternative to conventional magnetic recording. In heat assisted magnetic recording, a high coercivity magnetic material is used in conjunction with laser heating to lower the coercivity of the magnetic material prior to writing. Heat assisted magnetic recording requires a number of novel components that need to be optimized such as the laser delivery system, the thermomagnetic write head, the head-disk interface, and the magnetic media with stable thermal properties [21]. To accomplish heat assisted magnetic recording, a laser beam is first “delivered” to a waveguide on the head, which guides the laser to the near-field transducer to reduce the spot size and focus the laser on the desired spot. The laser heats the spot on the disk to a temperature near the Curie temperature, lowering its magnetic coercivity for subsequent writing. Then, during the cooling process, the recorded data are “frozen” [243]. Heat assisted magnetic recording can achieve higher magnetic recording density than conventional magnetic recording [18, 21, 243]. However, the high local temperatures along with high heating and cooling rates during thermal cycling can lead

to tribological problems such as lubricant degradation at the head-disk interface [21, 246-253].

Lim and Gellman [244] studied desorption and decomposition kinetics of Fomblin Zdol lubricants in a temperature range from 400 to 650°C. They concluded that perfluoropolyether lubricants with a molecular weight of less than 3,000 g/mol are more likely to desorb than decompose, while perfluoropolyether lubricants with higher molecular weight tend to decompose under laser irradiation. Kryder et al. [21] stated that lubricants with low molecular weight deplete under laser irradiation due to evaporation, while heavy molecular weight lubricants deplete due to decomposition, similar to the conclusions of Lim and Gellman [244]. Gauvin et al. [246] studied Zdol lubricant films under pulsed laser irradiation using a repetition rate of 3 MHz and a pulse duration of 200 ns. They observed that the photo-thermal stability of the lubricant film increases with an increase in the substitution ratio for the lubricant end groups. Tagawa et al. [247-249] experimentally studied lubricant depletion due to laser heating. They concluded that lubricant depletion greatly depends on lubricant thickness. Also, lubricant depletion occurred predominantly due to evaporation. Wang et al. [250] investigated square pulse laser heating for heat assisted magnetic recording technology, and observed higher thermal gradients in the heat affected zone when pulsed lasers were used instead of continuous-wave lasers. Lee et al. [251] observed that laser heating causes a change in disk surface properties, such as surface roughness and lubricant depletion. Ma et al. [252] modeled heat assisted magnetic recording using a continuous-wave laser with a wavelength of 785 nm and a spot diameter of 0.9 μm . They observed a lubricant depletion depth of approximately 8 Angstrom with volcano-like ridges along

the depleted track. They concluded that lubricant depletion under laser irradiation is strongly affected by the lubricant thickness and the bonding ratio. Li et al. [253] discussed the use of Raman spectroscopy to investigate temperature profiles occurring in an environment similar to heat assisted magnetic recording.

In addition to experimental studies, many numerical studies have been conducted to investigate the effect of laser irradiation on thin-film lubricants. Wu [245] developed a model to study the dynamics of perfluoropolyether lubricant under laser irradiation with laser power of 7 mW and a laser spot radius of 100 nm. He concluded that both evaporation and thermocapillary effects dominate lubricant depletion. Wu et al. [254] developed a finite element model to study lubricant depletion and reflow under laser heating and stated that their results agree well with experiments. Wu and Talke [255] investigated the effect of material properties on laser penetration depth and the resulting temperature distribution. They concluded that disk temperature distribution and lubricant depletion were mostly affected by thermal properties and the thickness of the magnetic layer. Zhou et al. [256] simulated lubricant depletion under laser irradiation. They concluded that for heat assisted magnetic recording, lubricants with high molecular weight and low polydispersity index would be optimal. Zhou et al. [257] improved Wu's model [245, 255] by including lubricant evaporation. They found that the lubricant evaporation coefficient decreases exponentially with temperature. Zeng et al. [258] studied lubricant depletion in heat assisted magnetic recording system by considering lubricant film thickness, evaporation enthalpy and surface tension. The authors concluded that the mechanism of lubricant depletion is related to evaporation and thermal capillary effects, similar to Wu [245]. Dahl et al. [259] developed a

continuum model considering the functional end groups of the lubricant and the viscosity of thin lubricant films. They concluded that lubricant deformation is predominantly affected by thermocapillary shear stress. Sarabi and Bogy [260] numerically studied the lubricant reflow in heat assisted magnetic recording as a function of lubricant film thickness and lubricant type. They observed that Z-tetraol 2200 and ZTMD (a type of multidentate perfluoropolyether lubricant) have a greater recovery time than Zdol 2000. In addition, they found that for different lubricants an optimum film thickness exists to achieve lubricant reflow and replenishment rate. Xu et al. [261] performed micro-magnetic simulations and observed that with decreasing pulse duration and increasing laser peak power, the thermal spot size decreases. Xu et al. [262-263] investigated the effect of pulsed laser heating with a near field transducer by solving the Landau-Lifshitz-Block equation. The results showed that pulsed laser heating with pulse duration of 100 ps can achieve an areal density greater than 4 Tb/in² for FePt media. Xu et al. [264] performed micro-magnetic simulations to study the effect of laser peak power, pulse duration, and repetition rate on the signal-to-noise ratio, and concluded that frequency jitter in the laser will affect the signal-to-noise ratio.

In addition to the above studies, investigations have been performed to study lubricant depletion using molecular dynamics simulations. Li et al. [265] modeled a disk surface using the so-called “coarse-grained bead spring” approach. They modeled the laser to be stationary and continuous-wave, i.e., they modeled a continuous, not-pulsed laser. Li et al. [266] also simulated a moving laser on a disk surface using a coarse-grained bead spring model. The laser was modeled as a continuous-wave laser. Both

studies concluded that lubricant depletion increases as a function of laser irradiation time and laser power.

In the present study, molecular dynamics was used to investigate the effect of laser heating on lubricant depletion for a stationary disk surface coated with perfluoropolyether lubricants. Unlike Ref. [265-266], the laser was modeled to be a pulsed laser instead of a continuous-wave laser. The effect of Gaussian pulse laser heating on lubricant depletion was compared with continuous-wave laser heating and square pulse laser heating. The maximum temperature of the irradiated lubricant molecules is studied along with lubricant depletion, lubricant evaporation and lubricant fragmentation as a function of laser peak power, laser pulse duration and laser repetition rate.

6.2 Molecular Dynamics Simulation

6.2.1 Disk-Lubricant Modeling

Similar to Ref. [93], a *coarse-grained bead spring* approach was used in the modeling of the disk surface and the lubricant layer. Figure 6.1 shows a schematic of the model.

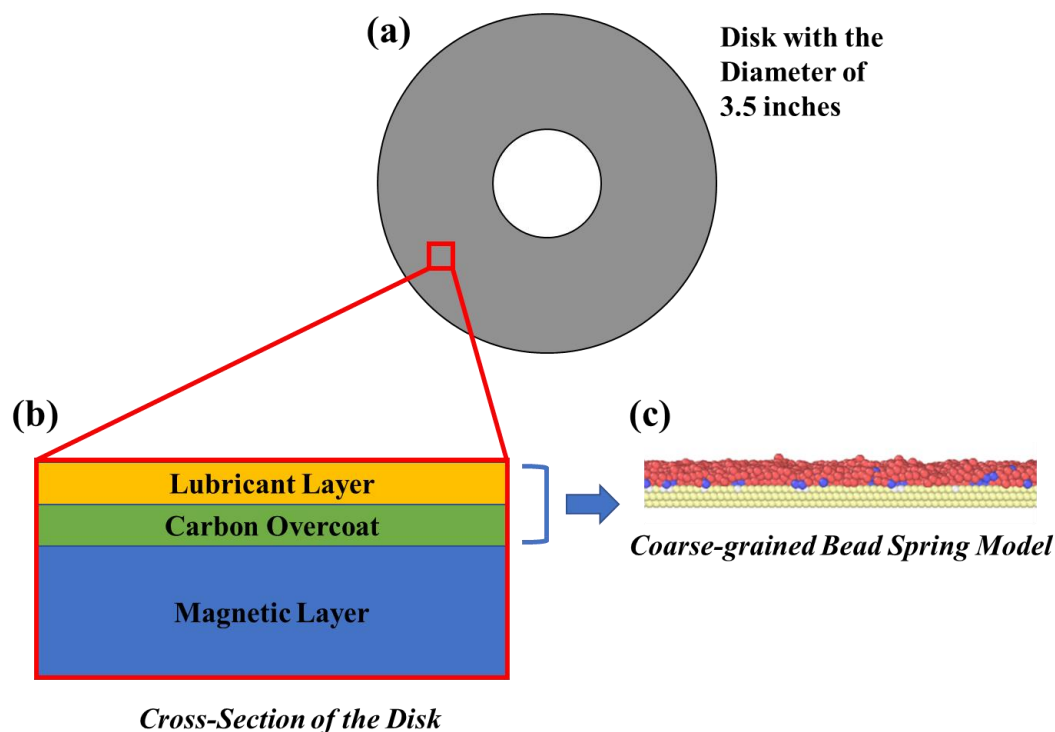


Figure 6.1 Schematic of the modeling process: (a) typical magnetic disk with diameter of 3.5 inches, (b) cross-section of the disk, and (c) coarse-grained bead spring model of the carbon overcoat with a thin lubricant layer.

To develop the molecular dynamics model, a small area of the disk shown in Figure 6.1(a) was considered (Figure 6.1(b)) and modeled using the coarse-grained bead spring approach (Figure 6.1(c)). The model consists of the disk layer of width and length of $200\sigma \times 200\sigma$ (approximately 140 nm x 140 nm). The lubricant layer was assumed to be 2σ (approximately 1.5 nm).

6.2.2 Potential Functions

To describe intermolecular and intramolecular interactions, different potential functions were used (Figure 6.2), including the Lennard-Jones (LJ) potential, the short-

range attractive polar (EXP) potential, the finitely extensible nonlinear elastic (FENE) potential and the quartic potential function.

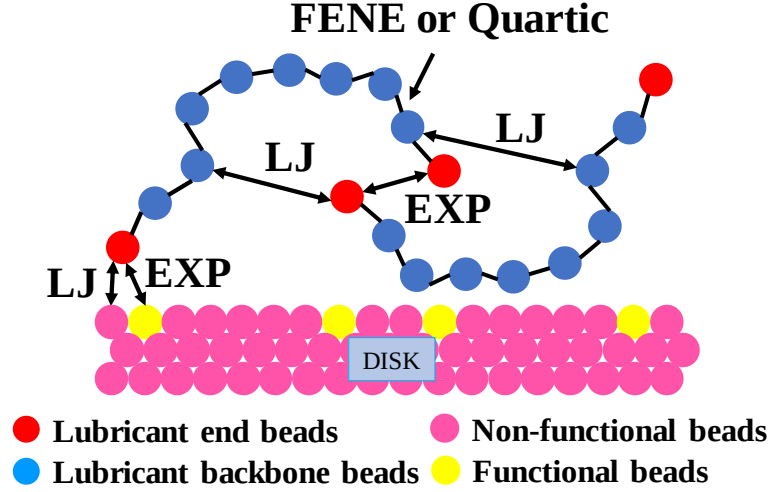


Figure 6.2 Schematic of intermolecular and intramolecular interactions among the modeled coarse-grained beads.

Intermolecular interactions were simulated using both the truncated 12-6 LJ potential function and the EXP potential function. For non-bonded Van-der-Waals force calculations, the LJ potential function was used, i.e.,

$$U_{LJ}^{Truncated} = 4\epsilon_{LJ} \left[\left(\frac{\sigma_{LJ}}{r} \right)^{12} - \left(\frac{\sigma_{LJ}}{r} \right)^6 - \left(\frac{\sigma_{LJ}}{r_c} \right)^{12} + \left(\frac{\sigma_{LJ}}{r_c} \right)^6 \right] \quad (3.14)$$

where r is the distance between two neighboring beads, σ is the bead diameter, ϵ is the potential well-depth, and r_c is the cutoff distance between two beads. In order to calculate polar attractive forces, the EXP potential function was used [167], i.e.,

$$U_{EXP} = -\epsilon^p \exp \left(-\frac{r - r_c}{d} \right) \quad (3.16)$$

where ϵ^p is the magnitude of the polar interaction and d is the decay length in the exponential function for short-ranged polar attraction. Intramolecular interactions were

described using two different potential functions. During the initial equilibrium step, the FENE potential function was used [159], i.e.,

$$U_{\text{FENE}} = \frac{1}{2} k_{\text{FENE}} r_0^2 \ln \left[1 - \left(\frac{r_{12}}{r_0} \right)^2 \right] \quad (3.6)$$

where K_{fene} is the nonlinear harmonic spring constant and R_0 is the maximum extent of the spring. After equilibration was reached, the quartic potential function was used during laser irradiation. This potential function allows to simulate bond breakage when the bond between two beads extends beyond the so-called “cutoff distance.” The quartic potential function is given by [160]:

$$U_{\text{quartic}} = k_q (r - R_c)^2 (r - R_c - B_1)(r - R_c - B_2) + U_0 + 4\varepsilon \left[\left(\frac{\sigma}{r_{12}} \right)^{12} - \left(\frac{\sigma}{r_{12}} \right)^6 \right] \quad (3.8)$$

where K_Q , B_1 , and B_2 are coefficients used to simulate the FENE potential function. When the bond length extends beyond the cutoff distance R_c , the potential energy reaches a local maximum and the bond breaks. In Table 6.1, the coefficients for the above potential functions are listed.

Table 6.1 Potential Function Coefficients

Name	Symbol	Value*
Bead diameter	σ_{LJ}	1.0 σ
Potential well-depth	ε_{LJ}	1.0 ε
LJ cutoff-distance	r_c	2.5 σ
Magnitude of polar interaction	ε^p	4 ε_{LJ}
Dist. between functional beads	D	0.3 σ
FENE spring constant	K_{fene}	30.0 ε/σ^2
FENE spring length	R_0	1.5 σ
Quartic spring constant	K_Q	1434.3 ε/σ^2
Quartic spring length	R_c	1.5 σ
Quartic coefficient #1	B_1	-0.7589 σ
Quartic coefficient #2	B_2	0.0 σ
Quartic coefficient #3	U_0	67.223 ε

*All units are in the LJ units [191]

We have used “LJ” units were used in this study with σ indicating length ($1\sigma \sim 0.7$ nm), ε indicating energy ($1\varepsilon \sim 10^{-21}$ J), and τ indicating time ($1\tau \sim 100$ ps) [191]. The mass of each PFPE lubricant bead was assumed to be 0.2 kg/mol. All calculations were done using the *Large-scale Atomic/Molecular Massively Parallel Simulator* (LAMMPS) software [191].

6.2.3 Pulsed Laser Modeling

In this study, the laser was assumed to be a pulsed laser rather than a continuous-wave laser as in Ref. [265-266]. To simulate a pulsed laser, the laser power was assumed to be Gaussian over time and space [250, 267-268], i.e.,

$$P(x, y, t) = P_{peak} \exp \left[-\frac{(t - t_0)^2}{2(\sigma_{pulse})^2} \right] \exp \left[-\frac{(x - x_0)^2 + (y - y_0)^2}{2\delta} \right] \quad (5.1)$$

where P_{peak} is the laser peak power, t_0 is the time at which the laser power reaches its peak power, and σ_{pulse} is the standard deviation of the laser pulse over time, defined as “full width at half maximum / $2\sqrt{2 \ln 2}$ ” [267]. *Full width at half maximum* (FWHM) is typically used to define the laser pulse duration. Also, x_0 and y_0 are the locations for the center point of the laser spot and 2δ is the radius of the laser spot. Figure 6.3 illustrates the laser pulse shape as a function of time and space.

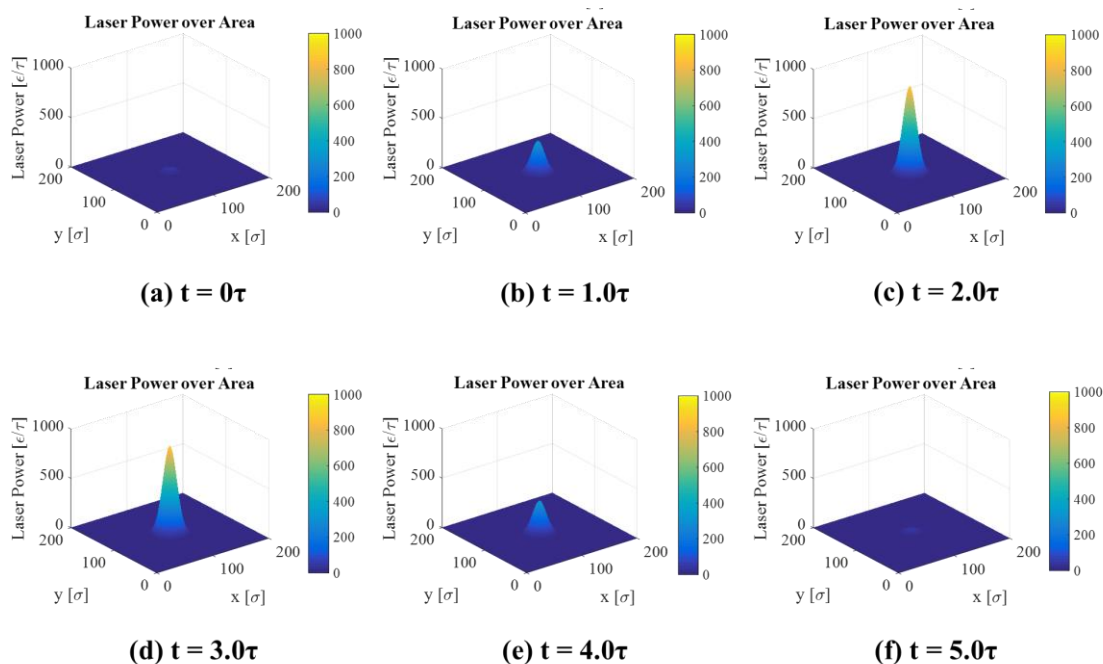


Figure 6.3 Illustration of a Gaussian pulse laser over space at different times (a) $t = 0\tau$, (b) 1.0τ , (c) 2.0τ , (d) 3.0τ , (e) 4.0τ , and (f) 5.0τ .

6.2.4 Molecular Dynamics Simulation

For the molecular dynamics simulation, the disk surface was divided into three areas, the laser spot region (a), the intermediate Newtonian region (b), and the outer thermostat region (c) (Figure 6.4).

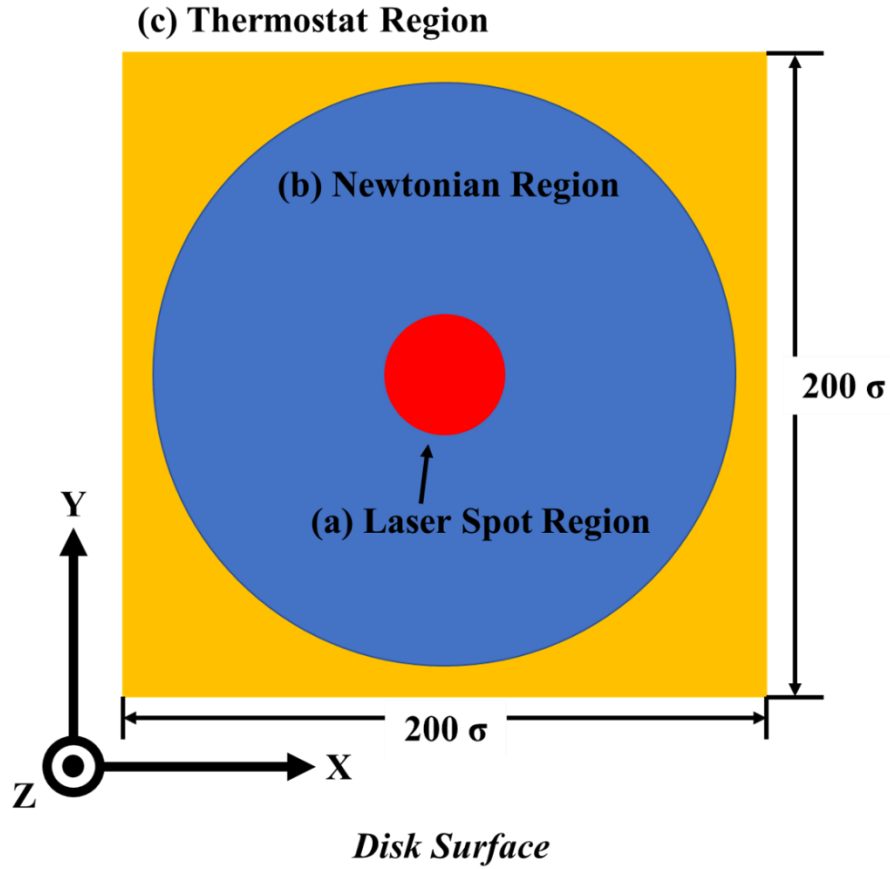


Figure 6.4 Molecular dynamics simulation model: (a) the laser spot region, (b) the intermediate Newtonian region, and (c) the outer thermostat region.

A $200\sigma \times 200\sigma$ disk area was modeled as shown in Figure 6.4. The central laser spot region is located at the center with a spot radius of 20σ ($r \leq 20\sigma$). This is the region in which the pulsed laser irradiates the lubricant molecules. The “Newtonian” region ($20\sigma < r \leq 90\sigma$) is the region in which lubricant molecules are free to move according to Newtonian dynamics. Lastly, the outer thermostat region ($90\sigma < r$) is the region where the temperature is controlled to be $1.0 \text{ } \epsilon/k_B$ using the Langevin thermostat to keep the modeled molecular dynamics system thermodynamically stable.

For the molecular dynamics simulation, a total number of 200,000 beads were used to model the disk surface with a thin lubricant layer of thickness 2σ (≈ 1.5 nm). 120,000 beads were used to model the diamond-like carbon surface, and 80,000 beads were used for the perfluoropolyether lubricant layer. Periodic boundary conditions were applied for both the x and y axis while a non-periodic “shrink-wrapped” boundary condition was used for the z axis. The “shrink-wrapped” boundary condition is used to include atoms that have moved far from their original positions [191]. The time step size Δt was chosen to be 0.005τ . The simulation was divided into two parts. In the first part, a total simulation time equivalent to 568,000 steps ($2,840\tau$) was used to equilibrate the simulation model at a temperature of $1.0\varepsilon/\tau$. For this part, the canonical ensemble was used. The canonical ensemble, also known as the *NVT* ensemble, keeps the number of beads (N), the system volume (V), and the temperature (T) constant. In the second part, a simulation time of $5,300\tau$ (corresponding to 1,060,000 steps) was used for both laser irradiation (60,000 steps or 300τ) and cooling (1,000,000 steps or $5,000\tau$). During the first 60,000 time steps, a laser pulse was treated as a stationary heat source with a Gaussian profile over time and space. The laser spot was assumed to be stationary, similar to Ref. [267]. Then, the heat source was removed from the simulation during the latter 1,000,000 time steps. The microcanonical ensemble (also known as the *NVE* ensemble) was used during the second simulation step. The *NVE* ensemble keeps the number of beads (N), the system volume (V), and the temperature (T) constant. The effect of laser irradiation was evaluated in terms of lubricant maximum temperature, lubricant depletion width, lubricant evaporation, and lubricant fragmentation. A post-processing step was performed at a time of 300τ , corresponding to roughly 30 ns. In

terms of laser-matter interaction, laser energy is first absorbed by electrons. Afterwards, it takes roughly 10 ps in order to transfer energy from the electrons to the phonons. This time is determined by the electron-phonon coupling constant [270-271]. After the energy has been transferred to the phonons, it takes on the order of nanoseconds to achieve equilibrium-like conditions in the entire system (electron and phonon subsystems). Therefore, we assume that the system has reached equilibrium after 30 ns.

In this investigation, we study the effect of a pulsed laser on lubricant depletion. We neglect the cooling down period in which lubricant reflow occurs. Lubricant reflow during the cooling phase, where the laser is not activated, has been investigated by Ref. [265-266] using molecular dynamics.

6.3 Results

In Figure 6.5(a), 6.5(b), and 6.5(c), molecular dynamics simulation results are shown for time $t = 0\tau$, 150τ , and 300τ , respectively, and laser parameters $P_{peak} = 1,400\epsilon/\tau$ (≈ 14 nW), $FWHM = 2.35\tau$ (≈ 235 ps), and $f_{pulse} = 0.2\tau^{-1}$ (≈ 2 GHz). The parameters were chosen to be similar to the laser parameters used in Ref. [261-266].

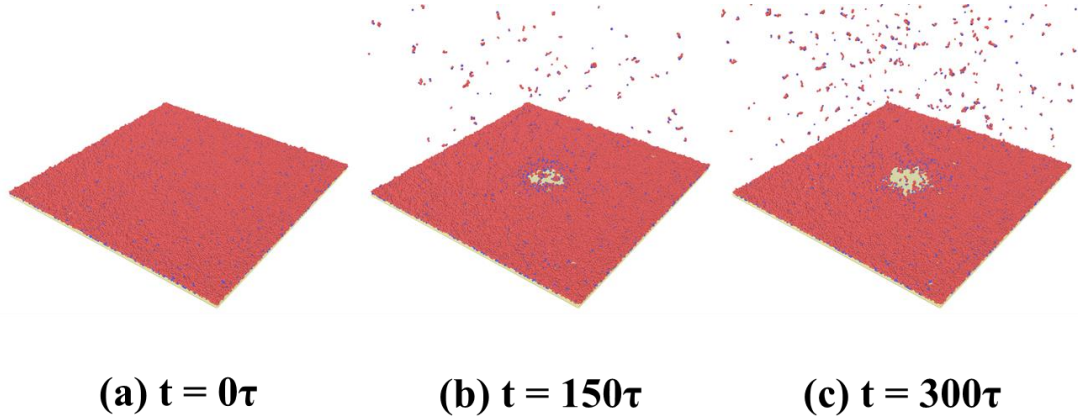


Figure 6.5 Molecular dynamics simulation with $P_{peak} = 1,400\epsilon/\tau$ (≈ 14 nW), $FWHM = 2.35\tau$ (≈ 235 ps), and $f_{pulse} = 0.2\tau^{-1}$ (≈ 2 GHz) for pulsed laser irradiation on the disk surface at (a) $t = 0\tau$, (b) $t = 150\tau$, and (c) $t = 300\tau$.

From Figure 6.5(b) and 6.5(c), we observe that a number of “dots” are present, corresponding to airborne molecules. The number of “dots” above the disk surface increases with time, indicating that the number of air-borne lubricant molecules increases with time due to laser heating. Figure 6.5(a) shows the initial state of the molecular dynamics simulation where lubricant depletion is absent, while Figure 6.5(b) and 6.5(c) show a near-circular area without lubricant as a result of laser irradiation at $t = 150\tau$ and $t = 300\tau$, respectively. This phenomenon is described as lubricant depletion. Lubricant molecules vibrate under the influence of supplied kinetic energy. If the supplied energy exceeds a fixed threshold, lubricant molecules break away from their

neighbors. This leads to evaporated lubricant molecules. If the vibrations become even larger, bonds between lubricant molecules can break, leading to fragmentation.

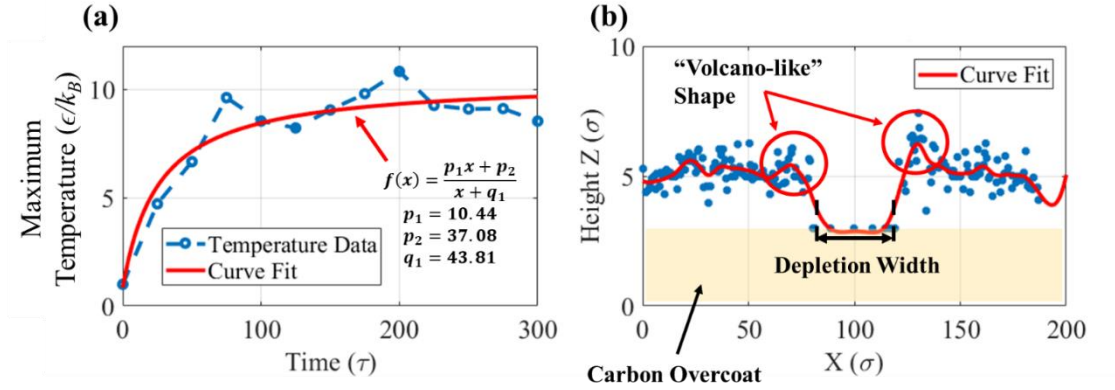


Figure 6.6 Molecular dynamics results showing (a) the maximum temperature in the lubricant layer versus time and (b) lubricant height distribution as a function position at time $t = 300\tau$.

Figure 6.6(a) shows the maximum temperature observed during laser irradiation on the disk surface from time $t = 0\tau$ to $t = 300\tau$. A curve fit of the form $f(x) = \frac{p_1 x + p_2}{x + q_1}$ was used, where $p_1 = 10.44$, $p_2 = 37.08$, and $q_1 = 43.81$. In addition, the lubricant depletion width was estimated in Figure 6.6(b). Here, lubricant depletion width is defined as the distance on the x-axis (Figure 6.6(b)) where the carbon overcoat is exposed. As can be seen in Figure 6.6(b), the edges of the region without lubricant are higher than the overall lubricant level, leading to a “volcano-like” shape. The formation of this volcano-like structure depends on the pulse duration. For ultra-short pulses with pulse duration of less than 10 ps, volcano-like structures are not observed. For pulse durations larger than 10 ps, evaporation, melting, and re-solidification can occur [269, 271]. The formation of volcano-like structures is similar to what was predicted by Wu

and Talke [255], observed by Tagawa et al. [248-249], and simulated by Li et al. [265-266] using molecular dynamics.

In addition to maximum temperature and lubricant depletion width, we have also investigated the effect of pulsed laser irradiation on lubricant depletion in terms of the number of evaporated lubricant beads and the number of fragmented lubricant chains. All lubricant beads that move freely above the disk surface were regarded to be in the vapor phase.

Figure 6.7-6.9 show molecular dynamics simulation results as a function of laser peak power P_{peak} , pulse duration $FWHM$, and repetition rate f_{pulse} .

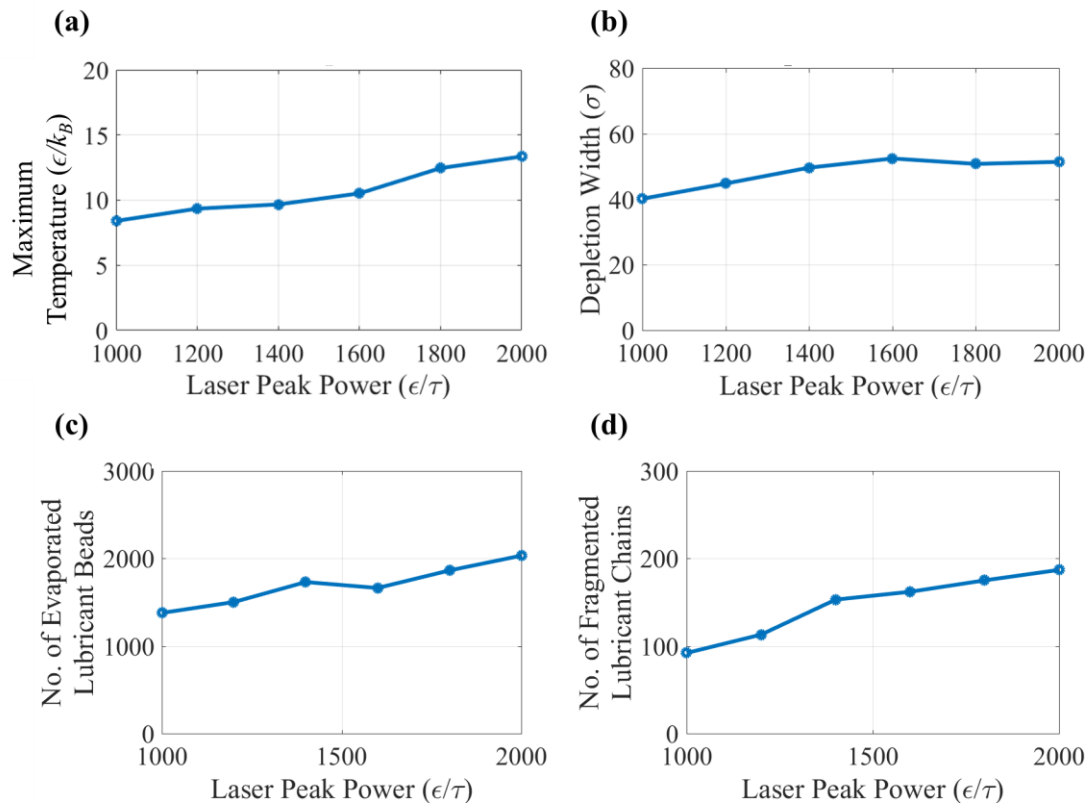


Figure 6.7 Effect of laser peak power on (a) maximum temperature, (b) lubricant depletion width, (c) number of evaporated lubricant beads, and (d) number of fragmented lubricant chains.

Figure 6.7 shows the maximum temperature, the depletion width, the number of evaporated lubricant beads, and the number of fragmented lubricant chains as a function of laser peak power P_{peak} , keeping pulse duration ($FWHM = 2.35\tau \approx 235$ ps)) and repetition rate ($f_{pulse} = 0.2\tau^{-1} \approx 2$ GHz)) constant. We note that all four parameters show a small increase with laser peak power.

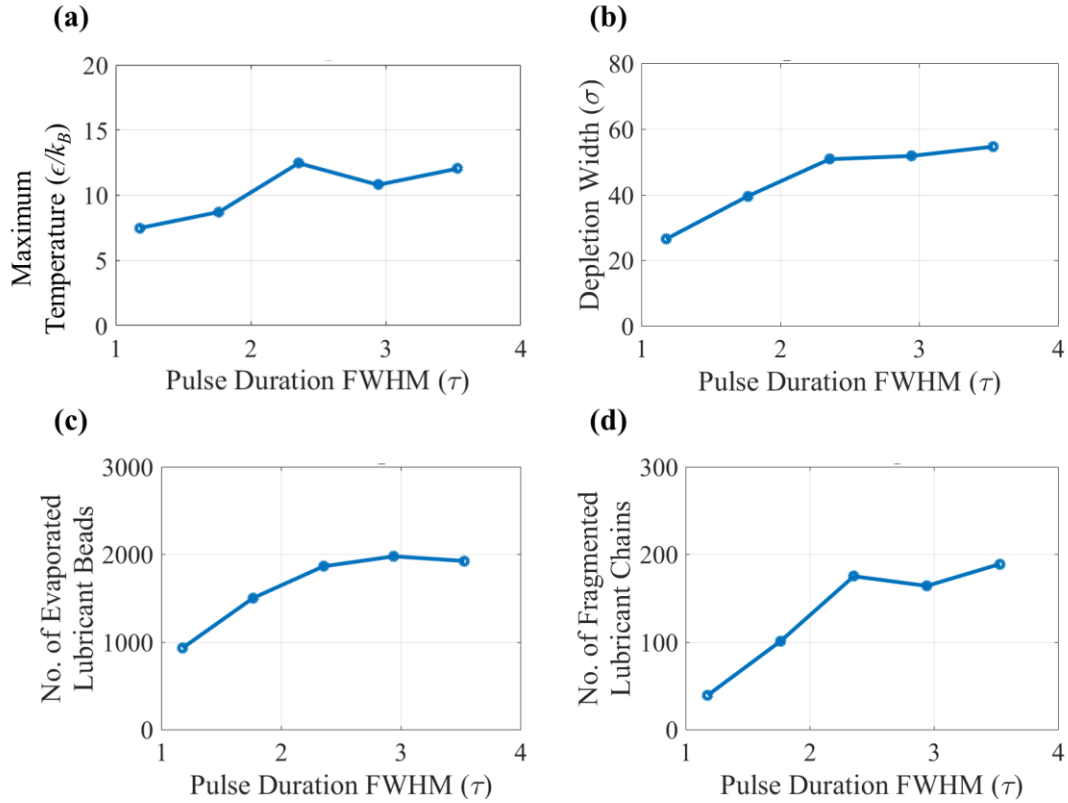


Figure 6.8 Effect of pulse duration on (a) maximum temperature in the lubricant layer, (b) depletion width, (c) number of evaporated lubricant beads, and (d) number of fragmented lubricant chains.

Figure 6.8 shows the maximum temperature, the depletion width, the number of evaporated lubricant beads, and the number of fragmented lubricant chains as a function of pulse duration $FWHM$, keeping laser peak power ($P_{peak} = 1,400\epsilon/\tau \approx 14$ nW)) and repetition rate ($f_{pulse} = 0.2\tau^{-1} \approx 2$ GHz)) constant. We observe that the maximum

temperature and the lubricant depletion width increase with pulse duration. The similar trend is observed for the number of evaporated lubricant beads and the number of fragmented lubricant chains as a function of pulse duration. We also observe that the effect of pulse duration is more significant than that of laser peak power.

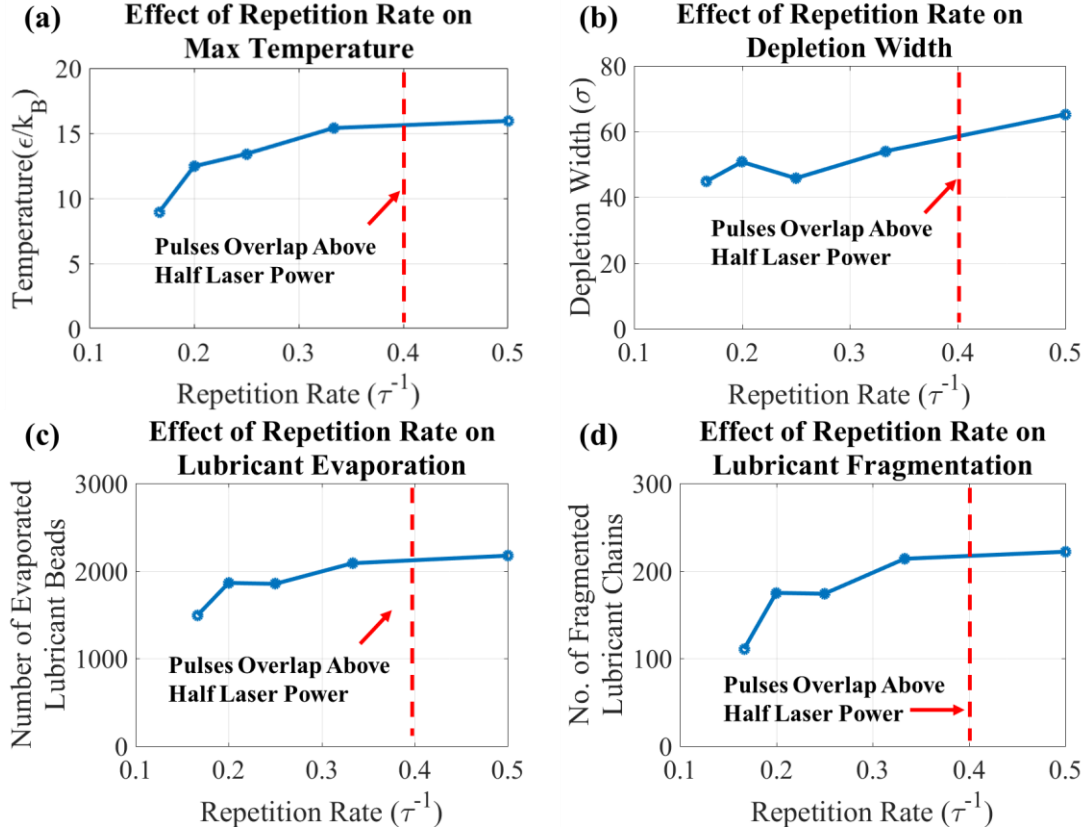


Figure 6.9 Effect of repetition rate on (a) maximum temperature, (b) lubricant depletion width, (c) number of evaporated lubricant beads, and (d) number of fragmented lubricant chains.

Figure 6.9 shows the maximum temperature, the depletion width, the number of evaporated lubricant beads, and the number of fragmented lubricant chains as a function of repetition rate f_{pulse} , keeping laser peak power ($P_{peak} = 1,400\epsilon/\tau \approx 14$ nW) and pulse duration ($FWHM = 2.35\tau \approx 235$ ps) constant. We observe that the maximum temperature, the depletion width, the number of evaporated lubricant beads and the

number of fragmented lubricant chains increase with repetition rate. It is important to note that laser pulses begin to overlap if the repetition rate is increased above a critical repetition rate.

In addition to a Gaussian pulse laser, we also simulated continuous-wave laser heating and square pulse laser heating in order to compare how different types of laser heating affect lubricant depletion. In Figure 6.10, laser power versus time is plotted as a function of pulse type. Figure 6.10(a) shows laser power for a continuous-wave laser, Figure 6.10(b) shows laser power for a Gaussian pulse laser, and Figure 6.10(c) shows laser power for a square pulse laser.

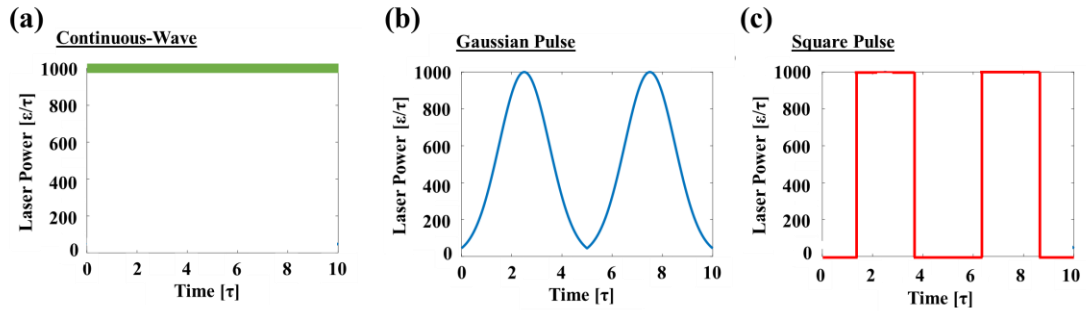


Figure 6.10 Laser power versus time for (a) Continuous-wave laser, (b) Gaussian pulse laser, and (c) square pulse laser.

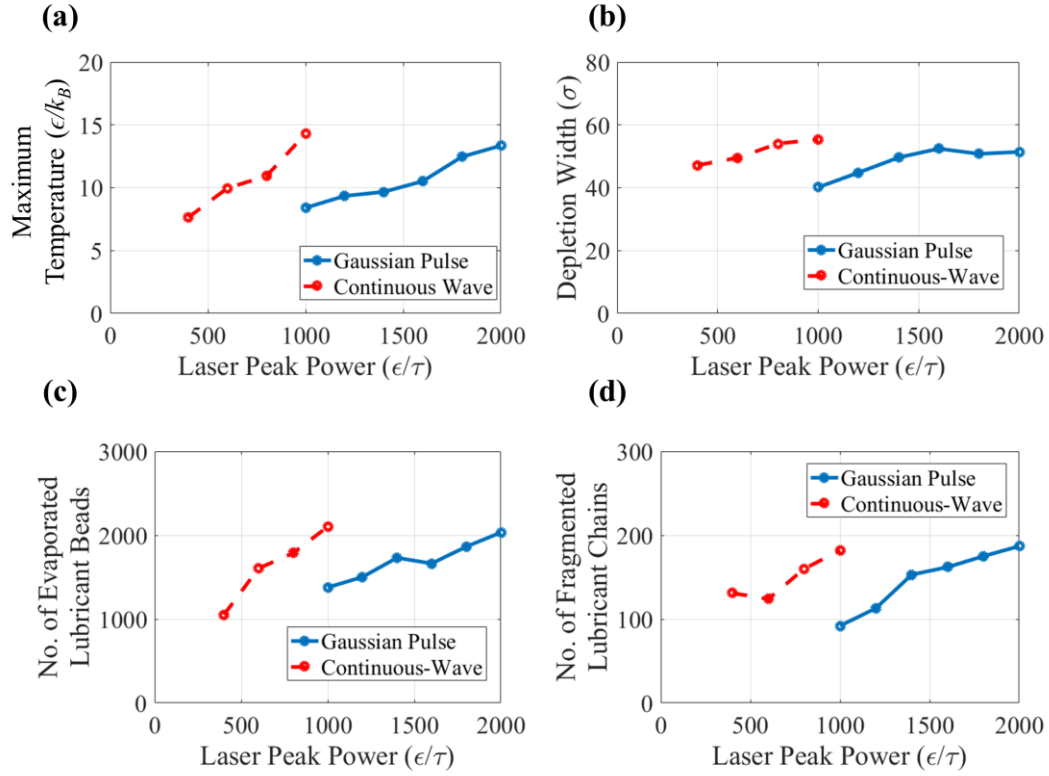


Figure 6.11 Comparison between a continuous-wave laser and a Gaussian pulse laser. Effect of laser peak power on (a) maximum temperature, (b) lubricant depletion width, (c) number of evaporated lubricant beads, and (d) number of fragmented lubricant chains.

Figure 6.11 shows the maximum temperature, the depletion width, the number of evaporated lubricant beads and the number of fragmented lubricant chains as a function of laser peak power. Continuous-wave lasers were investigated for laser peak power ranging from 400 to 1,000 ϵ/τ . Gaussian pulse lasers were simulated for laser peak power ranging from 1,000 to 2,000 ϵ/τ with pulse duration of 2.35τ (≈ 235 ps) and repetition rate of $0.2\tau^{-1}$ (≈ 2 GHz). We observe that the laser peak power to deplete a similar amount of lubricant molecules is smaller for continuous-wave lasers than for pulsed lasers.

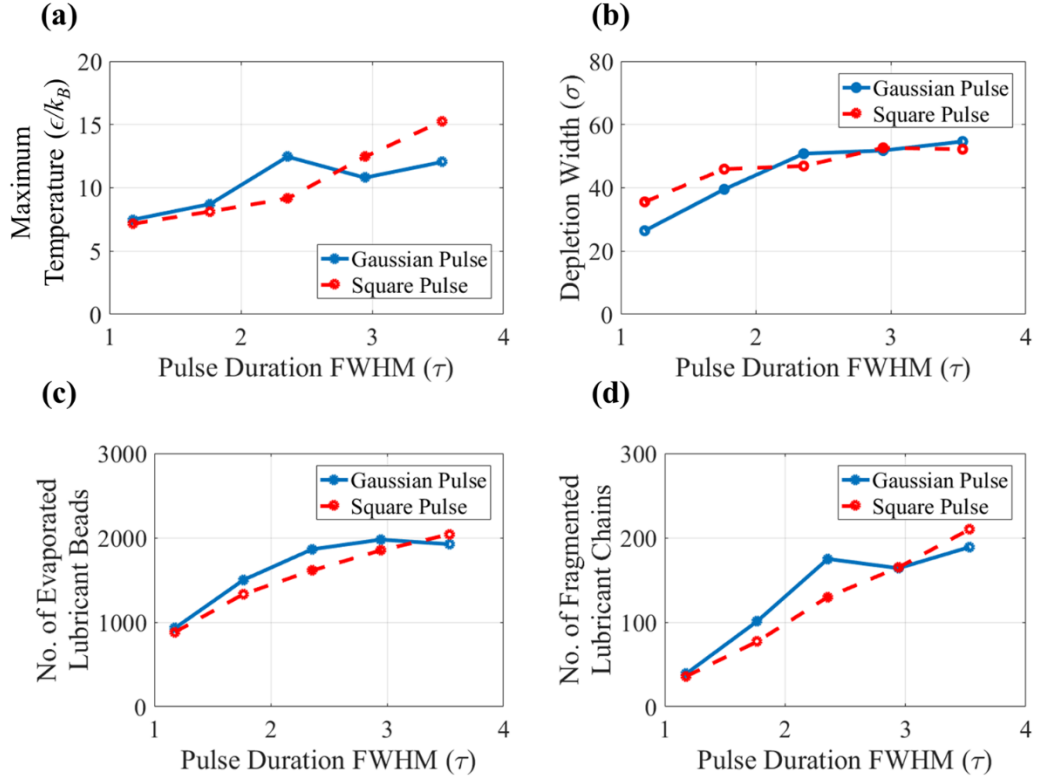


Figure 6.12 Comparison between a square pulse laser and a Gaussian pulse laser. Effect of pulse duration on (a) maximum temperature, (b) lubricant depletion, (c) number of evaporated lubricant beads, and (d) number of fragmented lubricant chains.

Figure 6.12 shows the maximum temperature, the depletion width, the number of evaporated lubricant beads and the number of fragmented lubricant chains as a function of pulse duration *FWHM*. Both square pulse lasers and Gaussian pulse lasers were investigated for pulse duration ranging from 1.18 to 3.53τ with laser peak power of $1,400\epsilon/\tau$ (≈ 14 nW) and repetition rate of $0.2\tau^{-1}$ (≈ 2 GHz). We observe that for the same pulse duration, square pulse lasers deplete a similar amount of lubricant molecules as Gaussian pulse lasers.

6.4 Discussion

Molecular dynamics simulations were performed to investigate pulsed laser heating on lubricant depletion. Due to spatial and temporal limitations inherent in molecular dynamics, the results for lubricant depletion, lubricant evaporation, and lubricant fragmentation must be considered qualitative rather than quantitative in nature. Our results show good agreement with experimental work by Tagawa et al. [247-249], theoretical prediction by Wu and Talke [255], and molecular dynamics simulation of continuous-wave laser irradiation by Li et al [265-266].

Lubricant depletion increases as a function of laser peak power, pulse duration and repetition rate as shown in Figure 6.7-6.9. Also, as can be seen in Figure 6.9(a), the maximum temperature approaches a nearly constant value as the repetition rate is increased. A similar trend is observed for the depletion width, the number of evaporated lubricant beads and the number of fragmented lubricant chains. This effect is a function of pulse overlapping, i.e., if the repetition rate is increased, pulses begin to overlap and approach the continuous-wave laser results. Figure 6.13 illustrates the “overlapping” of laser pulses at two different repetition rates, namely $0.2\tau^{-1}$ (≈ 2 GHz) and $0.5\tau^{-1}$ (≈ 5 GHz). “Overlapping” of pulses occurs when a second laser pulse begins before the first pulse is “completed”. In Figure 6.13, overlapped parts of the pulses are shown as shaded portions.

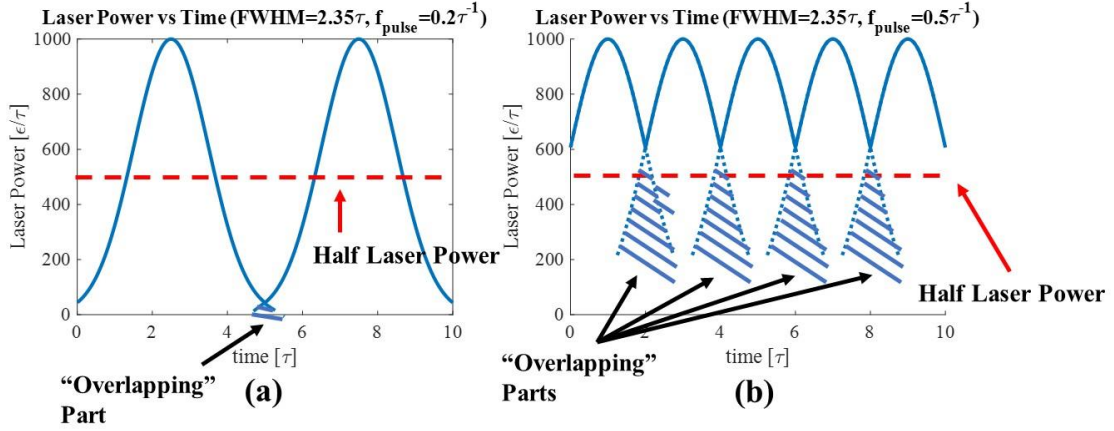


Figure 6.13 Laser pulse power as a function of time with $\text{FWHM} = 2.35\tau$ (≈ 235 ps) at the repetition rate (a) $f_{\text{pulse}} = 0.2\tau^{-1}$ (≈ 2 GHz) and (b) $f_{\text{pulse}} = 0.5\tau^{-1}$ (≈ 5 GHz).

For a repetition rate of $0.2\tau^{-1}$ (≈ 2 GHz), overlap of laser pulses is not significant (Figure 6.13(a)). When the repetition rate is increased to $0.5\tau^{-1}$ (≈ 5 GHz), laser pulses overlap above the half laser power (Figure 6.13(b)). The overlapping of laser pulses leads to heat accumulation. Due to the high repetition rate and the short time available for heat diffusion, the respective laser pulses cannot be treated as individual pulses. As a consequence, the behavior of a pulsed laser at high repetition rates approaches that of a continuous-wave laser. In other words, the average laser power increases with an increase in the laser repetition rate. At very high pulse repetition rates, the average laser power approaches the value of a continuous-wave laser.

In this study, two important assumptions were made. First, we assumed the laser pulse to be Gaussian over time and space. In order to understand the effect of the pulse shape on lubricant depletion, we performed additional molecular dynamics simulations with continuous-wave laser heating (similar to Ref. [265-266]) and square laser pulse heating as shown in Figure 6.10. We observed that at approximately half laser peak power, continuous-wave laser heating resulted in a similar number of evaporated

lubricant beads and fragmented lubricant chains as that of Gaussian pulse laser heating (Figure 6.11). This is because the average energy supplied from the laser is much less when the laser is pulsed compared to a continuous-wave laser. This agrees with the results reported by Xu et al. [261] and Wang et al. [250]. In contrast, square laser pulses resulted in a similar number of evaporated lubricant beads and fragmented lubricant chains when compared to a Gaussian pulse laser (Figure 6.12). The results indicate that a square pulse laser with the same pulse duration as a Gaussian pulse laser supplies a similar amount of energy, leading to similar lubricant depletion behavior.

Second, we assumed that both the disk and the laser are stationary. We believe that the main difference between the stationary and moving lasers is the volume of affected lubricant molecules. To verify this assumption, we performed molecular dynamics simulations with a moving laser source.

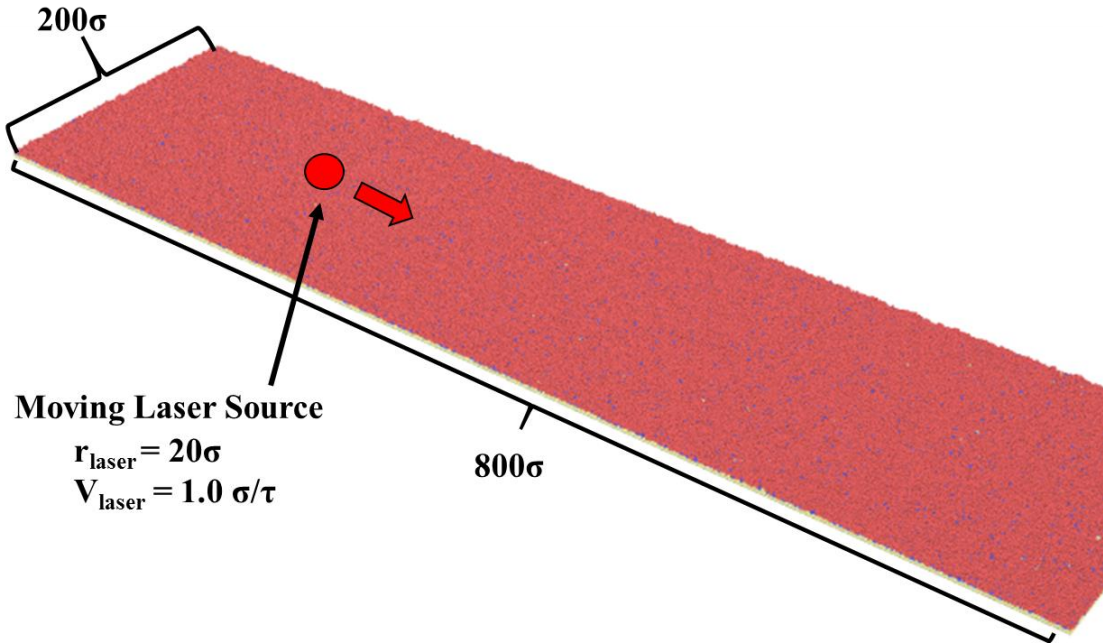


Figure 6.14 Molecular dynamics simulation with a moving laser source with a radius $r_{\text{laser}} = 20\sigma$ and $V_{\text{laser}} = 1.0\sigma/\tau$ (approximately 7 m/s).

A disk surface ($800\sigma \times 200\sigma$) with a 2σ -thick lubricant layer was modeled (Figure 6.14). The laser source of radius $r_{laser} = 20\sigma$ was simulated to move with a velocity $V_{laser} = 1.0\sigma/\tau$, equivalent to 7 m/s. The laser was pulsed with a pulse duration $FWHM = 2.35\tau$ (≈ 235 ps), a pulse repetition rate $f_{pulse} = 0.2\tau^{-1}$ (≈ 2 GHz), and a laser peak power P_{peak} of 2,000, 4,000, and 6,000 ϵ/τ , respectively. Figure 6.15 shows the number of evaporated lubricant beads versus laser peak power for a moving laser source.

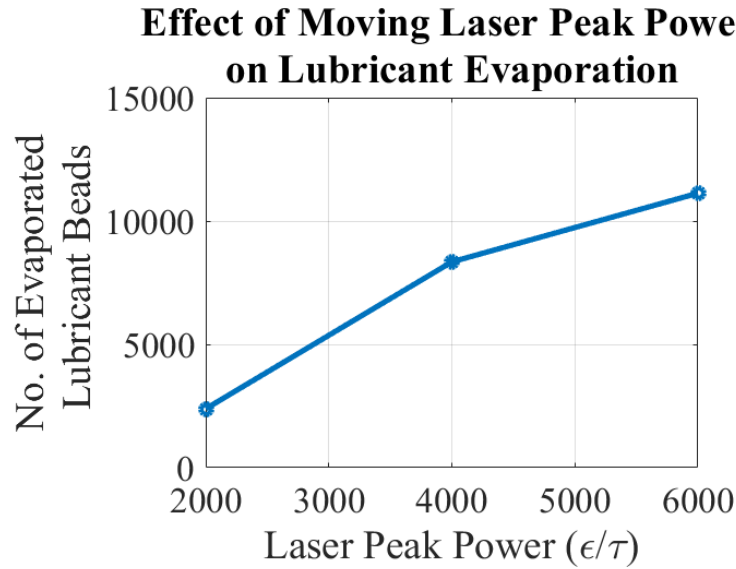


Figure 6.15 Number of evaporated lubricant beads as a function of laser peak power for a moving laser source.

The laser was pulsed for a duration of 300τ , equivalent to 60 laser pulses. The laser was simulated for laser peak power ranging from 2,000 to 6,000 ϵ/τ with a pulse duration of 2.35τ (≈ 235 ps) and a repetition rate of $0.2\tau^{-1}$ (≈ 2 GHz). The results show that lubricant evaporation increases as a function of laser peak power when the laser source moves relative to the stationary case. This is qualitatively the same as for the stationary disk case. Additional studies are required to fully evaluate the effect of a moving pulsed laser on lubricant depletion and degradation.

6.5 Summary

Molecular dynamics simulations were performed to investigate the effect of pulsed laser heating on lubricant depletion. Molecular dynamics simulations show good qualitative agreement with past experimental and numerical investigation with respect to the effect of laser irradiation on the lubricant depletion width, the number of evaporated lubricant beads and the number of fragmented lubricant chains. From the simulations, we conclude:

1. Molecular dynamics simulations prescribed in this paper show good qualitative agreement with previous experimental studies.
2. The maximum temperature, the depletion width, the number of evaporated lubricant beads, and the number of fragmented lubricant chains increase as a function of laser peak power, pulse duration and repetition rate.
3. The effect of repetition rate levels off if laser pulses overlap above the half laser power. In this case, a pulsed laser behaves similarly to a continuous-wave laser.
4. At half laser power, a continuous-wave laser depleted a similar amount of lubricant as a Gaussian pulse laser with repetition rate of $0.2\tau^{-1}$ (≈ 2 GHz).
5. When compared to a Gaussian pulse laser, a square pulse laser was found to deplete a similar amount of lubricant at the same pulse duration as a Gaussian pulse laser.

In this paper, we assumed that the laser spot is stationary. In heat assisted magnetic recording hard disk drives, the disk surface moves with a linear velocity of typically 20 m/s. Comparing studies from Li et al. [267] for a stationary laser and Li et

al. [229] for a moving laser, we observe that the number of evaporated lubricant beads as a function of laser peak power shows similar trends for both stationary and moving laser sources. To improve the understanding of the effect of pulsed laser heating on lubricant depletion, it will be necessary to incorporate the magnetic layer and heat sink layers in the model.

6.6 Acknowledgement

Chapter 6, in part is a reprint of the material as it appears in "Molecular Dynamics Simulation Study on the Effect of Laser Pulse Peak Power, Pulse Duration, and Repetition Rate on Lubricant Depletion," Seo, Young Woo, Andreas Rosenkranz, and Frank E. Talke, *In Preparation for Publication*. The dissertation author was the primary investigator and author of this paper.

Chapter 7 Summary and

Conclusions

As the head-disk spacing in current hard disk drives has been reduced to 1 nm, the head-disk interface has become increasingly more susceptible to contamination. In this dissertation, lubricant transfer and hydrocarbon oil contamination at the head-disk interface are studied.

First, the investigation of hydrocarbon contamination at the head-disk interface is discussed. For this study, a “three-step” hydrocarbon contamination mechanism is postulated. First, hydrocarbon oil molecules evaporate from the source, e.g., pivot actuator arm, and enter the air stream, becoming airborne. Then, airborne hydrocarbon molecules condense on the disk surface. When the head flies in close proximity to the disk surface, hydrocarbon molecules transfer from the disk surface to the head surface. Experimental investigation is performed using a spin-stand tester. Using atomic force microscopy, hydrocarbon droplets and crystals are observed on the disk surface. Optical microscopy and scanning electron microscopy are used to observe hydrocarbon contamination on the head surface. Energy-dispersive X-ray spectroscopy and time-of-flight secondary ion mass spectrometry verify that the contaminants found on the head surface are hydrocarbons, namely C_{32} and C_{36} . Lighter molecules, C_{24} and C_{28} , are not observed. In addition, molecular dynamics simulations are performed to further understand hydrocarbon contamination at the head-disk interface as a function of

temperature and chain length. The results show that with an increase in temperature, hydrocarbon transfer from the disk surface to the head surface increases. However, with an increase in hydrocarbon chain length, hydrocarbon transfer decreases. Also, hydrocarbon transfer is observed to occur predominantly in the form of evaporation. The “three-step” hydrocarbon contamination mechanism hypothesis is verified both experimentally and numerically. A “good” hydrocarbon oil is concluded to be one of the following types. The first type consists of hydrocarbons with low molecular weight and high volatility, allowing the hydrocarbon oil to easily evaporate from any adsorbed surface. The second type of “good” hydrocarbon oil consists of hydrocarbons with high molecular weight and low volatility. This type would not easily outgas from the pivot actuator arm.

Thereafter, molecular dynamics simulations of lubricant transfer and fragmentation at the head-disk interface are performed as a function of temperature, local pressure change and disk velocity. In this study, four types of lubricants are modeled. Type I lubricant consists of two functional end beads and eight backbone beads. Type II lubricant is as long as Type I lubricant with two functional end beads and eighteen backbone beads. Type III and Type IV lubricants have the same chain length as Type I lubricant. Type III lubricant has two functional end beads, two functional center beads, and six backbone beads. Type IV lubricant has four functional end beads and six backbone beads. The molecular dynamics simulation results show that with an increase in temperature, local pressure change and disk velocity, lubricant transfer and fragmentation increase. At low temperature range, Type III and Type IV lubricants exhibit much less lubricant transfer when compared to Type I and Type II lubricants.

Local pressure change is observed to influence lubricant fragmentation most significantly.

At the end of the dissertation, molecular dynamics simulations of pulsed laser irradiation on a stationary disk surface are performed to study the effect of pulsed laser peak power, pulse duration and repetition rate on lubricant depletion. The maximum temperature, the lubricant depletion width, the number of evaporated lubricant beads and the number of fragmented lubricant chains are observed to increase with an increase in laser peak power, pulse duration and repetition rate. Also, a pulsed laser is observed to behave similar to a continuous-wave laser with an increase in repetition rates. In addition, we simulated continuous-wave laser heating and square pulse laser heating in order to compare how different types of laser heating affect lubricant depletion. We observe that a smaller laser peak power is needed for continuous-wave laser heating to deplete a similar amount of lubricant molecules when compared to Gaussian laser heating at low repetition rate. We also observe that for the same pulse duration and repetition rate, both square pulse laser heating and Gaussian pulse laser heating deplete a similar amount of lubricant molecules. Also, the effect of pulsed laser heating on a moving disk surface is studied as a function of laser peak power. However, a further study is needed to enhance our understanding of the effect of pulsed laser heating on a moving disk.

In conclusion, the studies presented in this dissertation provide improved understanding of the mechanism behind lubricant transfer and hydrocarbon contamination at the head-disk interface under various conditions. The results provide a guideline to improve disk lubricants and hydrocarbon-based bearing oils.

Bibliography

- [1] Marr, Bernard. "Big Data: 20 Mind-Boggling Facts." Forbes, Forbes Magazine, 19 Nov. 2015, www.forbes.com/sites/bernardmarr/2015/09/30/big-data-20-mind-boggling-facts-everyone-must-read/#72d1384517b1.
- [2] "IBM 305 RAMAC." Wikipedia, Wikimedia Foundation, 23 July 2017, en.wikipedia.org/wiki/IBM_305_RAMAC.
- [3] Mearian, Lucas. "WD Ships World's First 10TB Helium-Filled Hard Drive." Computerworld, Computerworld, 2 Dec. 2015, www.computerworld.com/article/3011142/data-storage/wd-ships-worlds-first-10tb-helium-filled-hard-drive.html.
- [4] "Seagate Trims 2.5' Hard Drives to Just 7 Millimeters Thick." Geek.com, 8 Dec. 2009, www.geek.com/chips/seagate-trims-2-5-hard-drives-to-just-7-millimeters-thick-1010722/.
- [5] H. Zheng, "Investigation of bit patterned media, thermal flying height control sliders and heat assisted magnetic recording in hard disk drives," University of California, San Diego, 2011.
- [6] Y. Fu, "Tribological Study of Contact Interfaces in Hard Disk Drives," University of California, San Diego, 2016.
- [7] "Magnet." Wikipedia, Wikimedia Foundation, 29 Aug. 2017, en.wikipedia.org/wiki/Magnet#Magnetic_materials.
- [8] "Types of Magnetic Materials." Electronics Tutorials, 15 Nov. 2016, electronicspani.com/types-of-magnetic-materials/.
- [9] Bertram, H. Neal. Theory of magnetic recording. Cambridge University Press, 1994.
- [10] "Magnetic Hysteresis." Electronics Tutorial, www.electronicstutorials.ws/electromagnetism/magnetic-hysteresis.html.
- [11] Jean-Claude Peuzin (4). "Principles of Magnetic Recording." Springer, Springer New York, 1 Jan. 1970, link.springer.com/referenceworkentry/10.1007%2F978-0-387-23063-4_7.

- [12] McFadyen, I. R., E. E. Fullerton, and M. J. Carey. "State-of-the-art magnetic hard disk drives." *Mrs Bulletin* 31.5 (2006): 379-383.
- [13] Richter, H. J. "The transition from longitudinal to perpendicular recording." *Journal of Physics D: Applied Physics* 40.9 (2007): R149.
- [14] Piramanayagam, S. N. "Perpendicular recording media for hard disk drives." *Journal of Applied Physics* 102.1 (2007): 2.
- [15] Richter, H. J., A. Y. Dobin, O. Heinonen, K. Z. Gao, R. J. M. vd Veerdonk, R. T. Lynch, J. Xue. "Recording on bit-patterned media at densities of 1 Tb/in ^{2} and beyond." *IEEE Transactions on Magnetics* 42, no. 10 (2006): 2255-2260.
- [16] Al Mamun, Abdullah, GuoXiao Guo, and Chao Bi. *Hard disk drive: mechatronics and control*. Vol. 23. CRC press, 2006.
- [17] Toshiba: Press Releases 14 December, 2004, www.toshiba.co.jp/about/press/2004_12/pr1401.htm.
- [18] Rottmayer, Robert E., Sharat Batra, Dorothea Buechel, William A. Challener, Julius Hohlfeld, Yukiko Kubota, Lei Li. "Heat-assisted magnetic recording." *IEEE Transactions on Magnetics* 42, no. 10 (2006): 2417-2421.
- [19] Shiroishi, Y., K. Fukuda, I. Tagawa, H. Iwasaki, S. Takenoiri, H. Tanaka, H. Mutoh, and N. Yoshikawa. "Future options for HDD storage." *IEEE Transactions on Magnetics* 45, no. 10 (2009): 3816-3822.
- [20] Challener, W. A., Chubing Peng, A. V. Itagi, D. Karns, Wei Peng, Yingguo Peng, XiaoMin Yang. "Heat-assisted magnetic recording by a near-field transducer with efficient optical energy transfer." *Nature photonics* 3, no. 4 (2009): 220-224.
- [21] Kryder, Mark H., Edward C. Gage, Terry W. McDaniel, William A. Challener, Robert E. Rottmayer, Ganping Ju, Yiao-Tee Hsia, and M. Fatih Erden. "Heat assisted magnetic recording." *Proceedings of the IEEE* 96, no. 11 (2008): 1810-1835.
- [22] Piramanayagam, S. N., and Tow C. Chong, eds. *Developments in data storage: materials perspective*. John Wiley & Sons, 2011.
- [23] Eom, Hyo J. "Faraday's Law of Induction." *Primary Theory of Electromagnetics*. Springer Netherlands, 2013. 95-111.
- [24] Wallace, R. L. "The reproduction of magnetically recorded signals." *Bell Labs Technical Journal* 30, no. 4 (1951): 1145-1173.

- [25] Shi, W., L. Zhu, and D. Bogy. "Use of readback signal modulation to measure head/disk spacing variations in magnetic disk files." *IEEE transactions on magnetics* 23, no. 1 (1987): 233-240.
- [26] Rouse, Margaret. "What Is Magnetoresistive Head Technology? - Definition from WhatIs.com." SearchStorage, Apr. 2005, searchstorage.techtarget.com/definition/magnetoresistive-head-technology.
- [27] Takanashi, K. (2015) Fundamentals of Magnetoresistance Effects, in *Spintronics for Next Generation Innovative Devices* (eds K. Sato and E. Saitoh), John Wiley & Sons, Ltd, Chichester, UK. doi: 10.1002/9781118751886.ch1
- [28] Bajorek, C. "Magnetoresistive (MR) heads and the earliest MR head-based disk drives: Sawmill and Corsair." Computer History Museum, Mountain View, CA, Tech. Rep (2014).
- [29] Thomson, William. "On the electro-dynamic qualities of metals:--effects of magnetization on the electric conductivity of nickel and of iron." *Proceedings of the Royal Society of London* 8 (1856): 546-550.
- [30] McGuire, T., and R. L. Potter. "Anisotropic magnetoresistance in ferromagnetic 3d alloys." *IEEE Transactions on Magnetism* 11.4 (1975): 1018-1038.
- [31] M. N. Baibich, J. M. Broto, A. Fert, F. N. Van Dau, F. Petroff, P. Eitenne, G. Creuzet, A. Friederich, and J. Chazelas, "Giant magnetoresistance of (001)Fe/(001)Cr magnetic superlattices," *Phys. Rev. Lett.*, vol. 61, no. 21, pp. 2472–2475, 1988.
- [32] G. Binasch, P. Grunberg, F. Saurenbach, and W. Zinn, "Enhanced magnetoresistance in layered magnetic structures with antiferromagnetic interlayer exchange," *Phys. Rev. B*, vol. 39, no. 7, pp. 4828–4830, 1989.
- [33] E. Y. Tsybal and D. G. Pettifor, "Giant magnetoresistance in magnetic metallic multilayers," 1999. [Online]. Available: http://unlcms.unl.edu/cas/physics/tsybal/tsybal_files/Presentations/JMW-1999.pdf.
- [34] Julliere, Michel. "Tunneling between ferromagnetic films." *Physics letters A* 54.3 (1975): 225-226.
- [35] Tongsomporn, Damrongsak, Nitin Afzulpurkar, Brent Bargmann, Lertsak Lekawat, and Apirat Siritaratiwat. "An experimental study of head instabilities in TMR sensors for magnetic recording heads with adaptive flying height." *IEICE transactions on electronics* 91, no. 12 (2008): 1958-1965.

- [36] Introduction to Tribology – Friction, depts.washington.edu/nanolab/ChemE554/Summaries%20ChemE%20554/Introduction%20Tribology.htm.
- [37] B. Bhushan, Introduction to tribology, 2nd ed. New York: John Wiley & Sons, 2013.
- [38] Blau, Peter J. "Amontons' Laws of Friction." *Encyclopedia of Tribology*. Springer US, 2013. 71-71.
- [39] F. P. Bowden and D. Tabor, The friction and lubrication of solids, vol. 1. Oxford: Oxford university press, 2001.
- [40] Rubenstein, C. "A general theory of the surface friction of solids." *Proceedings of the Physical Society. Section B* 69.9 (1956): 921.
- [41] B. Bhushan, Principles and applications of tribology. New York: John Wiley & Sons, 2013.
- [42] Johnson, K. L. Contact Mechanics. Cambridge, Cambridge University Press, 1985.
- [43] Tabor, David. "The mechanism of rolling friction. II. The elastic range." *Proceedings of the Royal Society of London A: Mathematical, Physical and Engineering Sciences*. Vol. 229. No. 1177. The Royal Society, 1955.
- [44] Tabor, David. "Friction, lubrication and wear." *Surface and colloid science* 5 (1972): 245-312.
- [45] Archard, J. F. "Elastic deformation and the laws of friction." *Proceedings of the Royal Society of London A: Mathematical, Physical and Engineering Sciences*. Vol. 243. No. 1233. The Royal Society, 1957.
- [46] E. Rabinowicz, Friction and wear of materials. New York: Wiley, 1965.
- [47] N. K. Myshkin, M. I. Petrokovets, and A. V. Kovalev, "Tribology of polymers: adhesion, friction, wear, and mass-transfer," *Tribol. Int.*, vol. 38, no. 11, pp. 910–921, 2005.
- [48] J. A. Greenwood and D. Tabor, "Deformation properties of friction junctions," *Proc. Phys. Soc. Sect. B*, vol. 68, no. 9, p. 609, 1955.
- [49] Greenwood, J. A., and D. Tabor. "The properties of model friction junctions." *Inst. Mech. Eng. Proc. of Conference on Lubrication and Wear*, Paper. Vol. 92. 1957.

- [50] Bayer, R. G., P. A. Engel, and J. L. Sirico. "Impact wear testing machine." *Wear* 19.3 (1972): 343-354.
- [51] Halling, John. *Principles of tribology*. Macmillan, 1975.
- [52] Rabinowicz, E. "The wear coefficient—magnitude, scatter, uses." *ASME J. Lubr. Technol* 103.2 (1981): 188-194.
- [53] Suh, Nam P. "Tribophysics." *Prentice-Hall, Englewood Cliffs, New Jersey 07632, USA, 1986*. (1986).
- [54] Komvopoulos, K. N. N. P., N. Saka, and N. P. Suh. "The mechanism of friction in boundary lubrication." *Journal of tribology* 107.4 (1985): 452-462.
- [55] Holm, R. "Electrical Contacts, Stockholm: H." *Gerber Pub* (1946).
- [56] Archard, JeFoa. "Contact and rubbing of flat surfaces." *Journal of applied physics* 24.8 (1953): 981-988.
- [57] Buttery, T. C., and J. F. Archard. "Grinding and abrasive wear." *Proceedings of the Institution of Mechanical Engineers* 185.1 (1970): 537-551.
- [58] Burwell, John T. "Survey of possible wear mechanisms." *Wear* 1.2 (1957): 119-141.
- [59] Kovaříková, Ingrid, Beáta Szewczyková, Pavel Blaškoviš, E. Hodúlová, and E. Lechovič. "Study and characteristic of abrasive wear mechanisms." *Materials Science and Technology* [online].-ISSN (2009): 1335-9053.
- [60] Spurr, R. T., and T. P. Newcomb. "The friction and wear of various materials sliding against unlubricated surfaces of different types and degrees of roughness." *Proceedings of the Conference Lubrication and Wear*. 1957.
- [61] Avient, B. W. E., J. Goddard, and H. Wilman. "An experimental study of friction and wear during abrasion of metals." *Proceedings of the Royal Society of London A: Mathematical, Physical and Engineering Sciences*. Vol. 258. No. 1293. The Royal Society, 1960.
- [62] Lopa, M. *A Study of the Influence of Hardness, Rubbing Speed and Load on Abrasive Wear*. Diss. BS thesis, MIT, Cambridge, 1956.
- [63] Khrushchov, M. M., and M. A. Babichev. "An investigation of the wear of metals and alloys by rubbing on an abrasive surface." *ASME Friction Wear Mach* 11 (1956): 1-12.

- [64] Samuels, L. E. "The nature of mechanically polished metal surfaces: the surface deformation produced by the abrasion and polishing of 70: 30 brass." *Journal of the Institute of Metals* 85 (1956): 51-62.
- [65] Toporov, G. V. "The influence of structure on the abrasive wear of cast iron." *Friction and Wear in Machinery* 12 (1958): 39-59.
- [66] Rabinowicz, E., L. A. Dunn, and P. G. Russell. "The abrasive wear resistance of some bearing steels." *Lubr. Eng* 17 (1961): 587-593.
- [67] Rabinowicz, E., L. A. Dunn, and P. G. Russell. "A study of abrasive wear under three-body conditions." *Wear* 4.5 (1961): 345-355.
- [68] Thomas, T. R. "Characterization of surface roughness." *Precision Engineering* 3, no. 2 (1981): 97-104.
- [69] Hertz, Heinrich. "On the contact of elastic solids." *J. Reine Angew Math.* 92 (1881): 156-171.
- [70] Greenwood, J. A., and JB Pl Williamson. "Contact of nominally flat surfaces." In *Proceedings of the Royal Society of London A: Mathematical, Physical and Engineering Sciences*, vol. 295, no. 1442, pp. 300-319. The Royal Society, 1966.
- [71] Brunner, Ralf, Izhak Etsion, and Frank E. Talke. "A simple atomic force microscopy calibration method for direct measurement of surface energy on nanostructured surfaces covered with molecularly thin liquid films." *Review of Scientific Instruments* 80, no. 5 (2009): 055109.
- [72] Miller, Clint Matthew. "Adhesion and the surface energy components of natural minerals and aggregates." PhD diss., Texas A & M University, 2011.
- [73] Seo, Young Woo, Andrey Ovcharenko, Yongqi Yan, and Frank E. Talke. "Experimental Investigation of the Effect of Hydrocarbon Oil Contamination on a Disk Surface." In *ASME 2016 Conference on Information Storage and Processing Systems*, pp. V001T01A015-V001T01A015. American Society of Mechanical Engineers, 2016.
- [74] Owens, Daniel K., and R. C. Wendt. "Estimation of the surface free energy of polymers." *Journal of applied polymer science* 13, no. 8 (1969): 1741-1747.
- [75] Waltman, R. J. "The interactions between Z-Tetraol perfluoropolyether lubricant and amorphous nitrogenated-and hydrogenated-carbon surfaces and silicon nitride." *Journal of fluorine chemistry* 125, no. 3 (2004): 391-400.

- [76] B. J. Hamrock, S. R. Schmid, and B. O. Jacobson, *Fundamentals of fluid film lubrication*. New York: CRC press, 2004.
- [77] Kondo, Yuriko, Tahahiro Koyama, and Shinya Sasaki. "Tribological properties of ionic Liquids." *Ionic liquids-New aspects for the future*. InTech, 2013.
- [78] Pugh, Brinley. "Practical lubrication: an introductory text." (1970).
- [79] Hess, Fred C., and Arthur Louis Thomas. *Chemistry made simple*. Broadway Books, 2001.
- [80] Robert J. Ouellette and J. David Rawn, 2 - Part I: Functional Groups and Their Properties, In *Organic Chemistry*, Elsevier, Boston, 2014, Pages 41-74, ISBN 9780128007808, <https://doi.org/10.1016/B978-0-12-800780-8.00002-4>. (<http://www.sciencedirect.com/science/article/pii/B9780128007808000024>)
- [81] Tyndall, G. W., P. B. Leezenberg, R. J. Waltman, and J. Castenada. "Interfacial interactions of perfluoropolyether lubricants with magnetic recording media." *Tribology Letters* 4, no. 2 (1998): 103-108.
- [82] Zumdahl, Steven S. *Chemistry*. DC Heath, Lexington, MA, 1986. ISBN 0-669-04529-2.
- [83] Srivastava, Som Prakash. *Developments in lubricant technology*. John Wiley & Sons, 2014.
- [84] C. Mathew Mate, "Molecular tribology of disk drives," *Tribology Letters*, vol. 4, no. 2, pp. 119–123, 2000.
- [85] R. Z. Lei, A. J. Gellman, P. Jones, and Ryan Z. Lei; Andrew J. Gellman; Paul Jones, "Thermal stability of Fomblin Z and Fomblin Zdol thin Films on amorphous hydrogenated Carbon," *Tribology Letters*, vol. 11, no. 1, pp. 1–5, 2001.
- [86] G.W. Tyndall, P. B. Leezenberg, R. J.Waltman, and J. Castenada, "Interfacial interactions of perfluoropolyether lubricants with magnetic recording media," *Tribology Letters*, vol. 4, no. 2, pp. 103–108, 1998.
- [87] P. H. Kasai and V. Raman, "Lubricant Transfer in Disk Drives," *Tribology Letters*, vol. 48, no. 3, pp. 367–374, aug 2012.
- [88] T. E. Karis, G. W. Tyndall, and R. J. Waltman, "Lubricant Bonding Effects on Thin Film Disk Tribology," *Tribology Transactions*, vol. 44, no. 2, pp. 249–255, jan 2001.

- [89] J. Gui and B. Marchon, "Fly/stiction: mechanical instability of a head-disc interface," *Magn. IEEE Trans.*, vol. 34, no. 4, pp. 1804–1806, 1998.
- [90] C. Gao, P. Dai, and V. Vu, "Flying stiction, lubricant pick-up and carbon-overcoat wear of magnetic heads," *J. Tribol.*, vol. 121, no. 1, pp. 97–101, 1999.
- [91] Y. Ma and B. Liu, "Lubricant transfer from disk to slider in hard disk drives," *Appl. Phys. Lett.*, vol. 90, no. 14, p. 143516, 2007.
- [92] R. P. Ambekar, D. B. Bogy, and C. S. Bhatia, "Lubricant depletion and disk-to-head lubricant transfer at the head-disk interface in hard disk drives," *Journal of Tribology*, vol. 131, no. 3. p. 031901, 2009.
- [93] Y. W. Seo, D. Pan, A. Ovcharenko, M. Yang, and F. E. Talke, "Molecular dynamics simulation of lubricant transfer at the head-disk interface," *IEEE Transactions on Magnetics*, vol. 50, no. 11. pp. 1–4, 2014.
- [94] Wood, Roger. "Future hard disk drive systems." *Journal of magnetism and magnetic materials* 321.6 (2009): 555-561.
- [95] Bouchard, G., L. Lau, and F. Talke. "An investigation of non-repeatable spindle runout." *IEEE Transactions on Magnetics* 23.5 (1987): 3687-3689.
- [96] Blount, Walker C. "Fluid dynamic bearing spindle motors: Their future in hard disk drives." *IBM White Paper* (2007).
- [97] Seo, Young Woo, Andrey Ovcharenko, Daniel Bilich, and Frank E. Talke. "Experimental Investigation of Hydrocarbon Contamination at the Head–Disk Interface." *Tribology Letters* 65, no. 2 (2017): 54.
- [98] Fowler, D. E., Geiss, R. H., Eldridge, D., & Schreck, E. "Observation of slider droplet formation during fly stiction tests with a real time visualization instrument." *Magnetics, IEEE Transactions on* 35.5 (1999): 2409-2411.
- [99] Fowler, David E., and Roy H. Geiss. "Chemical contamination at the head-disk interface in a disk drive." *IEEE transactions on magnetics* 36.1 (2000): 133-139.
- [100] Akamatsu, Naotoshi, and Toshiaki Ohtani. "Study of the adsorption of siloxane and hydrocarbon contaminants onto the surfaces at the head/disk interface of a hard disk drive by thermal desorption spectroscopy." *Tribology Letters* 13.1 (2002): 15-20.
- [101] Sonoda, Koji. "Flying Instability due to Organic Compounds in Hard Disk Drive." *Advances in Tribology* 2012 (2012).

- [102]Raman, V., Nguyen, T., and Escobar J., “Reliability Enhancements in Hard Disk Drives Using In-Situ Vapor Phase Additives.” 40th Leeds-Lyon Symposium on Tribology & Tribochemistry Forum 2013. Oral presentation (2013).
- [103]Kasai, Paul H., and Vedantham Raman. "Hydrocarbon Transfer in Disk Drives."ASME 2014 Conference on Information Storage and Processing Systems. American Society of Mechanical Engineers, 2014.
- [104]Chen, Chao-Yuan, David B. Bogy, Tai Cheng, and C. Singh Bhalia. "Effect of the additive X-1P on the tribological performance and migration behavior of PFPE lubricant at the head-disk interface." IEEE transactions on magnetics 36, no. 5 (2000): 2708-2710.
- [105]B. Marchon, M. R. Khan, N. Heiman, P. Pereira, and A. Lautie, “Tribochemical wear on amorphous carbon thin films,” IEEE Transactions on Magnetics, vol. 26, no. 5, pp. 2670–2675, 1990.
- [106]J. Robertson, “Diamond-like amorphous carbon,” Materials Science and Engineering: R: Reports, vol. 37, no. 4-6, pp. 129–281, 2002.
- [107]B. Wei, B. Zhang, and K. E. Johnson, “Nitrogen-induced modifications in microstructure and wear durability of ultrathin amorphous-carbon films,” Journal of Applied Physics, vol. 83, no. 5, pp. 2491–2499, 1998.
- [108]A. R. Machcha, M. H. Azarian, and F. E. Talke, “An investigation of nano-wear during contact recording,” Wear, vol. 197, pp. 211–220, 1996.
- [109]A. Grill, “Tribology of diamondlike carbon and related materials: an updated review,” Surface and Coatings Technology, vol. 94-95, pp. 507–513, oct 1997.
- [110]Zhou, Weidong, Shengkai Yu, Wei Hua, and Kyaw Sett Myo. "A modified slip model for gas lubrication at nanoscale head-disk interface." Proceedings of the Institution of Mechanical Engineers, Part J: Journal of Engineering Tribology 227, no. 12 (2013): 1367-1375.
- [111]Wahl, Michael H. *Numerical and experimental investigation of the head/disk interface*. Diss. University of California, San Diego, 1994.
- [112]Duwensee, Maik. *Numerical and experimental investigations of the head/disk interface*. Diss. University of California, San Diego, 2007.
- [113]L. Matthes, “Experimental studies of the head-disk interface from a tribological and controls point of view for flying heights below 2 nm,” University of California, San Diego, 2016

- [114] Marion Brünglinghaus, ENS, European Nuclear Society. Mean Free Path, www.euronuclear.org/info/encyclopedia/m/mean-free-path.htm.
- [115] Fukui, S., and R. Kaneko. "Analysis of flying characteristics of magnetic heads with ultra-thin spacings based on the Boltzmann equation." *IEEE Transactions on Magnetics* 24.6 (1988): 2751-2753.
- [116] Y. Morinishi, T. S. Lund, O. V Vasilyev, and P. Moin, "Fully conservative higher order finite difference schemes for incompressible flow," *J. Comput. Phys.*, vol. 143, no. 1, pp. 90–124, 1998.
- [117] L. Wu and D. B. Bogy, "Unstructured adaptive triangular mesh generation techniques and finite volume schemes for the air bearing problem in hard disk drives," *J. Tribol.*, vol. 122, no. 4, pp. 761–770, 2000.
- [118] H. Li, H. Zheng, Y. Yoon, and F. E. Talke, "Air bearing simulation for bit patterned media," *Tribol. Lett.*, vol. 33, no. 3, pp. 199–204, 2009.
- [119] P. A. Salas and F. E. Talke, "Numerical simulation of thermal flying-height control sliders to dynamically minimize flying height variations," *Magn. IEEE Trans.*, vol. 49, no. 4, pp. 1337–1342, 2013.
- [120] Yeack-Scranton, C. E., V. D. Khanna, K. F. Etzold, and A. P. Praino. "An active slider for practical contact recording." *IEEE Transactions on Magnetics* 26, no. 5 (1990): 2478-2483.
- [121] Schultz, Brian E. "Thermal fly-height control (TFC) technology in Hitachi hard disk drives." *Hitachi Global Storage Technologies, San Jose* (2007): 4.
- [122] Zheng, Jinglin, David B. Bogy, Shuyu Zhang, and Wentao Yan. "Effects of altitude on thermal flying-height control actuation." *Tribology letters* 40, no. 3 (2010): 295-299.
- [123] "Candela™ 63xx." Candela 6300 Series Manual, KLA Tencor, www.kla-tencor.com/candela_6300.pdf/download.
- [124] "Candela™ 71xx." Candela 71xx Hard Disk Inspection - Hard Disk Defect Inspection | KLA-Tencor, www.kla-tencor.com/Transparent-Metal-Substrate-Inspection-Metrolo/candela-71xx.html.
- [125] Tompkins, Harland, and Eugene A. Irene. *Handbook of ellipsometry*. William Andrew, 2005.

- [126]Hinrichs, Karsten, and Klaus-Jochen Eichhorn, eds. *Ellipsometry of functional organic surfaces and films*. Vol. 52. Berlin: Springer, 2014.
- [127]Jung, Jesper, Jakob Bork, Tobias Holmgaard, and Niels Anker Kortbek. "Ellipsometry." *Aalborg University, Aalborg* (2004).
- [128]Ovcharenko, A., T. Karis, and J. P. Peng. "Correlation of Disk Topography Waves with Nanometer-Scale Lubricant Moguls and Magnetic Head Media Spacing." *Tribology Letters* 65, no. 4 (2017): 122.
- [129]"Scanning Electron Microscopy." How Does Scanning Electron Microscopy Work?, www.nanoscience.com/technology/sem-technology/.
- [130]Wells, Oliver C., and David C. Joy. "The early history and future of the SEM." *Surface and interface analysis* 38.12-13 (2006): 1738-1742.
- [131]De Broglie, Louis. "The wave nature of the electron." *Nobel lecture* 12 (1929): 244-256.
- [132]"Electron Microscopy Tutorial." Introduction to Electron Microscopy - Advanced Microscopy - Imaging Facilities - The University of Utah, advanced-microscopy.utah.edu/education/electron-micro/.
- [133]Window on a Small World, pubs.acs.org/subscribe/archive/tcaw/11/i06/html/06inst.html.
- [134]"Afm Modes 12-10." Wikipedia, commons.wikimedia.org/wiki/File:Afm_modes_12-10.png.
- [135]Li, Hong-Qiang. AFM Scanning Modes, 24 Apr. 1997, www.chembio.uoguelph.ca/educmat/chm729/afm/details.htm.
- [136]"Energy-Dispersive X-Ray Spectroscopy (EDS)." Characterization in Silicon Processing, 1993, p. 188., doi:10.1016/b978-0-08-052342-2.50020-6.
- [137]"MyScopetraining for Advanced Research." Background Information - What Is Energy Dispersive X-Ray Spectroscopy? | MyScope, www.ammrf.org.au/myscope/analysis/eds/.
- [138]"Bremsstrahlung." Wikipedia, Wikimedia Foundation, 30 July 2017, en.wikipedia.org/wiki/Bremsstrahlung.
- [139]"Characteristic X-Ray." Wikipedia, Wikimedia Foundation, 27 July 2017, en.wikipedia.org/wiki/Characteristic_X-ray.

- [140]“The Prashant Kamat Laboratory.” Physical Characterization Facilities || The Prashant Kamat Lab at the University of Notre Dame, www3.nd.edu/~kamatlab/facilities_physchar.html.
- [141] “Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS).” Techniques, 16 May 2017, serc.carleton.edu/research_education/geochemsheets/techniques/ToF-SIMS.html.
- [142]Fearn, Sarah. *An Introduction to Time-of-flight Secondary Ion Mass Spectrometry (ToF-SIMS) and Its Application to Materials Science*. Morgan & Claypool Publishers, 2015.
- [143]“Biomarker Analysis (Molecular Imaging) of Small Samples Using Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS).” Biomarker Analysis, www.geomuseum.uni-goettingen.de/people/vthiel/tof_sims/index.shtml.
- [144]Pan, Deng, Andrey Ovcharenko, Min Yang, Filippo Radicati, and Frank E. Talke. "Effect of pitch and roll static angle on lubricant transfer between disk and slider." *Tribology Letters* 53, no. 1 (2014): 261-270.
- [145]Fermi, E., J. Pasta, S. Ulam, and M. Tsingou. "Los Alamos Report No." LA-1940 (1955): 978.
- [146]Alder, Berni J., and T E. Wainwright. "Studies in molecular dynamics. I. General method." *The Journal of Chemical Physics* 31.2 (1959): 459-466.
- [147]Rahman, A. "Correlations in the motion of atoms in liquid argon." *Physical Review* 136.2A (1964): A405.
- [148]Beveridge, D. L., M. Mezei, P. K. Mehrotra, F. T. Marchese, G. Ravi-Shankar, T. Vasu, and S. Swaminathan. "Molecular-based study of fluids." *Advances in Chemistry* 204 (1983): 297-351.
- [149]Tolman, Richard Chace. *The principles of statistical mechanics*. Courier Corporation, 1938.
- [150]Guardian Staff. “Physicist Erwin Schrödinger's Google Doodle Marks Quantum Mechanics Work.” *The Guardian*, Guardian News and Media, 12 Aug. 2013, www.theguardian.com/technology/2013/aug/12/erwin-schrodinger-google-doodle.
- [151]Schrödinger, Erwin. "An undulatory theory of the mechanics of atoms and molecules." *Physical Review* 28.6 (1926): 1049.

- [152] Arya, Gaurav. "Molecular Mechanics." NANO 204. 2014.
- [153] P. Haynes, "Linear-scaling methods in ab initio quantum-mechanical calculations," University of Cambridge, 1998
- [154] Goedecker, Stefan, and L. Colombo. "Efficient linear scaling algorithm for tight-binding molecular dynamics." *Physical Review Letters* 73.1 (1994): 122.
- [155] Foulkes, W. Matthew C., and Roger Haydock. "Tight-binding models and density-functional theory." *Physical review B* 39.17 (1989): 12520.
- [156] Fedders, P. A., D. A. Drabold, and Stefan Klemm. "Defects, tight binding, and first-principles molecular-dynamics simulations on a-Si." *Physical Review B* 45.8 (1992): 4048.
- [157] Car, Richard, and Mark Parrinello. "Unified approach for molecular dynamics and density-functional theory." *Physical review letters* 55.22 (1985): 2471.
- [158] Griebel, Michael, Stephan Knapek, and Gerhard Zumbusch. "Numerical Simulation in Molecular Dynamics: Numerics." *Algorithms, Parallelization, Applications (New York, 2007)* (2007).
- [159] Sexton, B. A., A. E. Hughes, and N. R. Avery. "A spectroscopic study of the adsorption and reactions of methanol, formaldehyde and methyl formate on clean and oxygenated Cu (110) surfaces." *Surface science* 155.1 (1985): 366-386.
- [160] Stevens, Mark J. "Interfacial fracture between highly cross-linked polymer networks and a solid surface: effect of interfacial bond density." *Macromolecules* 34.8 (2001): 2710-2718.
- [161] Ethane,
ursula.chem.yale.edu/~chem220/chem220js/STUDYAIDS/movies/ethane.html.
- [162] Waheed, Numan, M. J. Ko, and G. C. Rutledge. "Molecular simulation of crystal growth in long alkanes." *Polymer* 46.20 (2005): 8689-8702.
- [163] Garrett, Reginald H.; Grisham, Charles M. (2016). *biochemistry*(sixth ed.). University of Virginia. pp. 12–13.
- [164] Jones, John Edward. "On the determination of molecular fields. I. From the variation of the viscosity of a gas with temperature." *Proceedings of the Royal Society of London A: Mathematical, Physical and Engineering Sciences*. Vol. 106. No. 738. The Royal Society, 1924.

- [165] Jones, John Edward. "On the determination of molecular fields. II. From the equation of state of a gas." *Proceedings of the Royal Society of London A: Mathematical, Physical and Engineering Sciences*. Vol. 106. No. 738. The Royal Society, 1924.
- [166] Coulomb (1785a) "Premier mémoire sur l'électricité et le magnétisme," *Histoire de l'Académie Royale des Sciences*, pages 569-577
- [167] Weaver, Jason F., Anders F. Carlsson, and Robert J. Madix. "The adsorption and reaction of low molecular weight alkanes on metallic single crystal surfaces." *Surface Science Reports* 50.4 (2003): 107-199.
- [168] T. P. Straatsma & J. A. McCammon (1990) Molecular Dynamics Simulations with Interaction Potentials Including Polarization Development of a Noniterative Method and Application to Water, *Molecular Simulation*, 5:3-4, 181-192, DOI: 10.1080/08927029008022130
- [169] Arya, Gaurav. "Statistical Mechanics." *NANO* 204. 2014.
- [170] Oliveira, César R. de, and Thiago Werlang. "Ergodic hypothesis in classical statistical mechanics." *Revista Brasileira de Ensino de Física* 29.2 (2007): 189-201.
- [171] Callaway, David JE, and Aneesur Rahman. "Microcanonical ensemble formulation of lattice gauge theory." *Physical Review Letters* 49.9 (1982): 613.
- [172] Langevin Thermostat, cms.mpi.univie.ac.at/vasp/vasp/Langevin_thermostat.html.
- [173] Allen, Mike P., and Dominic J. Tildesley. *Computer simulation of liquids*. Oxford university press, 1989.
- [174] B. Hess, H. Bekker, H. Berendsen, and J. Fraaije, *LINCS: A linear constraint solver for molecular simulations*, *J. Comput. Chem.*, 18 (1997), pp. 1463–1472.
- [175] Nosé, Shūichi. "A molecular dynamics method for simulations in the canonical ensemble." *Molecular physics* 52.2 (1984): 255-268.
- [176] Wood, W. W. "NpT-Ensemble Monte Carlo Calculations for the Hard-Disk Fluid." *The Journal of Chemical Physics* 52.2 (1970): 729-741.
- [177] Adams, D. J. "Grand canonical ensemble Monte Carlo for a Lennard-Jones fluid." *Molecular Physics* 29.1 (1975): 307-311.

- [178]Moin, Parviz. *Fundamentals of engineering numerical analysis*. Cambridge University Press, 2010.
- [179]Grubmüller, Helmut, Helmut Heller, Andreas Windemuth, and Klaus Schulten. "Generalized Verlet algorithm for efficient molecular dynamics simulations with long-range interactions." *Molecular Simulation* 6, no. 1-3 (1991): 121-142.
- [180]Arya, Gaurav. "Molecular Dynamics." *NANO* 204. 2014.
- [181]Van Gunsteren, Wilfred F., and H. J. C. Berendsen. "A leap-frog algorithm for stochastic dynamics." *Molecular Simulation* 1.3 (1988): 173-185.
- [182]Martys, Nicos S., and Raymond D. Mountain. "Velocity Verlet algorithm for dissipative-particle-dynamics-based models of suspensions." *Physical Review E* 59.3 (1999): 3733.
- [183]Chialvo, Ariel A., and Pablo G. Debenedetti. "On the use of the Verlet neighbor list in molecular dynamics." *Computer physics communications* 60.2 (1990): 215-224.
- [184]"CUT-OFFS AND NEIGHBOUR LISTS." CUT-OFFS AND NEIGHBOUR LISTS, reaktiveplasmen.rub.de/files/lehre/md/02-2.pdf.
- [185]Agarwal, Anshul, Lorenz T. Biegler, and Stephen E. Zitney. "Simulation and optimization of pressure swing adsorption systems using reduced-order modeling." *Industrial & Engineering Chemistry Research* 48.5 (2008): 2327-2343.
- [186]Kmiecik, Sebastian, Dominik Gront, Michal Kolinski, Lukasz Wieteska, Aleksandra Elzbieta Dawid, and Andrzej Kolinski. "Coarse-grained protein models and their applications." *Chem. Rev* 116, no. 14 (2016): 7898-7936.
- [187]Baron, Riccardo, Daniel Trzesniak, Alex H. de Vries, Andreas Elsener, Siewert J. Marrink, and Wilfred F. van Gunsteren. "Comparison of Thermodynamic Properties of Coarse - Grained and Atomic - Level Simulation Models." *ChemPhysChem* 8, no. 3 (2007): 452-461.
- [188]Boniecki, Michal J., Grzegorz Lach, Wayne K. Dawson, Konrad Tomala, Pawel Lukasz, Tomasz Soltysinski, Kristian M. Rother, and Janusz M. Bujnicki. "SimRNA: a coarse-grained method for RNA folding simulations and 3D structure prediction." *Nucleic acids research* 44, no. 7 (2016): e63-e63.

- [189]Jhon, Myung S., Pil Seung Chung, Robert L. Smith, and Lorenz T. Biegler. "A description of multiscale modeling for the head-disk interface focusing on bottom-level lubricant and carbon overcoat models." *Advances in Tribology 2013* (2013).
- [190]Noid, W. G., Jhih-Wei Chu, Gary S. Ayton, Vinod Krishna, Sergei Izvekov, Gregory A. Voth, Avisek Das, and Hans C. Andersen. "The multiscale coarse-graining method. I. A rigorous bridge between atomistic and coarse-grained models." *The Journal of chemical physics* 128, no. 24 (2008): 244114.
- [191]Plimpton, Steve. "Fast parallel algorithms for short-range molecular dynamics." *Journal of computational physics* 117.1 (1995): 1-19. <http://lammps.sandia.gov/index.html>
- [192]Stupak Jr, J. J., Chao, G. H., Moe, E., & Mayberry, K. W. "Disk drive spindle motor." U.S. Patent No. 5,373,407. 13 Dec. 1994.
- [193]Dauber, Edwin G., Christian E. Bailey, and Robert L. Sassa. "Adsorbent assembly for removing gaseous contaminants." U.S. Patent No. 5,593,482. 14 Jan. 1997.
- [194]Beecroft, Harold. "Filter system for type II HDD." U.S. Patent No. 5,406,431. 11 Apr. 1995.
- [195]Elerath, Jon G., and Michael Pecht. "Enhanced reliability modeling of RAID storage systems." *Dependable Systems and Networks, 2007. DSN'07. 37th Annual IEEE/IFIP International Conference on*. IEEE, 2007.
- [196]Smith, Gordon James. "Contamination control on actuator arms in a disk drive." U.S. Patent No. 6,665,150. 16 Dec. 2003.
- [197]Jesh, Mark S., and Peter R. Segar. "The effect of vapor phase chemicals on head/disk interface tribology." *Tribology transactions* 42.2 (1999): 310-316.
- [198]Gao, Chao, Peihua Dai, and Vinh Vu. "Flying stiction, lubricant pick-up and carbon-overcoat wear of magnetic heads." *Journal of tribology* 121.1 (1999): 97-101.
- [199]Seo, Young Woo, Andrey Ovcharenko, and Frank E. Talke. "Simulation of Hydrocarbon Oil Contamination at the Head-Disk Interface Using Molecular Dynamics." *Tribology Letters* 61.3 (2016): 1-10.
- [200]Marchon, B., Karis, T., Dai, Q., & Pit, R. (2003). A model for lubricant flow from disk to slider. *IEEE transactions on magnetics*, 39(5), 2447-2449.

- [201]Guo, X. C., Raman, V., Karis, T. E., & Yao, Y. Z. (2007). Flyability failures due to siloxanes at the head-disk interface revisited. *IEEE transactions on magnetics*, 43(6), 2223-2225.
- [202]Schmidt, R., Griesbaum, K., Behr, A., Biedenkapp, D., Voges, H.-W., Garbe, D., Paetz, C., Collin, G., Mayer, D. and Höke, H. 2014. Hydrocarbons. Ullmann's Encyclopedia of Industrial Chemistry. 1–74.
- [203]Haynes, William M., ed. *CRC handbook of chemistry and physics*. CRC press, 2014.
- [204]Nozaki, K., Saihara, R., Ishikawa, K., & Yamamoto, T. (2007). Structure of normal alkane evaporated films: molecular orientation. *Japanese Journal of Applied Physics*, 46(2R), 761.
- [205]Tanaka, K., Ishikawa, K., Nozaki, K., Urakami, N., & Yamamoto, T. (2008). Structures of Multilayered Thin Films of Long-Chain Molecules: X-ray Scattering Study. *Polymer journal*, 40(10), 1017-1024.
- [206]Vollhardt, K. Peter C., and Neil E. Schore. *Organic chemistry: structure and function*. Macmillan, 2007
- [207]Yasuda, T., T. Okuno, and H. Yasuda. "Contact angle of water on polymer surfaces." *Langmuir* 10.7 (1994): 2435-2439.
- [208]Stalder, A. F., Kulik, G., Sage, D., Barbieri, L., & Hoffmann, P. (2006). A snake-based approach to accurate determination of both contact points and contact angles. *Colloids and surfaces A: physicochemical and engineering aspects*, 286(1), 92-103.
- [209]Taylor, M., Urquhart, A. J., Zelzer, M., Davies, M. C., & Alexander, M. R. (2007). Picoliter water contact angle measurement on polymers. *Langmuir*, 23(13), 6875-6878.
- [210]Chirico, R. D., An, N., Steele, W. V., Strube, M. M., & Tsonopoulos, C. (1989). The vapor pressure of n-alkanes revisited. New high-precision vapor pressure data on n-decane, n-eicosane, and n-octacosane. *Journal of Chemical and Engineering Data*, 34(2), 149-156.
- [211]Morgan, David L., and Riki Kobayashi. "Direct vapor pressure measurements of ten n-alkanes in the 10-C 28 range." *Fluid Phase Equilibria* 97 (1994): 211-242.
- [212]Paserba, Kris R., and Andrew J. Gellman. "Kinetics and energetics of oligomer desorption from surfaces." *Physical review letters* 86.19 (2001): 4338.

- [213]Gellman, Andrew J., and Kris R. Paserba. "Kinetics and mechanism of oligomer desorption from surfaces: n-alkanes on graphite." *The Journal of Physical Chemistry B* 106.51 (2002): 13231-13241.
- [214]Paul, Wolfgang, Do Y. Yoon, and Grant D. Smith. "An optimized united atom model for simulations of polymethylene melts." *The Journal of chemical physics* 103.4 (1995): 1702-1709.
- [215]Shimizu, Thoru, and Takashi Yamamoto. "Melting and crystallization in thin film of n-alkanes: A molecular dynamics simulation." *The Journal of Chemical Physics* 113.8 (2000): 3351-3359.
- [216]Waheed, N., M. S. Lavine, and G. C. Rutledge. "Molecular simulation of crystal growth in n-eicosane." *The Journal of chemical physics* 116.5 (2002): 2301-2309.
- [217]Yamamoto, Takashi, Koji Nozaki, Aki Yamaguchi, and Naohito Urakami. "Molecular simulation of crystallization in n-alkane ultrathin films: Effects of film thickness and substrate attraction." *The Journal of chemical physics* 127, no. 15 (2007): 154704.
- [218]Anwar, Muhammad, Francesco Turci, and Tanja Schilling. "Crystallization mechanism in melts of short n-alkane chains." *The Journal of chemical physics* 139.21 (2013): 214904.
- [219]R.P. Ambekar, D.B. Bogy, and C.S. Bhatia, "Lubricant Depletion and Disk-to-Head Lubricant Transfer at the Head-Disk Interface in Hard Disk Drives," *ASME J. Tribol.*, vol. 131, pp. 031901, 2009
- [220]Y. Tagaya, Y. Mitsuya, S. Ogata, H. Zhang, and K. Fukuzawa, "Effects of Molecular Conformations and Functional Endgroups on Nanoscale Mobility of Lubricant Molecules on Magnetic Disks," *MHS*, 10.1109/MHS.2006.320267, 2006
- [221]M. Fukuda, S. Komatsu, H. Zhang, K. Fukuzawa, and S. Itoh, "Coarse-Grained Molecular Dynamics Simulations of Adhesion on UV-Patterned Nanometer-Thick Liquid Lubricant Films," *MHS*, 10.1109/MHS.2010.5669554, 2010
- [222]Lei, Ryan Z., Andrew J. Gellman, and Christopher F. McFadden. "Alkane Contamination Effects on PFPE Lubricant Bonding to a-CH₃ Overcoats." *Langmuir* 17.20 (2001): 6240-6247.
- [223]Da, Y. (2005). "Study of Chemical Contamination at Head/Disk Interface." (Master's thesis). Retrieved from <http://scholarbank.nus.edu.sg/handle/10635/14736>.

- [224]Guo, Q., Izumisawa, S., Phillips, D. M., and Jhon, M. S. (2003). "Surface morphology and molecular conformation for ultrathin lubricant films with functional end groups". *Journal of applied physics*, 93(10), 8707-8709. K. Kremer and G.S. Grest, "Dynamics..."
- [225]Tyndall, G. W., Waltman, R. J., & Pocker, D. J. (1998). "Concerning the interactions between Zdol perfluoropolyether lubricant and an amorphous-nitrogenated carbon surface." *Langmuir*, 14(26), 7527-7536.
- [226]Deoras, Saurabh K., and Frank E. Talke. "Slider-lubricant interactions for low flying sliders." *IEEE transactions on magnetics* 39.5 (2003): 2471-2473.
- [227]Canchi, Sripathi Vangipuram, and David B. Bogy. "Experiments on slider lubricant interactions and lubricant transfer using TFC sliders." *Microsystem technologies* 18.9-10 (2012): 1517-1523.
- [228]Pan, Deng, Andrey Ovcharenko, Raj Tangaraj, Min Yang, and Frank E. Talke. "Investigation of lubricant transfer between slider and disk using molecular dynamics simulation." *Tribology Letters* 53, no. 1 (2014): 373-381.
- [229]Chen, Chao-Yuan, Walton Fong, David B. Bogy, and C. Singh Bhatia. "Lubricant thickness effect on tribological performance of ZDOL lubricated disks with hydrogenated overcoats." *Tribology Letters* 7, no. 1 (1999): 1-10
- [230]Bogy, David B., and C. Singh Bhatia. "The fragmentation mechanisms and thermal stability of ZDOL lubricant on hydrogenated carbon overcoats." *TECHNICAL BRIEFS* (2000): 458.
- [231]Zhao, X., B. Bhushan, and C. Kajdas. "Lubrication studies of head-disk interfaces in a controlled environment Part 2: Degradation mechanisms of perfluoropolyether lubricants." *Proceedings of the Institution of Mechanical Engineers, Part J: Journal of Engineering Tribology* 214, no. 6 (2000): 547-559.
- [232]Tao, Zhenhua, and Bharat Bhushan. "Bonding, degradation, and environmental effects on novel perfluoropolyether lubricants." *Wear* 259.7 (2005): 1352-1361.
- [233]Deb Nath, S. K., and C. H. Wong. "Study of the thermal fragmentation of PFPEs lubricants on a thin DLC film using finitely extensible nonlinear elastic potential based molecular dynamics simulation." *Journal of Nanotechnology* 2014 (2014).
- [234]Pan, Deng, Andrey Ovcharenko, Jih-Ping Peng, and Hongyuan Jiang. "Effect of lubricant fragments on lubricant transfer: a molecular dynamics simulation." *IEEE Transactions on Magnetism* 50, no. 9 (2014): 1-5.
- [235]Marchon, Bruno. "Lubricant design attributes for subnanometer head-disk clearance." *IEEE Transactions on Magnetism* 45.2 (2009): 872-876.

- [236]Li, Ning, Yonggang Meng, and David B. Bogy. "Effects of PFPE lubricant properties on the critical clearance and rate of the lubricant transfer from disk surface to slider." *Tribology Letters* 43.3 (2011): 275-286.
- [237]Guo, X-C., B. Knigge, B. Marchon, R. J. Waltman, M. Carter, and J. Burns. "Multidentate functionalized lubricant for ultralow head/disk spacing in a disk drive." *Journal of applied physics* 100, no. 4 (2006): 044306.
- [238]Sonoda, Koji, Daisuke Shirakawa, Takayuki Yamamoto, and Jun Itoh. "The tribological properties of the new structure lubricant at the head–disk interface." *IEEE transactions on magnetics* 43, no. 6 (2007): 2250-2252.
- [239]Shirakawa, D., K. Sonoda, and K. Ohnishi. "A study on design and synthesis of new lubricant for near contact recording." *IEEE transactions on magnetics* 43.6 (2007): 2253-2255.
- [240]Fukui, S., and R. Kaneko. "Analysis of ultra-thin gas film lubrication based on linearized Boltzmann equation: first report—derivation of a generalized lubrication equation including thermal creep flow." *Journal of Tribology* 110.2 (1988): 253-261.
- [241]Liu, Nan, and David B. Bogy. "Air-bearing shear force in the head–disk interface of hard disk." *Tribology letters* 35.2 (2009): 121-125.
- [242]Wei, J., Fong, W., Bogy, D.B. and Bhatia, C.S., 1998. The decomposition mechanisms of a perfluoropolyether at the head/disk interface of hard disk drives. *Tribology Letters*, 5(2), pp.203-209.
- [243]Thiele, J-U., Kevin R. Coffey, M. F. Toney, J. A. Hedstrom, and A. J. Kellock. "Temperature dependent magnetic properties of highly chemically ordered Fe 55–x Ni x Pt 45 L1 0 films." *Journal of applied physics* 91, no. 10 (2002): 6595-6600.
- [244]Lim, Min Soo, and Andrew J. Gellman. "Kinetics of laser induced desorption and decomposition of Fomblin Zdol on carbon overcoats." *Tribology international* 38.6 (2005): 554-561.
- [245]Wu, Lin. "Modelling and simulation of the lubricant depletion process induced by laser heating in heat-assisted magnetic recording system." *Nanotechnology* 18.21 (2007): 215702.
- [246]Gauvin, M., H. Zheng, B. Suen, J. Lee, H. J. Kang, and F. E. Talke. "Enhanced photo-thermal stability of modified PFPE lubricants under laser beam exposure." *IEEE Transactions on Magnetism* 47, no. 7 (2011): 1849-1854.

- [247]Tagawa, Norio, Ryo Kakitani, Hiroshi Tani, Naoyasu Iketani, and Ikuo Nakano. "Study of lubricant depletion induced by laser heating in thermally assisted magnetic recording systems—Effect of lubricant film materials." *IEEE Transactions on Magnetics* 45, no. 2 (2009): 877-882.
- [248]Tagawa, Norio, Hideki Andoh, and Hiroshi Tani. "Study on lubricant depletion induced by laser heating in thermally assisted magnetic recording systems: effect of lubricant thickness and bonding ratio." *Tribology letters* 37.2 (2010): 411-418.
- [249]Tagawa, N., and H. Tani. "Lubricant depletion characteristics induced by rapid laser heating in thermally assisted magnetic recording." *IEEE Transactions on Magnetics* 47.1 (2011): 105-110.
- [250]Wang, Yiming, Tobias Maletzky, Eric X. Jin, Dayu Zhou, Joe Smyth, and Moris Dovek. "Pulsed thermally assisted magnetic recording." *IEEE Transactions on Magnetics* 49, no. 2 (2013): 739-743.
- [251]Lee, Sungae, Shahrukh Niazi, and Chang-Dong Yeo. "The change in surface properties of magnetic recording media under pulsed laser application." *Tribology Letters* 47.1 (2012): 57-65.
- [252]Ma, Yansheng, Xiuying Chen, and Bo Liu. "Experimental study of lubricant depletion in heat assisted magnetic recording over the lifetime of the drive." *Tribology Letters* 47.2 (2012): 175-182.
- [253]Li, Longqiu, Benjamin Suen, and Frank E. Talke. "Investigation of Temperature Dependence of Raman Shift of Diamond-Like Carbon Coatings Used in Heat-Assisted Magnetic Recording." *IEEE Transactions on Magnetics* 51.11 (2015): 1-4.
- [254]Wu, Haoyu, Alejandro Rodriguez Mendez, Shaomin Xiong, and David B. Bogy. "Lubricant reflow after laser heating in heat assisted magnetic recording." *Journal of Applied Physics* 117, no. 17 (2015): 17E310.
- [255]Wu, Lin, and Frank E. Talke. "Modeling laser induced lubricant depletion in heat-assisted-magnetic recording systems using a multiple-layered disk structure." *Microsystem technologies* 17.5-7 (2011): 1109-1114.
- [256]Zhou, Weidong, Yan Zeng, Bo Liu, Shengkai Yu, Wei Hua, and Xiaoyang Huang. "Evaporation of polydisperse perfluoropolyether lubricants in heat-assisted magnetic recording." *Applied physics express* 4, no. 9 (2011): 095201.

- [257] Zhou, Weidong, Yan Zeng, Bo Liu, Shengkai Yu, and Xiaoyang Huang. "A model for laser induced lubricant depletion in heat-assisted magnetic recording." *Tribology Letters* 45, no. 3 (2012): 411-416.
- [258] Zeng, Yan, Weidong Zhou, Xiaoyang Huang, and Shengkai Yu. "Numerical study on thermal-induced lubricant depletion in laser heat-assisted magnetic recording systems." *International Journal of Heat and Mass Transfer* 55, no. 4 (2012): 886-896.
- [259] Dahl, Joanna Bechtel, and David B. Bogy. "Lubricant flow and evaporation model for heat-assisted magnetic recording including functional end-group effects and thin film viscosity." *Tribology Letters* 52.1 (2013): 27-45.
- [260] Sarabi, Soroush, and David B. Bogy. "Effect of Functional End-Groups on Lubricant Reflow in Heat-Assisted Magnetic Recording (HAMR)." *Tribology Letters* 65.1 (2017): 15.
- [261] Xu, B. X., Z. H. Cen, J. H. Goh, J. M. Li, Y. T. Toh, J. Zhang, K. D. Ye, and C. G. Quan. "Performance benefits from pulsed laser heating in heat assisted magnetic recording." *Journal of Applied Physics* 115, no. 17 (2014): 17B701.
- [262] Xu, Baoxi, Hongtao Wang, Zhanhong Cen, Zhejie Liu, Jianming Li, Yeow Teck Toh, Kaidong Ye, Jing Zhang, and Hongzhi Yang. "Analysis of Heat-Assisted Magnetic Recording to Density of 4 Tb/in²." *IEEE Transactions on Magnetics* 50, no. 11 (2014): 1-4.
- [263] Xu, Baoxi, Hongtao Wang, Zhanhong Cen, and Zhejie Liu. "4–5 Tb/in Heat-Assisted Magnetic Recording by Short-Pulse Laser Heating." *IEEE Transactions on Magnetics* 51, no. 6 (2015): 1-5.
- [264] Xu, Baoxi, Hongtao Wang, Zhanhong Cen, Zhejie Liu, Jianming Li, Kaidong Ye, Jing Zhang, and Hongzhi Yang. "Simulation Study of Pulse Laser Quality Effects on Recording Performances of Heat-Assisted Magnetic Recording by Short-Pulse Laser Heating." *IEEE Transactions on Magnetics* 51.11 (2015): 1-5.
- [265] Li, Yong, Chee How Wong, Bei Li, Shengkai Yu, Wei Hua, and Weidong Zhou. "Lubricant evolution and depletion under laser heating: a molecular dynamics study." *Soft Matter* 8, no. 20 (2012): 5649-5657.
- [266] Li, B., and C. H. Wong. "Molecular dynamics studies of lubricant depletion under moving laser heating: Effects of laser power and film thickness." *Tribology International* 92 (2015): 38-46.
- [267] Hirlimann, C. "Pulsed optics." *Femtosecond Laser Pulses* (2005): 25.

- [268]Diels, Jean-Claude, and Wolfgang Rudolph. Ultrashort laser pulse phenomena. Academic press, 2006.
- [269]Wellershoff, S.S., Hohlfeld, J., GÜdde, J. and Matthias, E., 1999. The role of electron–phonon coupling in femtosecond laser damage of metals. *Applied Physics A*, 69(1), pp.S99-S107.
- [270]Chen, J.K., Latham, W.P. and Beraun, J.E., 2005. The role of electron–phonon coupling in ultrafast laser heating. *Journal of laser applications*, 17(1), pp.63-68.
- [271]Lasagni, A., D’Alessandria, M., Giovanelli, R. and Mücklich, F., 2007. Advanced design of periodical architectures in bulk metals by means of Laser Interference Metallurgy. *Applied Surface Science*, 254(4), pp.930-936.