Molecular dynamics study on tribological behaviors of DLC films

Bai, Lichun

2016

Bai, L. (2016). Molecular dynamics study on tribological behaviors of DLC films. Doctoral thesis, Nanyang Technological University, Singapore.

<http://hdl.handle.net/10356/69320>

<https://doi.org/10.32657/10356/69320>

**NANYANG
TECHNOLOGICAL
UNIVERSITY**

**MOLECULAR DYNAMICS STUDY ON TRIBOLOGICAL
BEHAVIORS OF DLC FILMS**

BAI LICHUN

**INTERDISCIPLINARY GRADUATE SCHOOL
ENERGY RESEARCH INSTITUTE @ NTU (ERI@N)**

2016

**MOLECULAR DYNAMICS STUDY ON TRIBOLOGICAL
BEHAVIORS OF DLC FILMS**

BAI LICHUN

**Interdisciplinary Graduate School
Energy Research Institute @ NTU (ERI@N)**

**A thesis submitted to the Nanyang Technological University in
partial fulfilment of the requirement for the degree of**

Doctor of Philosophy

2016

Statement of Originality

I hereby certify that the work embodied in this thesis is the result of original research and has not been submitted for a higher degree to any other University or Institution.

9 December 2016
.....

Date

Bai Lichun
.....

Bai Lichun

Acknowledgements

I would like to express my sincere gratitude and appreciation to my supervisor Assistant Professor Zhou Kun for his tremendous support, guidance and encouragement. This research would be impossible without his instructive advice and help. His rigorous attitude towards scientific research deeply impresses me, and his strict training on both scientific thinking and writing strongly benefits me.

I would also like to express my deepest gratitude to my co-supervisor Dr. Narasimalu Srikanth for his continuous advice and encouragement. His persistent guidance and help make this research possible.

I sincerely acknowledge the Interdisciplinary Graduate School of Nanyang Technological University for providing the Research Scholarship and its High Performance Computing Center for computational support.

I am thankful to Dr. Zhang Yongwei, Dr. Sha Zhendong and Dr. Pei Qingxiang from the Institute of High Performance Computing, Agency for Science, Technology and Research, Singapore for their insightful comments and suggestions. Many thanks also go to my friends Dr. Liu Bo and Mr. Tang Chao for their valuable suggestions about my research works.

Last but not the least, I would like to express my sincere gratefulness to my parents and my wife Li Ling for their love and encouragement and to my sisters for their unconditional supports.

Table of Contents

Acknowledgements	I
Table of Contents	III
Abstract.....	V
List of Publications	IX
List of Figures.....	XI
List of Tables	XV
List of Symbols	XVII
Chapter 1. Introduction.....	1
1.1. Background	1
1.2. Motivations	4
1.3. Objectives	7
1.4. Dissertation outline	7
Chapter 2. Literature review	9
2.1. Fundamentals of tribology	9
2.1.1. Friction and wear	9
2.1.2. Tribology under two-body and three-body contact	11
2.1.3. Tribology at the nanoscale.....	19
2.2. Tribological behaviors of DLC films.....	24
2.2.1. Operational condition influence	24
2.2.2. Lubrication influence.....	31
2.3. MD simulation	34
2.3.1. Principles	34
2.3.2. Simulation of tribology at the nanoscale	38
2.4. Summary	44
Chapter 3. Tribological behaviors of DLC films under two-body contact	45
3.1. Modelling.....	45
3.1.1. Atomistic configuration.....	45
3.1.2. Simulation methods	47
3.2. Results and discussions.....	50
3.2.1. Contact interface.....	50
3.2.2. Load effect.....	52
3.2.3. Velocity effect	63
3.2.4. Surface roughness effect.....	66

3.3. Summary	70
Chapter 4. Tribological behaviors of DLC films under three-body contact.....	73
4.1. Modelling.....	73
4.1.1. Atomistic configuration.....	73
4.1.2. Simulation methods	75
4.2. Results and Discussions	76
4.2.1. Contact interface.....	76
4.2.2. Load effect.....	77
4.2.3. Velocity effect	82
4.2.4. Particle effect.....	87
4.3. Summary	91
Chapter 5. Influence of the hydrogen atmosphere on tribological behaviors of DLC films .	93
5.1. Modelling.....	93
5.2. Results and discussions.....	95
5.2.1. Friction forces and atomic configuration.....	95
5.2.2. Friction temperatures and element diffusions	102
5.2.3. Graphitization and atom density	106
5.3. Summary	114
Chapter 6. Influence of the graphene lubrication on tribological behaviors of DLC films	117
6.1. Modeling.....	117
6.2. Results and discussions.....	120
6.2.1. Friction force	120
6.2.2. Load capacity.....	129
6.2.3. Effect of defects in graphene.....	133
6.3. Summary	136
Chapter 7. Conclusions and recommendations.....	139
7.1. Conclusions and contributions	139
7.2. Recommendations.....	141
References.....	143

Abstract

Diamond-like carbon (DLC) films that are a type of amorphous solids exhibit excellent mechanical properties and superior tribological performances and thus can be used as the coating of workpieces to improve their wear resistance and reduce their surface friction. The tribological behaviors of the DLC films are sensitive to many factors such as the film compositions, operational parameters and environment. These sensitivities highly complicate the tribological mechanisms of the DLC films and largely degrade their reliability and performances. Due to the difficulty to observe the evolution of the contact interfaces, particularly their detailed atomic structures at the nanoscale, investigation of the tribological mechanisms of the DLC films is challenging. Molecular dynamics (MD) simulation is a powerful technique used to investigate the nanoscale physical and chemical phenomena which can hardly be observed in experiments. This PhD dissertation adopts MD simulation as the main approach to investigate the nanoscale tribological mechanisms of DLC films under different operational conditions.

The effects of the load, velocity and the surface roughness of DLC films on their tribological behaviors are studied for two-body contact cases in which a diamond tip slides against a DLC film. It is found that the increase of the load can induce transition of wear from adhesive to abrasive and highly increase wear rate of the film. Its friction force follows the macroscale Bowden-Tabor model at a small load, but diverges from such model at a large load due to the formation of transfer layers. This keeps consistent with experimental observations in literature and thus demonstrates that the macroscale tribological mechanisms are still valid at the nanoscale. The friction force and wear rate of the film decrease with the velocity due to the reduction of the sliding depth of the diamond

tip and number of bonds at the contact interface. The increase of the surface roughness causes that the friction force of the film increases while its wear rate shows a nonmonotonic dependence on the roughness due to the competitions between the adhesive and abrasive wear. This nonmonotonic dependence indicates the existence of a minimum wear of the DLC films and thus shows the difference of their nanoscale tribology from that at the macroscale.

The effects of third particles at the interface between DLC films on their tribological behaviors are studied by relative sliding two films with a rigid particle located between them. It is found that friction and wear of the films are determined by adhesion at a small load but dominated by both adhesion and ploughing at a large load. A high velocity can increase the friction of the film but decrease its wear, due to the response of its networks to a high strain rate indicated by such velocity. This indicates that both the surface adhesion and the mechanical response of the DLC films play significant roles in their tribological behaviors at the nanoscale. The friction and wear of the film are also highly influenced by the shape of the particle and its size which can influence its movement mode and wear mechanisms.

The effects of testing atmospheres are studied by simulating the friction behaviors of DLC films with the presence of environmental H atoms. It is found that the friction mechanisms depend on the friction temperature. At low friction temperatures, H atoms are concentrated near contact interfaces, and their passivations highly reduce the interfacial adhesion and friction force. However, at high friction temperatures, the diffusions of H atoms and graphitization of the DLC film as well as its thermal expansions cause a wide region with easy-shear properties, thus resulting in a low friction force. This indicates that

besides the H-passivations the H diffusions can also reduce the friction force of the DLC films by tailoring structures and properties of their sliding interface, providing a new explanation for the low friction of these films in the H₂ environment.

Graphene is a single layer of carbon atoms arranged into a honeycomb lattice structures. Since its discovery, graphene has found itself wide applications in nanotechnologies due to its superior mechanical properties including the ultrahigh mechanical strength and superior lubrication performances. One of these applications is to use graphene as a lubrication material to isolate the contact between surface asperities. Simulation of the lubrication of graphene for DLC films shows that its lubrication performance can be improved by the increase of its layer number but degraded by its defects. Under a small normal force, though the puckering effect has been induced, the superlubrication of the graphene can be preserved as indicated by the ultralow friction force. Under a large normal force, the friction force increases due to the tribochemical reactions of graphene and the tribopairs. The tribochemical reactions highly influence the structural stability of the graphene and thus terminate its superlubrication. The simulation also demonstrates that the size increase of the graphene can largely increase its friction force by promoting the puckering effect. This shows that the small-sized graphene may exhibit a better lubrication performance than that with a large size.

This PhD dissertation has investigated the tribological behaviors of DLC films under the influence of operational conditions. The results help to understand the tribological mechanisms of the DLC films and promote their wide applications in future.

List of Publications

- **L. Bai**, N. Srikanth, E. A. Korznikova, J. A. Baimova, S. V. Dmitriev and K. Zhou. 2016. Wear and Friction Between Smooth or Rough Diamond-like Carbon Films and Diamond Tips. *Wear* (accepted).
- **L. Bai**, N. Srikanth, G. Kang and K. Zhou. 2016. Influence of Third Particle on the Tribological Behaviors of Diamond-like Carbon Films. *Scientific Reports* 6: 38279.
- **L. Bai**, N. Srikanth, B. Zhao, B. Liu, Z. Liu and K. Zhou. 2016. Lubrication Mechanisms of Graphene for DLC Films Scratched by a Diamond Tip. *Journal of Physics D: Applied Physics* 49: 485302.
- **L. Bai**, N. Srikanth, H. Wu, F. Liu, B. Liu and K. Zhou. 2016. Effect of Environmental Hydrogen Atoms on the Tribological Behaviors of Diamond-like Carbon Films. *Tribology International* 99: 258–266.
- **L. Bai**, N. Srikanth, H. Wu, Y. Liu, B. Liu and K. Zhou. 2016. Investigation on Tensile Behaviors of Diamond-like Carbon Films. *Journal of Noncrystalline Solids* 443: 8–16.
- **L. Bai**, Z. Sha, N. Srikanth, Q. Pei, X. Wang, D. J Srolovitz and K. Zhou. 2015. Friction Between Silicon and Diamond at the Nanoscale. *Journal of Physics D: Applied Physics* 48: 255303.

List of Figures

Fig. 2.1. Schematic of a hard asperity sliding against a soft material (Rabinowicz, 1965).	13
Fig. 2.2. Stick-slip friction force as a function of time or distance (Bhushan, 2013a).	15
Fig. 2.3. Abrasive model of a hard conical asperity sliding against a soft surface.	18
Fig. 2.4. Schematic of wear process of two relatively sliding surfaces with (a) trapped third particles and (b) rolling particles (Bhushan, 2013a).	18
Fig. 2.5. Phase diagram of confined liquid layers during the stick-slip friction process (Bhushan et al., 1995).	21
Fig. 2.6. Schematic of the wear process by atom-by-atom attritions (Bhaskaran et al., 2010).	23
Fig. 2.7. Optical image of transfer layers on the surface of counterpart at different loads (Wang et al., 2013).	25
Fig. 2.8. Illustration of the friction reduction mechanisms by H-passivations of DLC films (Erdemir and Donnet, 2006).	27
Fig. 2.9. The humidity effect on the friction coefficient of DLC films (Donnet and Erdemir, 2007).	29
Fig. 2.10. Effect of DLC films on the friction coefficient of components in a lubricated condition (Donnet and Erdemir, 2007).	33
Fig. 2.11. Flowchart of MD simulation (Li, 2005).	36
Fig. 2.12. Illustration of the commensurate contact (a) - (b) and incommensurate contact (c) - (d), where (a) and (b) are tilted view, and (c) and (d) are upper view (Hod, 2012).	40
Fig. 2.13. Atomic configuration of contact at the nanoscale (Mo et al., 2009): (a) and (b) are atomic configuration, (c) is the outline of the contact area.	41
Fig. 2.14. Mechanisms of friction reduction of DLC films by H-passivations (Hayashi et al., 2011).	43
Fig. 2.15. Formation of graphene-like layers at interfaces between DLC films (Ma et al., 2011).	44
Fig. 3.1. Configuration of the friction model with (a) a front view and (b) a side view. .	46
Fig. 3.2. Number of bonds n_b at the contact interface with different loads F_n (a) before and (b) during the sliding.	51
Fig. 3.3. Evolution of the contact between the diamond tip and the DLC film with the load of (a) 2.9 nN and (b) 290 nN when the sliding distance L increases from 0 Å to 100 Å.	52

Fig. 3.4. (a) Load F_n dependence of friction force F_f and (b) its correlation with the number of bonds n_b at the contact interface; (c) comparison of MD simulation (solid line) and the Bowden-Tabor model (dashed or dotted line). The prediction of this model is also plotted as the dotted line in (b).....	54
Fig. 3.5. Contours of atom displacement with the load of (a) 2.9 nN and (b) 290 nN during stable friction. The large atoms are belonged to the diamond tip, and the small atoms are those of the DLC film.	55
Fig. 3.6. (a) Evolution of the fraction of sp^2 atoms f_1 in the DLC film with sliding distance L , and (b) the dependence of average friction temperature T_f on the load F_n	57
Fig. 3.7. (a) Evolution of the number of worn atoms N in DLC films with the sliding distance L , and (b) the dependence of the wear rate k on load F_n	59
Fig. 3.8. (a) Dependence of the wear rate k of DLC films on their friction forces F_f ; (b) comparison between MD simulation and the Archard law in term of the relation of k with the number of contact bonds n_b ; (c) the sliding depth h dependence of the difference between MD simulation and the Archard law.	61
Fig. 3.9. Effect of sliding velocities v_s on (a) the friction force F_f , (b) the number of bonds n_b at the contact interface and (c) the relation between the F_f and the n_b	64
Fig. 3.10. (a) Effect of sliding velocities v_s on the wear rate k and (b) its relation with the bond number n_b at the contact interface.....	66
Fig. 3.11. Effect of surface roughness of the DLC film on (a) its friction force F_f , (b) wear rate k and (c) number of bonds n_b at the contact interface.	69
Fig. 4.1. Atomic configuration of the simulation model with (a) a front view and (b) a side view. The model consists of two relative sliding DLC films with a third particle located between them.	74
Fig. 4.2. Atomic configuration of the friction process with a spherical particle.	77
Fig. 4.3. Effect of loads F_n of the DLC film on (a) its friction force F_f , (b) the number of contact bonds n_b and (c) the relation between F_f and n_b	80
Fig. 4.4. Effect of loads F_n of the DLC film on (a) its wear rate k , (b) the sliding depth of the spherical particle h and (c) the relation between k and h	81
Fig. 4.5. Effect of velocities v_s of the DLC film on (a) its friction force F_f and (b) the number of contact bonds n_b	83
Fig. 4.6. Atomic configuration with different velocities v_s : (a) 2 Å/ps and (b) 10 Å/ps. .	83
Fig. 4.7. Effect of velocities v_s of the DLC film on (a) its wear rate k and (b) the sliding depth h of the spherical particle.	84
Fig. 4.8. Formation process of worn atoms at a high velocity v_s of 10 Å/ps. The dark-red color in the figure highlights the networks attached to the third particle.	85

Fig. 4.9. Effect of velocities v_s of the DLC film on its (a) number of new sp^2 atoms Δn_{sp^2} and (b) friction temperature T_f .	86
Fig. 4.10. Atomic configuration with (a) cubic and (b) cuboidal particles during the friction process.	89
Fig. 4.11. Effect of the shape of the third particle on the friction and wear of DLC films.	90
Fig. 5.1. Schematic of the simulation model.	94
Fig. 5.2. Effect of H atoms on friction forces with various velocities and loads: (a) $v_s = 1$ Å/ps, $F_n = 100$ MPa, (b) $v_s = 1$ Å/ps, $F_n = 1$ GPa and (c) $v_s = 5$ Å/ps, $F_n = 100$ MPa.	97
Fig. 5.3. Atomistic configuration of the interfacial evolution before the friction stabilization for $v_s = 1$ Å/ps and $F_n = 100$ MPa. A thin straight slab is highlighted in red color as a marker to indicate the material deformations caused by sliding.	100
Fig. 5.4. Atomistic configuration of the interfacial evolution after the friction stabilization for $v_s = 1$ Å/ps and $F_n = 100$ MPa. A similar marker is defined to show the material deformation as in Fig. 5.3.	101
Fig. 5.5. Effect of H atoms on the friction temperature with various velocities and loads: (a) $v_s = 1$ Å/ps, $F_n = 100$ MPa, (b) $v_s = 1$ Å/ps, $F_n = 1$ GPa and (c) $v_s = 5$ Å/ps, $F_n = 100$ MPa.	103
Fig. 5.6. Evolution of the width of H-distributed regions with simulation time for various sliding velocities and loads: (a) $v_s = 1$ Å/ps, $F_n = 100$ MPa, (b) $v_s = 1$ Å/ps, $F_n = 1$ GPa and (c) $v_s = 5$ Å/ps, $F_n = 100$ MPa.	105
Fig. 5.7. Effect of H atoms on the fraction of sp^3 atoms f_2 for various velocities and loads: (a) $v_s = 1$ Å/ps, $F_n = 100$ MPa, (b) $v_s = 1$ Å/ps, $F_n = 1$ GPa and (c) $v_s = 5$ Å/ps, $F_n = 100$ MPa.	108
Fig. 5.8. Effect of H atoms on the density of C atoms for different velocities and loads: (a) $v_s = 1$ Å/ps, $F_n = 100$ MPa, (b) $v_s = 1$ Å/ps, $F_n = 1$ GPa and (c) $v_s = 5$ Å/ps, $F_n = 100$ MPa.	110
Fig. 6.1. Illustration of the atomistic model with (a) a front view and (b) a top view. In the model, a diamond tip scratches a DLC film which is passivated by H atoms and fully covered by graphene.	118
Fig. 6.2. Effect of graphene on the friction force F_f of (a) the DLC film and (b) the DLC-H film.	123
Fig. 6.3. Atomic configuration of the simulation system with single-layer graphene at an indentation depth h of (a) 2 Å, (b) 3.5 Å and (c) 6 Å, respectively. The bonds are generated with a cutoff of 1.9 Å which corresponds to the first minimum in the radial distribution function of carbon materials.	124
Fig. 6.4. Cross-sectional images of atom position in graphene.	125

Fig. 6.5. The number of bonds between the single-layer graphene and DLC film n_1 and between this graphene and the diamond tip n_2 when the graphene is set with (a) free boundary and (b) pinned boundary; (c) configuration of the bond between the graphene and the DLC film.	126
Fig. 6.6. (a) The bond number between graphene and the DLC film n_1 , between graphene and the diamond tip n_2 and between graphene layers n_3 and (b) the configuration of the system with bilayer graphene at the h of 5 Å.....	129
Fig. 6.7. Evolution of the friction force F_f with the normal force F_n for (a) the DLC film and (b) the DLC-H film.	132
Fig. 6.8. (a) The contact configuration of the system with 10% defects in graphene, (b) the effect of the defects of graphene on the friction force F_f and (c) its dependence on the normal force F_n for the DLC film when single graphene layer is used.	135

List of Tables

Table 2.1. Friction coefficients and wear rates for diamond coatings and various DLC films.....	31
Table 3.1. Variables in the simulation and their values	50
Table 4.1. Variables in the simulation and their values.....	77
Table 4.2. Effect of particle radius on the friction and wear of DLC films.....	89

List of Symbols

Symbols	Physical meaning
c	Constant in the nanoscale friction law
f_1	Fraction of sp^2 atoms
f_2	Fraction of sp^3 atoms
F_n	Normal force
F_f	Friction force
h	Sliding depth
k	Wear rate
k_1	Adhesive wear rate
k_2	Abrasive wear rate
L	Sliding distance
m	Number of graphene layers
n_b	Number of bonds
n_{sp^2}	Number of sp^2 atoms
N	Number of wear atoms
R_q	Root mean square surface roughness
T_f	Friction temperature
v_s	Sliding velocity
v_n	Normal velocity
V	Wear volume
w	Width of the sliding region
w_H	Width of the H-distributed region
ρ_H	Density of H atoms
ρ_C	Density of C atoms
η	Fraction of defects in graphene

Chapter 1. Introduction

Diamond-like carbon (DLC) films have excellent mechanical and tribological properties and thus can be employed as solid lubricants of workpieces to reduce their surface friction and improve their wear resistance. The wide applications of the DLC films have raised significant demands to understand their tribological mechanisms. In this chapter, a brief introduction is firstly conducted on tribological behaviors of the DLC films. Subsequently, the motivations and objectives for this PhD dissertation are presented, and the dissertation organization is then outlined.

1.1. Background

DLC films are a type of amorphous solids and consist of a mixture of sp^2 - and sp^3 -hybridized carbon atoms. These films have excellent mechanical properties, superlow friction coefficient and superior wear and corrosion resistance (Donnet, 1998). Therefore, the DLC films are can be used to improve wear resistance and reduce surface friction of workpieces and highly increase their reliability and lifetime. For example, the DLC films can be a suitable wear-resistant layer on plastic products such as sunglass lenses which are made of polycarbonate (Kimock and Knapp, 1993); these films have been used in a hard-disk driving system to improve its wear resistance and reduce the friction between magnetic disks and heads (Robertson, 2001; Kokaku *et al.*, 1993); these films are also employed to prevent wear for razor blades and metal cutting tools including lathe inserts and milling cutters and increase lifetime for bearings, cams and cam followers in the automobile industry (Kurokawa *et al.*, 1987; Erdemir *et al.*, 2006). Because of the wide applications

of the DLC films, their tribological mechanisms have attracted tremendous attentions in the past decades and have also been the theme of numerous studies.

It has been found that the exceptional wear resistances of DLC films are due to their high hardness which indicates a high resistance to plastic deformations and thus suppresses the formations of wear debris. The excellent friction behaviors of the DLC films are commonly due to the formation of graphitic transfer layers on the surface of their counterparts (Liu *et al.*, 1996a). Such layer that is easy to shear can isolate the direct contact between these films and their counterparts and cause the friction reduction (Bai *et al.*, 2011).

The tribological behaviors of DLC films depend on their compositions such as the sp^3/sp^2 ratio and the doping elements. The sp^3/sp^2 ratio is commonly used to characterize the microstructures of these films. The higher ratio commonly indicates a larger fraction of sp^3 bonds in such films and their higher hardness (Irmer and Dorner - Reisel, 2005). Since the sp^3/sp^2 ratio of the DLC films is sensitive to their deposition equipment and parameters, the mechanical properties of such films commonly vary case-by-case and their wear behaviors are diverse in the literature (Grill, 1997; Bull, 1995). The doping elements also highly influence the tribological behaviors of the DLC films by influencing their surface properties. For example, the hydrogenation of these films can highly reduce their friction by passivating dangling bonds on their surfaces and even induce the occurrence of superlubricity; the silver-doped films exhibit a superlow friction due to the diffusions of silver from the subsurface to the surface at a high friction temperature (Wang *et al.*, 2012).

Tribological behaviors of DLC films can also be influenced by many operational conditions such as the load, velocity, environment and lubrication (Bai *et al.*, 2011; Grill 1997; Donnet 1998). The effect of the load and velocity is mainly due to the fact that they

highly influence the formation of transfer layers by changing friction temperatures which eventually dominate the graphitization of the DLC films. The environment can influence the tribological behaviors of these films mainly by changing their contact interface. For example, such films exhibit a superlow friction in a hydrogen atmosphere (H_2) due to their surface passivations by H atoms (Fontaine *et al.*, 2004; Fontaine *et al.*, 2001); these films show a low friction in a sand-dust environment due to the rolling of the sand particles (Qi *et al.*, 2011a; Qi *et al.*, 2010). Lubricants are commonly employed to reduce the sensitivity of the DLC films to their compositions and operational conditions. These films show stable friction and wear behaviors in a lubricated condition and exhibit a complex boundary-lubrication mechanism which involves the effects of both the lubricants and films (Liu *et al.*, 2013; Liu *et al.*, 2011a; Liu *et al.*, 2011b).

The previous studies mainly investigated the tribological behaviors of DLC films by analyzing their macroscale tribological mechanisms via experimental methods. It should be noticed that the macroscale tribology actually happens as interactions between surface asperities at a small scale (Mo *et al.*, 2009; Eder *et al.*, 2015). These asperity interactions should be responsible for the fundamental tribological mechanisms of the DLC films, however, are invisible due to the limitations of the macroscale experimental methods.

As a result, many fundamental mechanisms at the microscale and nanoscale are still unclear. For example, the formation process of transfer layers during the running-in period of the DLC films always lacks clear understanding; the dependence of the formation of their wear debris on operational parameters such as velocity and load is rarely reported; sensitivities of the tribological behaviors of the DLC films to their working environment need to be explored by analyzing the contact interface; the effect of lubricants and

particularly their additives on the interfacial evolution of the DLC films is seldom studied. Hence, it is of great significance to investigate the tribological behaviors of these films at a small scale.

This significance is also highly raised by the applications of DLC films in a miniaturized component or machine. For instance, these films have been used to improve the wear resistances of tips for atomic force microscope (AFM) which has been used to nanomechanically machine surfaces with an atomic-scale roughness (Yan *et al.*, 2015); such films are also coated to components in a microelectromechanical system (MEMS) or nanoelectromechanical system (NEMS) to increase their wear resistances (Tambe and Bhushan, 2004). The DLC films at the small scales exhibit a tribological behavior different from that at macroscales and such behavior is unsuitable to be interpreted by the macroscale tribological mechanisms.

Therefore, investigations of the friction and wear of DLC films at a microscale especially nanoscale can highly improve the understanding of their tribological mechanisms and promote their wide applications.

1.2. Motivations

Nanoscale tribology of materials highly depends on their surface properties which eventually determine the adhesions at their contact interface and their contact area. Such adhesions are caused by atomic interactions and lead to a nonzero contact area and a high friction force even for a zero load (Eder *et al.*, 2015). As a result, it is commonly concluded that the nanoscale friction is linearly proportional to the contact area but has a nonlinear relation with the load, which is regarded as the friction law at the nanoscale (Mo *et al.*,

2009). The validation of this conclusion for the tribology of DLC films may be highly influenced by the formation of their graphitic transfer layers and easy-shear properties of such layers, which is of great scientific significance and thus should be investigated.

The high adhesion at interfaces between DLC films dominates their wear at the nanoscale. Such nanoscale wear can also be caused by abrasion with an extremely high load (Gnecco *et al.*, 2002). The transition of the nanoscale wear from adhesive to abrasive may be caused by the graphitization of the DLC films and the formation of their transfer layers. Investigation of such transition can uncover the nanoscale wear mechanisms of the DLC films and bridge the gap between their wear at different scales.

The nanotribological behaviors of DLC films are highly influenced by third-particles which may be the resultants during the friction process or sand-dust particles coming from the environment. The existence of a small number of the third-particles can highly increase the contact stresses and largely degrade the surface of the DLC films. Moreover, the interfacial adhesion between such films and their graphitization also highly change their tribological behaviors by influencing the motion of the third-particles. The tribological mechanism of the DLC films with the presence of third particles is not well explored and thus becomes another motivation in this study.

The atmosphere dependence of the tribological behaviors of DLC films is commonly attributed to the occurrence of tribochemical reactions, while the effect of atmosphere-element diffusions into the films on such dependence is ignored (Fontaine *et al.*, 2001; Fontaine *et al.* 2004). This can be exemplified by the low friction of the DLC films in a H₂ environment. Such low friction is commonly due to the H-passivations which result in van der Waals forces at the contact interface, and it is usually neglected the fact that the H

atoms can diffuse into the DLC films and highly reduce their shear modulus by enhancing their viscoplastic properties. Such diffusions have been rarely considered and thus their effect still lacks a clear understanding.

The sensitivity of the tribological behaviors of DLC films to their compositions and working atmospheres can be eliminated by using other lubricants. Graphene has excellent lubrication properties and superior chemical inertness and thus is capable of lubricating the DLC films with different compositions in various atmospheres (Filleter *et al.*, 2009). Therefore, graphene has a huge potential to stabilize the friction and wear of the DLC films. The lubrication mechanisms of graphene for these films are hardly studied in experiments due to its atomic-size thickness and thus should be investigated at the nanoscale.

It is evident that investigations of the above issues of DLC films are beneficial to understand their tribological mechanisms and promote their wide applications. These investigations are difficult to be conducted in experiments due to the nanoscale sizes but can be easily realized by simulation. This is because the fast development in computer science and technology has allowed atomistic models to simulate phenomena under a realistic situation. Many phenomena at the nanoscale can be well predicted by using either first-principle simulation or molecular dynamics (MD) simulation. Compared with the first-principle simulation, the MD simulation is capable of modeling systems with relatively large sizes and thus has been employed to simulate the tribological phenomenon at the nanoscale in this study.

In fact, it is always challenging for the MD simulation to accurately predict parameters in experiments, due to the large gap between the simulation and experiments at the time and length scales. However, the MD simulation can investigate physical and chemical

phenomena in a realistic situation and thus is still able to provide an atomic understanding about mechanisms of these experimental phenomena.

1.3. Objectives

The present research works are focused on the tribological mechanisms of DLC films by using MD simulation. The effects of working conditions and lubrication of graphene on the tribological behaviors of the DLC films are considered. The main objectives of the present research works are set as follows:

- To investigate the nanotribological behaviors of DLC films under different working conditions and with the lubrication of graphene;
- To study the friction and wear laws governing the tribological mechanisms of DLC films at the nanoscale;
- To explore fundamental mechanisms to link the tribological behaviors of DLC films at different scales;
- To provide guidance for applications of DLC films with the lubrication of two-dimensional materials in tough working conditions.

1.4. Dissertation outline

This PhD dissertation contains seven chapters. Following this introduction chapter, a literature review about the principle of tribology, tribological behaviors of DLC films and the MD simulation is conducted. Chapter 3 illustrates the investigation of tribological behaviors of DLC films under a two-body contact condition. In Chapter 4, the study focuses on the tribological behaviors of these films under a three-body contact condition.

Chapter 5 presents the influence of environmental hydrogen atoms on the tribological behaviors of the films. Chapter 6 deals with the lubrication of graphene for the film scratched by a diamond tip. Chapter 7 gives the conclusions of this dissertation and the recommendations for future works.

Chapter 2. Literature review

Friction and wear of DLC films are caused by the interactions of asperities at their contact interfaces during their relative sliding. Investigations of these interactions can help to uncover tribological mechanisms of such films. However, these interactions of asperities are common at the nanoscale and thus hardly studied in experiment. MD simulation can model the nanoscale tribology, since they are capable of monitoring the evolution of contact interfaces and providing information on the element diffusions and phase transformations. In this chapter, the fundamentals of tribology are firstly introduced. Then a review is conducted on tribological behaviors of the DLC films. Finally, the principles of the MD simulation are presented and their applications in modeling the nanoscale tribology are briefly illustrated.

2.1. Fundamentals of tribology

2.1.1. Friction and wear

The word *tribology* was initially derived from the Greek word *tribos* meaning rubbing, and thus the literal translation means “the science of rubbing”. In current dictionaries, tribology is defined as the science and technology of interacting objects during their relative motions and involves friction, wear and lubrication science. Friction is the resistance to relative motions of objects, and wear is the surface damage or material removal from one or both of their surfaces. Lubrication can reduce the friction and wear by using lubricants.

For components in a machine, high friction and wear highly degrade their surface and thus decrease their lifetime. Such degradations can be largely suppressed under a

lubrication condition. Therefore, tribology always relates with the reliability of machines ranging from spacecraft to household appliances. This determines the great economic significance of tribology. It has been reported that losses caused by tribology take about 4% of gross national product in United States, and about one third of the energy in the world is consumed by tribology (Bhushan, 2013a). Research and better designs of tribology are able to save about 1% gross national product in an industrialized nation (Jost, 1976). Therefore, tribology has highly attracted worldwide attentions.

The first study of tribology was conducted by the renaissance engineer and artist Leonardo da Vinci (Dowson, 1979). He firstly deduced rules for the motion of a rectangular block sliding over a flat surface. Such rules were rediscovered by the French scientist Guillaume Amontons (Bhushan, 2013a). He found that the friction force has a direct proportion to the normal load and is independent of the apparent contact area. The physicist Charles-Augustin Coulomb further reported that the friction force is independent of velocity after the commencement of motion (Coulomb, 1821). These pioneering observations became foundations of tribology and highly promoted its development.

Inventions of microscopes have promoted the rapid development of tribology. With these microscopies, it was found that many micro and nanoscale asperities exist on a macroscale smooth surface (Myers, 1962). The interactions between surface asperities of materials dominate their friction and wear. Therefore, investigations of these asperity interactions are capable of uncovering tribological mechanisms and have been the main research theme of the modern tribology (Bhushan, 2000).

The wear of materials was only empirically described to have a relation of with their mechanical properties such as hardness and elastic modulus for a long time. The fast

development of wear happened last century. With inventions of many kinds of microscopes, wear processes can be clearly examined, such as the formation of wear particles and transfer layers, crack propagations and delamination process (Sin *et al.*, 1979; Suh, 1973; Suh, 1977).

It should be noticed that both friction and wear are a systemic response instead of properties of materials. This is because both the friction and wear are influenced by operational conditions such as load, velocity, humidity, pairs of tribomaterials and atmosphere (Holmberg and Mathews, 1994). For example, sometimes a high friction is assumed to definitely relate with a high wear. The assumption is not universally correct because the friction is caused by interactions of surface asperities while the wear of materials relates with their mechanical properties (Bhushan, 2013a). This can be easily proved by the fact that polymers show low friction and high wear while ceramic materials exhibit high friction and low wear.

2.1.2. Tribology under two-body and three-body contact

Tribology can be categorized according to the contact conditions including solid-solid sliding, elastohydrodynamic lubrication and boundary lubrication (Bhushan, 2013a). Since DLC films are mainly used as solid lubricants in machine, their tribology mainly happens in a solid-solid contact condition. Therefore, the solid-solid sliding tribology is reviewed in the following sections.

The tribology of materials is regarded as the interaction between their surfaces. In some cases, a third particle from outside or generated during the wear processes can be present at the interface between these materials. Particularly, for DLC films in a sand-dust

environment, the sand particles at their interfaces highly influence their tribological behaviors. Due to the significance of the third particle on the tribological behaviors of the DLC films, both the tribology with the two-body contact and three-body contact are reviewed. This is different from the literature which commonly reviews the three-body tribology as a part of abrasion (Bhushan, 2013a).

Friction under a two-body contact condition is mainly dominated by adhesion and deformation. The adhesion friction commonly happens for metals and some ceramic materials (Bowden and Tabor, 1942; Bowden and Tabor, 1973). Under a large load, strong interactions (even cold welding) of surface asperities of metals can be caused and highly increase their interfacial adhesions. In this case, the relative sliding of metals requires a lateral force to overcome their interfacial adhesion. The lateral force that is friction force F_f can be obtained by

$$F_f = A_r \tau_a , \quad (2.1)$$

where τ_a is the average shear strength of the asperity contact and A_r the real contact area which is calculated by summing up the area for every asperity contact.

Friction can also be caused by deformation. During the friction process, asperities of the harder surface penetrate into the other soft surface and cause grooves by ploughing. As a result, the increase of the friction is induced because of the plastic deformation of the soft surface (Rigney and Hirth, 1979).

The friction caused by deformation can be understood by a simple model (Rabinowicz, 1965), as shown in Fig. 2.1. Under a large load, the rigid conical asperity penetrates into the lower material and thus causes its plastic deformations. Assuming that the yielding

strength of the lower material is isotropic, the forces along the horizontal and normal directions and the friction coefficient can be obtained as

$$F_n = pA_l, \quad (2.2)$$

$$F_f = pA_p, \quad (2.3)$$

$$\mu = \frac{F_f}{F_n} = \frac{A_p}{A_l}, \quad (2.4)$$

where F_n is the normal force, F_f the horizontal force that is the friction force, μ the friction coefficient, p the yield pressure of material, and A_l and A_p the projected area of the asperity contact along the normal and horizontal directions, respectively.

Fig. 2.1. Schematic of a hard asperity sliding against a soft material (Rabinowicz, 1965).

The Eq. 2.4 may be used to simply evaluate friction coefficient of materials particularly metals when they are experiencing ploughing. It should be noticed that the piling up of materials ahead of the asperity is neglected in the model. This results in that the friction coefficient predicted by Eq. 2.4 is smaller than experimental results in some cases (Rabinowicz, 1965).

Both the adhesion and deformation-induced friction describe the kinetic friction which is observed during the stable sliding of surfaces. In fact, when these surfaces are in contact under a large load, the lateral force required to initiate their relative sliding is commonly higher than the kinetic friction force and named as the static friction. The static friction is caused by interfacial adhesions which determine its time dependence (Rowe, 1960). A long rest time for the contact surfaces highly increases their interfacial adhesions by causing the formation of metallic or covalent bonds across their contact interface. With the commencement of the sliding, such interfacial adhesion is strong enough to cause plastic deformations and creeps of materials near the interface, thus highly increasing the friction force.

When the static friction between two materials is much larger than their kinetic friction, their relative sliding velocity fluctuates largely (Bhushan, 2013a), as shown in Fig. 2.2. Such fluctuation is called stick-slip friction and highly depends on the intrinsic properties of materials in contact as well as test conditions. During the sticky period, the interfaces between the materials are strongly bonded, thus highly increasing their friction force by inducing their deformation. When the stress reaches the strength of the interfacial adhesion, relatively slip of the materials happens. The periodic stick-slip friction can be seen in many situations such as squeal and chatter in bearings, jerking of brakes and earthquakes.

Stick-slip friction is undesirable in machines due to the frequent presence of large friction. Several methods have been developed to eliminate or prevent the stick-slip friction (Bhushan, 1980). For examples, one can design mechanical systems with a small compliance by using stiff springs and increasing both the inertias of sliding components and the system damping; lubricants can be used to avoid the stick-slip phenomenon by

reducing static friction and thus eliminating its difference with kinetic friction (Bhushan, 2013a).

Friction of materials has a close relation with their wear, since their friction energy is partly dissipated by plastic deformation or delamination during their wear. Different friction mechanisms indicate the existence of various principles of wear. The basic principles of wear include adhesion, abrasion, fatigue, chemical reactions, impact by erosion and percussion and electrical-arc-induced wear (Bisson, 1969). Commonly, at least two or more kinds of wear occur simultaneously, which highly complicates the wear analysis. It is noticed that two thirds of all wear in the industrial fields happen in the form of adhesion and abrasion. Therefore, a review of these two wear mechanisms will be conducted in this dissertation.

Fig. 2.2. Stick-slip friction force as a function of time or distance (Bhushan, 2013a).

Adhesive wear occurs when adhesion at the interface between materials is strong enough to deform them. As a result, a surface fragment may detach from the one material and attach to the other one (Archard, 1953). The adhesive wear commonly happens

between metals (Archard, 1980), due to the fact that the asperity welding of metals is easily induced under a large load.

The mechanisms of adhesive wear have been investigated for decades. Among these investigations, the mechanism proposed by Archard is most well-known. He suggested that shearing between two materials occurs at their original interface (Archard, 1953), due to the fact that the interfacial adhesion strength is commonly smaller than the mechanical strength of asperities. In some cases, the interfacial strength is much higher and can cause the break of surface asperities, leading to the detachment of a surface fragment and thus the formation of wear debris.

The equation of adhesive wear was commonly obtained based on the experimental results. It is found that the wear volume can be calculated as

$$V = \frac{kF_n L}{H}, \quad (2.5)$$

where V is the wear volume, F_n the load, L the sliding distance, H the hardness of the worn surface and k the wear coefficient (Holm, 2013). Eq. 2.5 was later verified by Archard via a theoretical model in which the contact was assumed to be plastic (Archard, 1953). Hence, the formula is also called Archard equation. The Archard equation has been validated by many experimental results and thus used widely to predict the wear volume of materials. The assumption of plastic deformations in the Archard equation can be verified by examining the wear track. For example, for a stainless steel sample after adhesive wear, adhesive debris is evidently pullout from the sample, and both its surface and subsurface experience severe plastic deformations.

Abrasive wear under the two-body contact condition happens when a hard surface slides against a soft surface. In this case, the asperities of the hard surface can penetrate

into the soft one and cause its plastic deformation or fracture (Moore, 1974). The abrasive wear widely occurs in the mechanical operations such as cutting, turning and grinding.

The wear volume caused by abrasion can be evaluated based on a simple model raised by Rabinowicz (Rabinowicz, 1965), as shown in Fig. 2.3. In this model, a rigid conical asperity slides against a soft and flat surface. A groove with uniform depth is ploughed on the soft surface. By assuming that the soft surface yields during the ploughing, the abrasive wear volume can be calculated by

$$V = \frac{2F_n L \tan \theta}{\pi H}, \quad (2.6)$$

where F_n is the load, L the sliding distance and H the hardness of the soft surface.

Eq. 2.6 is obtained based on a simple situation. It was further found that abrasive wear can also be rewritten with a similar formation of Archard equation as

$$V = \frac{k_1 F_n L}{H}, \quad (2.7)$$

where k_1 is the wear coefficient includes all the influences such as geometry of asperities. The k_1 is commonly two to three orders of magnitude larger than the wear coefficient of adhesion wear, which indicates that the abrasive wear is quite undesirable in machines and should be avoided during their working.

The three-body tribology happens with the presence of third particles. Such particles may come from the environment such as the desert. Moreover, these particles may also be the resultants formed during the adhesive and abrasive wear, due to the fact that many wear debris distributed on the wear track actually become third particles influencing the friction and wear.

Fig. 2.3. Abrasive model of a hard conical asperity sliding against a soft surface (Bhushan, 2013a).

Fig. 2.4. Schematic of wear process of two relatively sliding surfaces with (a) trapped third particles and (b) rolling particles (Bhushan, 2013a).

The mechanisms of three-body tribology highly depend on the mechanical properties of third particles. For the particles that are softer than the other two materials, these particles highly yield and thus become flat or fragmented during the wear process (Khrushchov, 1974). When the third particles are harder than the other two materials, such particles may be trapped by one of the two materials and plough another one (Bhushan *et al.*, 1985), as shown in Fig. 2.4. In this case, the mechanisms of the three-body tribology are similar to those of two-body abrasive tribology. The rolling of the third particles is

present, when the load is small or the other two materials have smooth surfaces. In some situations, these particles spend almost 90% of the time rolling. In this case, the rolling particles highly reduce the friction and wear, because such particles act as bearings to lubricate the relative sliding materials. It has been reported that the wear coefficient under three-body contact conditions is at least one order of magnitude smaller than that in two-body contact conditions (Rabinowicz *et al.*, 1961).

2.1.3. Tribology at the nanoscale

It has been discussed that macroscale tribology of materials is caused by interactions between their surface asperities which are at the micro or nanoscale. Investigations of these interactions can significantly improve the understanding of macroscale tribology and thus bridge the gap between science of tribology and its applications in engineering (Bhushan, 1999; Bhushan, 2013b). Moreover, the micro/nano-miniaturizations of machines such as NEMS and MEMS highly increase demands to understand the tribological phenomena at the nanoscale (Bhushan, 2000; Bhushan, 2012). As a result, the importance of the nanoscale tribology has been long recognized.

The rapid development of science and technology makes it easy to investigate nanoscale tribology. Many tip-based microscopies invented in the last century such as surface force apparatus (SFA), scanning tunneling microscope (STM), atomic force and friction force microscopes (AFM and FFM) can be used to study the nanoscale tribological phenomena. The emergence of these microscopes has highly improved the understanding of the nanoscale tribology by shedding light into atomic-scale energetics, dynamics, thermodynamics, structure of materials and their rheological properties (Bhushan, 1998).

Nanoscale friction is quite different from friction at the macroscale. It has been reported that the nanoscale friction is sensitive to properties of outermost surface-layers of materials instead of their bulk mechanical properties which dominate the macroscale friction (Kim and Kim, 2009). The outermost surface-layers may be the adsorbed gas, capillary junction, contamination and oxide layer, and their properties are determined by many factors such as temperature, humidity, working atmosphere and even sliding history.

Mate *et al.* (1987) firstly studied the nanoscale friction by exploring the frictional interactions between a sharp tungsten tip and a graphite substrate via an AFM. Their study showed a typical stick-slip friction behavior and demonstrated that such behavior is an essence of the nanoscale friction. This was later proved by many studies. For example, Akamine *et al.* (1990) obtained the saw tooth shaped stick-slip friction when using an AFM tip to scanning an Au film; Fujisawa *et al.* (1993) further found that the stick-slip friction during the relatively sliding of a Si_3N_4 tip and a mica substrate is attributed to the zigzag motion of such tip.

Stick-slip friction is also present for a confined liquid film which has a small thickness. The stick-slip friction is attributed to the periodic melt and freeze of the confined liquid film during its shear deformation (Bhushan *et al.*, 1995), as shown in Fig. 2.5. Under a small strain, the film stays in a frozen state and exhibits solid-like properties, leading to that the sliding hardly happens inside the frozen film and thus causes a sticking friction. When the strain energy is high enough to induce the melt of such film, it exhibits liquid-like behaviors and thus causes the slipping friction.

Nanoscale friction highly depends on the velocity. Tambe *et al.* (2005) reported that a mediate velocity can reduce the friction of silicon by suppressing the formation of meniscus

at the contact interface while a high velocity largely increases the friction by inducing deformation and fractures of surface asperities. They also found that structures of materials influence the velocity dependence of their nanoscale friction. For example, the friction force of DLC films decreases with the velocity, due to their graphitization and the formation of an easy-shear transfer layer.

Fig. 2.5. Phase diagram of confined liquid layers during the stick-slip friction process (Bhushan *et al.*, 1995).

Similar to the macroscale friction, nanoscale friction also has a positive proportion to contact area at the sliding interface (Bhushan and Sundararajan, 1998). Nair *et al.* (2008) reported that nanotexturing of amorphous silicon can reduce its friction coefficient from 0.5 to 0.05, due to the fact that the texturing highly reduces the contact area and thus decreases the interfacial adhesion.

The decrease of scales generally reduces friction. This is because a small scale can increase the indentation hardness and elastic modulus of materials and thus reduce their contact area under the same load (Bhushan and Kulkarni, 1996). Moreover, a small

apparent contact area at the small scale highly reduces the number of third-particles trapped at the contact interface and largely avoids the occurrence of ploughing (Tambe and Bhushan, 2004).

Similar to the nanoscale friction of materials, their nanoscale wear is also sensitive to properties of their outermost surface-layers (Bhushan and Kwak, 2007; Gnecco *et al.*, 2002). Since the properties of such outermost surface-layers are influenced by many factors such as atmosphere, temperature and contamination, such sensitivity determines that the nanoscale wear of materials cannot be calculated by Archard equation which only considers the effect of their load and hardness (Bhaskaran *et al.*, 2010). Therefore, the development of a generalized model for the nanoscale wear is always a huge challenge to researchers.

AFM has been commonly used to investigate the nanoscale wear. This is because the AFM can accurately measure extremely small forces and visualize surface morphologies with a resolution below 1 Å (Cho, 2009). Moreover, the tip-based scanning technique in the AFM is efficient to investigate the asperity sliding against a surface (Pham *et al.*, 2010). Such investigation is beneficial to bridge the gap of tribology at different scales.

Chung *et al.* (2003) studied the effect of humidity on wear behaviors of Si and Si₃N₄ tips. They found that the humidity can accelerate the wear of these tips by increasing adhesive forces at contact interfaces. The increase of the adhesions is due to the formation of meniscus (Liu *et al.*, 2010). The humidity effect can be changed by velocity. A high velocity can highly suppress the formation of meniscus and thus induce the occurrence of abrasive wear (Tambe and Bhushan, 2005a).

Gotsmann *et al.* (2008) investigated the wear behaviors of a single Si tip sliding against a flat polymer surface. They reported that nanoscale wear proceeds as a continuous atom-by-atom attrition without the presence of fracture. This attrition process cannot be well explained by the Archard equation, thus indicating the essential difference between the nanoscale and macroscale wear. The atom-by-atom attrition was later verified by Bhaskaran *et al.* (2010). They found that the nanoscale wear can be explained by the Arrhenius theory which is commonly employed to interpret the probabilities of chemical reactions. This theory demonstrates that an atom has a high possibility to be worn if its kinetic energy can overcome the energy barrier (denoted as ΔG in Fig. 2.6). The shear stress enhanced by the friction force can highly decrease this energy barrier and thus promote the generation of worn atoms.

Fig. 2.6. Schematic of the wear process by atom-by-atom attritions (Bhaskaran *et al.*, 2010).

2.2. Tribological behaviors of DLC films

Tribological behaviors of DLC films highly depend on the chemical and physical phenomena at the sliding interface (Liu *et al.*, 1996b). Such phenomena can be influenced by many factors such as doping elements of these films, their working parameters and environment and lubrication (Erdemir and Donnet, 2006). As a result, the tribological mechanisms of the DLC films are always complicated.

Since this PhD dissertation is devoted to exploring a fundamental explanation of tribological mechanisms of DLC films, a brief review will be conducted for the effect of operational conditions including working parameters and environment. The lubrication of other lubricants on DLC films will also be reviewed, due to the fact that such lubrication can highly change the chemical and physical phenomena at the sliding interface. The effects of other factors such as doping elements will be ruled out, since these factors can highly influence the mechanical properties of DLC films and induce complex phase transformations and chemical reactions, thus largely complicating their tribological mechanisms.

2.2.1. Operational condition influence

A high load of DLC films decreases both their friction coefficient and wear rate. These decreases can be explained by graphitization and formation of transfer layers (Wang *et al.*, 2013). The high load can improve the graphitization level of these films by increasing their friction temperature (Wang *et al.*, 2013; Bai *et al.*, 2011). Moreover, under the high load, transfer layers are easily formed on the counterpart surfaces of these DLC films (Fig. 2.7). These layers exhibit easy-shear properties due to their high graphitization level (Bai *et al.*,

2011; Liu, 1997; Erdemir, 2004; Liu *et al.*, 1996b). As a result, the transfer layers are capable of isolating the DLC films and their counterparts, leading to the sliding inside such layers.

The effect of loads on wear behaviors of DLC films can be well explained from the point of energy dissipation (Fouvry *et al.*, 2003). At a large load, more friction energies are dissipated by graphitization of the DLC films and the thermal conduction due to the large contact area. In this case, the friction energy dissipated by wear including crack propagations and kinetic energies of wear debris highly decreases, thus leading to a significant reduction of the wear rate at the large load (Ramalho and Miranda, 2006).

Fig. 2.7. Optical image of transfer layers on the surface of counterpart at different loads (Wang *et al.*, 2013).

Wear behaviors of DLC films under different loads can also be interpreted by an entropy-based theory (Ling *et al.*, 2002). It has been reported that the entropy is proportional to the wear rate, due to the fact that the friction and wear are actually a non-equilibrium thermodynamics process (Aghdam and Khonsari, 2011). For the DLC films, their entropies decrease with their load, mainly due to the high friction temperature which

reduces entropy consumptions (Amiri and Khonsari, 2010). The small entropies of DLC films at a large load keep consistent with their small wear rate.

Besides a high load, a high velocity of DLC films also reduces their friction force and wear rate. This is because the high velocity can induce a rapid deformation of surface asperities and generate a large amount of friction energy in a short time. These energies are mainly dissipated by temperature rising on the surface of the DLC films and their graphitization (Fouvry *et al.*, 2003). This highly promotes the formation of transfer layers and ensures their easy-shear properties, thus reducing wear rate and friction coefficient of the DLC films.

The chemical reactions at sliding interfaces between DLC films and their tribopairs influence the velocity dependence of their tribological behaviors. This can be demonstrated by exemplifying wear tests in different atmospheres. With a high velocity, the friction coefficient in air decreases while that in nitrogen almost keeps constant (Vercammen *et al.*, 1999). This is because surface oxidations of the DLC films in air can increase their interfacial adhesion. At a high velocity, the time is insufficient for the chemical absorptions of oxygen molecules and thus suppress oxidations of the DLC films. This suppression is beneficial for the decrease of interfacial adhesions of these films and thus reduces their friction forces. However, their interfacial adhesions almost keep constant in a nitrogen environment due to the chemical inertness of nitrogen molecules, thereby leading to a constant friction force (Erdemir *et al.*, 2000).

It is evident that the atmosphere highly changes the tribological behaviors of DLC films by influencing their chemical and physical states at their contact interfaces. Hydrogenated DLC films commonly exhibit low friction force and wear rate in an inert gas

atmosphere such as N_2 , Ar and CO_2 (Erdemir and Donnet, 2006). This is because these inert gas molecules hardly influence the H-passivations of dangling σ bonds at contact interfaces of the DLC films. As a result, the H-passivations always cause a small interfacial adhesion, thus ensuring a low friction force (Fig. 2.8).

The non-hydrogenated DLC films commonly exhibit short lifetime in an inert atmosphere (Erdemir and Donnet, 2006). This is due to the fact that the dangling σ bonds exist at the contact interface of these films. Such bonds are difficult to be efficiently passivated by the inert gas molecules and thus can cause strong interfacial adhesion strengths, resulting in a high friction of the DLC films and their failure.

Fig. 2.8. Illustration of the friction reduction mechanisms by H-passivations of DLC films (Erdemir and Donnet, 2006).

Tribological behaviors of DLC films in vacuum highly depend on their H content. A high H content causes a low friction and even the presence of superlubricity which means the friction coefficient is smaller than 0.01 (Andersson *et al.*, 2003b). This low friction is due to the H-passivation of interfacial dangling σ bonds. Although a high H content of the

DLC films is beneficial to their tribological behaviors, such high H content also degrades their mechanical properties and may influence their wear behaviors. This indicates the existence of an optimal H content in the DLC films.

Due to the significance of H-passivations to low friction of DLC films, their tribological behaviors in a H₂ environment have attracted wide attentions. It was found that a high pressure of H₂ can largely reduce the friction force of the DLC films (Andersson *et al.*, 2003a; Donnet *et al.*, 2001). This is because the H₂ molecules can be decomposed into active H atoms during the friction process. Such H atoms efficiently passivate the interfacial dangling bonds of the DLC films and thus largely reduce their interfacial adhesion.

Oxygen highly influences the tribological behaviors of DLC films by degrading their H-passivations. This is because the oxidation reactions at the sliding interface can easily remove the H atoms, increasing interfacial adhesion (Kim *et al.*, 2006). The oxidations of carbon atoms also enhance their departure from the DLC films and thus increases their wear rate.

Water molecules also significantly influence the tribological behaviors of DLC films. It has been reported that when the pressure of water vapor increases, the friction force of the hydrogenated films increases while that of the non-hydrogenated films decreases (Fig. 2.9) (Enke *et al.*, 1980; Tagawa *et al.*, 2004; Andersson *et al.*, 2003b). These different friction behaviors are due to the effect of water molecules on the interfacial adhesion. For the hydrogenated films, the absorption of water molecules on their interfaces can remove H atoms and increase their interfacial adhesion, leading to the increase of friction force (Donnet and Erdemir, 2007). For the non-hydrogenated films, the absorbed water molecule

passivates their dangling σ bonds at the interfaces and reduce their bonding strength. Such absorption actually induces the formation of water layers at the interface of the DLC films (Donnet and Erdemir, 2007). These layers act as liquid lubricants for the films, thus decreasing their friction force and wear rate.

Sand-dust environment has attracted intense attentions due to the worldwide explorations to outer space. For example, when the robotic car moves on moon, the sand particles can attach to bearings and gears of the car and thus cause their severe wear and even failure (Wickman, 2007). Moreover, the desertification of earth also raises the significance of machine reliability in a sand-dust environment (Reynolds *et al.*, 2007).

Fig. 2.9. The humidity effect on the friction coefficient of DLC films (Donnet and Erdemir, 2007).

Table 2.1. Friction coefficients and wear rates for diamond coatings and various DLC films. (Erdemir and Donnet, 2006).

	Diamond coatings	Hydrogen free DLC	Hydrogenated DLC	Modified/doped DLC
Atomic structure	sp ³	sp ² & sp ³	sp ² & sp ³	sp ² & sp ³
Hydrogen content	-	>1%	10-50%	
μ in vacuum	0.02-1	0.3-0.8	0.007-0.05	0.03
μ in dry N ₂	0.03	0.6-0.7	0.001-0.15	0.007
μ in dry air 5-15% RH	0.08-0.1	0.6	0.025-0.22	0.03
μ in humid air 15-95%	0.05-0.15	0.05-0.23	0.02-0.5	0.03-0.4
μ in water	0.002-0.08	0.07-0.01	0.01-0.7	0.06
μ in oil		0.03	0.1	0.1
k in vacuum	1-1000	60-400	0.0001	
k in dry N ₂	0.1-0.2	0.1-0.7	0.00001-0.1	
k in dry air 5-15% RH	1-5	0.3	0.01-0.04	
k in humid air 15-95%	0.04-0.06	0.0001-400	0.01-1	0.01-1
k in water	0.0001-1		0.002-0.2	0.15
k in oil	-	-	-	0.1

*k refers to wear rate [$10^{-6}\text{mm}^3(\text{Nm})^{-1}$].

DLC films exhibit an excellent lubrication for the components in a sand-dust environment. Such lubrication performance depends on the parameters such as load and the radius of sand particles (Qi *et al.*, 2010). The presence of sand particles can generally decrease the friction force of the DLC films, due to the rolling movement of these particles.

The large-sized sand particles can highly reduce the friction force of these films but increase their wear rate. This is because the large-sized particles can roll easily during the friction process while also causes a high contact stress to the films and thus cause their severe abrasive wear (Qi *et al.*, 2011a). It has been found that a high load can reduce the wear rate of the films by causing the fragmentation of the sand particles (Qi *et al.*, 2011b). This is because these fragmentations make the sand layer become smooth and thus reduce the contact stress of the films.

2.2.2. Lubrication influence

The sensitivity of tribological behaviors of DLC films to their composition and working atmosphere determines that only few of them can work alone during their applications for a long time. These sensitivities indicate that the employment of other lubricants is necessary to improve and stabilize the friction and wear of the DLC films. Therefore, it is significant to investigate the tribological behaviors for these films in a boundary-lubricated condition. This investigation is also pursued due to the real working conditions of the DLC films. Commonly, it is not economically viable to coat all workpieces in a machine. As a result, the DLC-coated workpieces still work under the lubrication condition and use the lubricants supplied for uncoated workpieces.

Tribological behaviors of DLC films under a lubricated condition follow a standard Stribeck curve (Czichos and Habig, 2010), as shown in Fig. 2.10. It is evident that compared with steel the DLC films can highly reduce the friction coefficient in a boundary-lubricated condition and ensure a fast transition of lubrication from boundary-lubricated to elastohydrodynamics (EHD). Therefore, the DLC films generally exhibit a better

tribological behavior than bare workpiece surfaces in either dry sliding or lubrication conditions. For extreme cases such as complete loss of lubricants and the malfunction of lubricating system, the DLC films can efficiently improve the friction and wear resistance of components over a wide range of the load, velocity and temperature and thus highly extend their lifetime.

It should be noticed that DLC films coated on the surface of steel have negligible effects of its friction and wear under EHD and hydrodynamics conditions (Donnet and Erdemir, 2007). This is attributed to that solid/solid contact is absent in the EHD and hydrodynamics conditions and the friction is determined by physically intrinsic properties of lubricants as liquid.

Under a boundary-lubricated condition, the DLC/steel pairs exhibit a smooth and low friction coefficient at the beginning of friction (Podgornik *et al.*, 2003; Podgornik *et al.*, 2005). This is due to the fact that the steel surface can be smoothed rapidly by the hard DLC films and thus cause the formation of graphitic transfer layers. However, the DLC/DLC pairs show a relatively long running-in period (Donnet and Erdemir, 2007), which is attributed to that two hard surfaces in contact take a long time to accommodate to each other.

Under boundary-lubricated conditions, the friction and wear of hydrogenated DLC films are insensitive to the liquid lubricants, their additive type and concentration (Donnet and Erdemir, 2007). This is due to the fact that these films are inert and hardly react with the lubricants and their additives. However, a high dependence can be observed for the metal-doped DLC films. When the liquid lubricants contain the sulfur-based additives, such additives can react with the graphitic transfer layers and form a new type of tribofilm

such as MoS₂ and WS₂ for Mo- and W-doped DLC films, respectively (Podgornik *et al.*, 2005; de Barros' Bouchet *et al.*, 2005; Miyake *et al.*, 2004). These new tribofilms have laminar structures and are easy to shear, thus highly reducing friction.

Fig. 2.10. Effect of DLC films on the friction coefficient of components in a lubricated condition (Donnet and Erdemir, 2007).

Additive concentration largely influences the tribological behaviors of the metal-doped DLC films. For example, when concentration of the sulfur-based additive is low, its quantity is insufficient to support the formation of dense MoS₂ or WS₂ films; when such concentration is high, sulfur-rich films that have high shear resistances are formed (Donnet and Erdemir, 2007). Both the extremely low and high additive concentrations can largely increase the friction force. As a result, a mediate concentration of the additive is commonly required to achieve the low friction by causing the fast formation of dense easy-shear tribofilms.

Recently, the emerging two-dimensional materials such as graphene have attracted wide attentions due to their superior mechanical properties and superlow friction

coefficient. It was found that such two-dimensional materials can work as additives of lubricants for DLC films to largely reduce their friction coefficient and increase their lifetime (Liu *et al.*, 2012; Liu *et al.*, 2011a; Liu *et al.*, 2011b). This is due to the fact that flakes of the two-dimensional materials tend to agglomerate at the interface between the DLC films and their counterparts. Such agglomerates are easy to shear and thus highly reduce the shear resistance.

2.3. MD simulation

2.3.1. Principles

MD simulation is a technique to determine the evolution of a system based on given initial positions of atoms and their velocities and predict its fast non-equilibrium processes (Rapaport, 2004). As a result, the MD simulation has been widely used to investigate material properties such as tribological behaviors, deformation mechanisms and atomic diffusions.

MD simulation is conducted based on the Newton equation of motion

$$m_i \frac{\partial^2 \vec{r}_i}{\partial t^2} = \vec{F}_i, \quad (2.8)$$

where m_i , $\vec{r}_i$ and $\vec{F}_i$ are the mass of the i -th atom, its position and force vectors, respectively; t is the time. For the i -th atom, its acceleration obtained from the Newton's equation of motion can help to update its velocities and positions by performing a step-by-step numerical integration of such equation. As a result, the velocities and positions of all the atoms in a system can be obtained by repeating such calculations and integrations. The whole process of the MD simulation is to repeatedly predict movements of the atoms and

monitor the thermodynamics states of systems and will be stopped when the quantities of interest such as the trajectory, temperature, pressure and density of materials have been recorded. The procedure of the MD simulation is shown in Fig. 2.11.

It is noticed that the acceleration of an atom is calculated based on the forces imposed by its surrounding neighbors. Such calculation is significant to ensure the accuracy and simplicity of MD simulation. These forces can be obtained according to their relation with interatomic potential as

$$\vec{F}_i = -\frac{\partial V}{\partial \vec{r}_i} , \quad (2.9)$$

with

$$V(r^{3N}) = \sum_{j=1}^N V_1(r_j) + \sum_{i<j}^N V_2(r_i, r_j) + \sum_{i<j<k}^N V_3(r_i, r_j, r_k) + \dots , \quad (2.10)$$

where V is the interatomic potential, and V_1 , V_2 and V_3 are one-, two- and three-body interactions, respectively. The V_1 is commonly absent unless an external field is present. The V_2 is purely pairwise interaction which is sufficient to describe the atomic interactions in some cases. V_3 usually considers the effect of the bonding environment of atoms and thus is capable of evaluating many physical and chemical properties of materials by evaluating their bond breaks and formations.

In this dissertation, interactions among carbon atoms are described by Tersoff and AIREBO potentials. This is because these potentials can accurately describe phase transformations in carbon-based materials and their physical and mechanical properties. Both the Tersoff and AIREBO potentials are briefly introduced as follows.

Fig. 2.11. Flowchart of MD simulation (Li, 2005).

(a) Tersoff potential

The Tersoff potential was firstly developed by Tersoff based on the concept of bond order (Tersoff, 1988; Tersoff, 1989). He found that the strength of a bond between two atoms is varied and depends on their local environment such as their coordination number which indicates the number of nearest neighbor atoms. The atoms with many neighbors possess weaker bonds than those with few neighbors. The Tersoff potential is capable of describing interatomic interactions within semiconductor systems such as silicon and carbon materials.

The Tersoff potential has a form shown as

$$V = \frac{1}{2} \sum_i \sum_{i \neq j} f_c(r_{ij}) [A_{ij} V^{(R)}(r_{ij}) - B_{ij} V^{(A)}(r_{ij})] , \quad (2.11)$$

with

$$f_c(r_{ij}) = \begin{cases} 1, & r_{ij} \leq R - D \\ \frac{1}{2} - \frac{1}{2} \sin\left[\frac{\pi(r_{ij} - R)}{2D}\right], & R - D < r_{ij} < R + D \\ 0, & r_{ij} > R + D \end{cases}, \quad (2.12)$$

where the f_c is the cutoff function to ensure that only the nearest neighbor interactions are considered in the Tersoff potential; R and D are parameters used to justify the nearest neighbors; the $V^{(R)}(r_{ij})$ and $V^{(A)}(r_{ij})$ functions are terms to represent the repulsive and attractive interactions, respectively. Detailed expression of these two functions can refer to the literature (Tersoff, 1988).

(b) AIREBO potential

The adaptive intermolecular reactive empirical bond order (AIREBO) potential was developed to model chemical reactions and physical transformations in condensed-phase hydrocarbon systems such as polymers, graphite, diamond and amorphous carbon materials (Stuart *et al.*, 2000). This potential is derived from the reactive empirical bond order (REBO) potential which can model breaks and formation of covalent bonds in the carbon and hydrocarbon systems (Brenner *et al.*, 2002). The AIREBO potential further considers the nonbonded and dihedral-angle interactions which are also the Torsion contribution. The nonbonded interactions are represented by van der Waals interactions which exist between two passivated molecules or atoms. Inclusion of the nonbonded interactions into the AIREBO potential ensures that it can help to simulate chemical reactions in which interactions between two atoms may change from van der Waals forces to covalent bonds. The AIREBO potential has a form as

$$V = \frac{1}{2} \sum_i \sum_{j \neq i} [E_{ij}^{REBO} + E_{ij}^{LJ} + \sum_{k \neq i, j} \sum_{l \neq i, j, k} E_{kijl}^{TORSION}] , \quad (2.13)$$

with

$$E_{ij}^{REBO} = V_R(r_{ij}) - B_{ij} V_A(r_{ij}) , \quad (2.14)$$

where the $V_R(r_{ij})$ and $V_A(r_{ij})$ are the repulsive and attractive terms, respectively; the parameter B_{ij} represents the atomic environment which influences the bond order; the LJ term indicates the Lennard-Jones potential which represents van der Waals interactions. More details of the REBO, LJ and Torsion terms can refer to the literature (Stuart *et al.*, 2000).

In this PhD thesis, the MD simulation is conducted by the Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) which is an open-source code. LAMMPS is capable of simulating solid-state matter, soft materials and coarse-grained or mesoscopic systems and can also work as a parallel simulator to model phenomenon at the atomic, meso and continuum scale (Plimpton *et al.*, 2007). Moreover, LAMMPS is easy to be modified or extended with new capabilities such as new force fields, atom types and boundary conditions. Therefore, LAMMPS has a high efficiency and flexibility and thus has been widely used to simulate many chemical and physical phenomena.

2.3.2. Simulation of tribology at the nanoscale

MD simulation is capable of tracking the trajectories of atoms and studying nanoscale phenomena which are hardly observed in experiment, and thus can be used to investigate the nanoscale tribology and uncover its mechanisms. Many studies by MD simulation have been reported to investigate the nanoscale tribology by considering the effect of factors

such as lattice orientation, load, velocity, temperature and contact area (Zhang and Tanaka, 1997; Dong *et al.*, 2013a; Family *et al.*, 2000; Braun and Naumovets, 2006; Szlufarska *et al.*, 2008; Vanossi *et al.*, 2011). It has been reported that the lattice orientation of materials influences their friction by inducing the contact interface with commensurate or incommensurate patterns (Dong *et al.*, 2013a). The commensurate contact pattern usually induces a high friction, while the incommensurate contact pattern can cause a low friction which is also called structural lubricity. The difference between these two contact patterns can be seen in Fig. 2.12 where both the upper and lower layers are graphene (Hod, 2012). Different contact patterns can be obtained by rotating the upper layer. For the commensurate contact pattern, the atom positions of two layers coincide from an upper view. However, such coincidence is absent for the incommensurate contact pattern (Dong *et al.*, 2013a).

Dong *et al.* (2011) elucidated the mechanisms of friction dependent on contact patterns by analyzing the stress distributions on the contact interface. They found that the commensurate contact only shows homogeneous positive shear stresses while the incommensurate contact exhibits positive and negative shear stresses in different regions. These positive and negative stresses can induce a partial slip in subsets of the incommensurate contact interface, thus easily causing sliding at the contact interface and highly reducing the friction.

Contact area at the nanoscale still highly influences the friction. Mo *et al.* (2009) found that the real contact area at the nanoscale is not a circular or continuum area but discretely distributes around atoms on the contact interface (Fig. 2.13). The real contact area can be calculated by summing up all the discrete areas and has a linear proportion to the friction

force. Therefore, the friction law at the nanoscale can be denoted as

$$F_f = \tau A , \quad (2.15)$$

where F_f is the friction force, τ shear stress at the contact interface and A the real contact area. The Eq. 2.15 has a same form as the Bowden-Tabor term at the macroscale and thus demonstrates its validation at the nanoscale (Bowden and Tabor, 1942; Eder *et al.*, 2015).

Fig. 2.12. Illustration of the commensurate contact (a) - (b) and incommensurate contact (c) - (d), where (a) and (b) are tilted view, and (c) and (d) are upper view (Hod, 2012).

Load also highly influences friction at the nanoscale. It has been found that the load has a linear relation with the friction when the adhesion at the contact interface is weak while such relation becomes nonlinear for a strong interfacial adhesion. This is because the increased interfacial adhesion can change the relation of the load and contact area from linear to nonlinear. Moreover, a zero load cannot eliminate friction, due to the fact that contact area is nonzero because of the interfacial adhesions. Elimination of the friction requires a negative load that is a pull force to overcome the interfacial adhesions to obtain

a zero contact area.

Fig. 2.13. Atomic configuration of contact at the nanoscale (Mo *et al.*, 2009): (a) and (b) are atomic configuration, (c) is the outline of the contact area.

A high temperature commonly causes the friction reduction. This is due to the fact that such high temperature can highly reduce the shear modulus of materials. Moreover, the high temperature can largely decrease the energy barrier to realize sliding at contact interfaces and thus reduce the shear resistance and the friction force (Dong *et al.*, 2013b).

A high velocity may reduce the nanoscale friction by increasing the friction temperature at the contact interface. However, this is not true and can be influenced by details in the MD simulation such as the potential defined, test conditions and materials. For example, in a Cu/Fe system, the friction force increases for the velocity below a critical value while decreases when the velocity is larger than such value (Lin *et al.*, 2012).

MD simulation has also been used to investigate tribological mechanisms of DLC films in past decades by considering the effect of their element passivations and graphitization.

For non-hydrogenated DLC films, many dangling σ bonds exist on their surface. The contact of such films can cause the formation of many covalent C-C bonds across their contact interface by tribochemical reactions. These bonds induce a strong interfacial adhesion and highly increase the friction force of the DLC films (Schall *et al.*, 2009; Harrison *et al.*, 2008; Gao *et al.*, 2002). It was further found that the unsaturated sp atoms are initiation sites for the tribochemical reactions (Gao *et al.*, 2002; Schall *et al.*, 2009).

The interfacial adhesion can be highly reduced when the surface of DLC films is passivated by H atoms. This is because such H-passivations can highly reduce the amount of surface dangling σ bonds (Hayashi *et al.*, 2011; Bai *et al.*, 2012), as shown in Fig. 2.14. In this case, the interactions at the contact interfaces of the DLC films are dominated by van der Waals forces between H atoms, thus causing a low friction force. It was found that the H-passivations also promote the cleavage of the C-C bonds across the contact interface (Hayashi *et al.*, 2011). Such cleavages also contribute to the friction reduction. Moreover, the tribochemical reactions also cause the low friction (Gao *et al.*, 2002). These reactions may induce the formation of H₂ molecules at the interface between DLC films and thus significantly reduce their interfacial adhesion.

Gao *et al.* (2002) found that friction forces of thick and thin DLC films are almost identical and demonstrated that the thickness of these films hardly influences their tribological behaviors at the nanoscale. This indicates that the friction of the DLC films is dominated by their structures near their surfaces.

The graphitization of DLC films is also responsible for their low friction at the nanoscale. Such graphitization can induce the presence of a soft layer which has a small elastic modulus and thus is easy to shear, resulting in the friction reduction (Gao *et al.*,

2002; Harrison *et al.*, 2008). It is also found that the graphitization can induce the presence of a graphene-like layer (Fig. 2.15) at a large load (Ma *et al.*, 2014; Ma *et al.*, 2011; Ma *et al.*, 2009). Such layer highly reduces the friction force of the DLC films, due to the weak interfacial adhesion dominated by van der Waals interactions.

Fig. 2.14. Mechanisms of friction reduction of DLC films by H-passivations (Hayashi *et al.*, 2011).

The graphitization of DLC films was commonly caused by the instability of their structure at high temperatures. Kunze *et al.* (2014) reported that sp^3 - sp^2 transitions of the DLC films can also happen during their elastic deformation. It was later found that sp^3 atoms with sp^2 neighbors are the initiation sites for these sp^3 - sp^2 transitions (Bai *et al.*, 2016b).

The wear mechanisms of DLC films have only been studied in few MD simulation studies. Kunze *et al.* (2014) reported that the soft layer caused by graphitization of the DLC films is the precursor to their wear debris. Sha *et al.* (2013) found that wear of these films is linearly proportional to their normal load and sliding distance and is mainly caused by

shear tractions. Such tractions can induce mass accumulations at the trailing end of contact and lead to a cluster detachment process.

Fig. 2.15. Formation of graphene-like layers at interfaces between DLC films (Ma *et al.*, 2011).

2.4. Summary

The fundamentals of tribology including friction and wear are reviewed and the tribology under two-body and three-body contact are discussed in detail. Unique phenomena of nanoscale tribology are also briefly presented. Particular attentions are devoted to the tribological mechanisms of DLC films in different operational and lubricated conditions. The principles of MD simulation as well as its applications in the nanoscale tribology are introduced.

Chapter 3. Tribological behaviors of DLC films under two-body contact

A fundamental analysis of the tribological behaviors of DLC films is hardly conducted in experiment. This is because their friction and wear are caused by the interactions between nanoscale surface asperities that are difficult to be evaluated by equipment. This chapter investigates the tribological behaviors of the DLC films at the nanoscale by considering the effect of the load, velocity and their surface roughness. The interactions between surface asperities are investigated in details, and the friction and wear laws governing the tribological behaviors of the DLC films at the nanoscale are demonstrated.

3.1. Modelling

3.1.1. Atomistic configuration

The simulation system consists of a diamond tip sliding against a DLC film, as shown in Fig. 3.1b. The sliding is realized by setting the diamond tip with a velocity v_s along the x -direction and a normal load F_n along the z -direction. The periodic conditions of the system are set along the x and y -directions.

The diamond tip that is a half-sphere with a radius of $15 \text{ \AA}$ is located in the middle of the DLC film along the y -direction. Moreover, this tip is set as a rigid body to keep its geometry unchanged during the simulation. The DLC film has dimensions of $237 \times 42 \times 26 \text{ \AA}^3$. Such film is divided into three layers along the z -direction according to their functions. The bottom layer with a thickness of $3 \text{ \AA}$ is always fixed to keep the film static. The middle layer with a thickness of $3 \text{ \AA}$ is coupled to a thermostat that keeps a constant temperature at 300 K by recalling the velocities of atoms. The rest that is the top layer keeps in contact with the diamond tip. Atoms in the top layer are free to move according to the forces of

their neighbors. More details of the simulation model can refer to our previous studies (Bai *et al.*, 2015; Bai *et al.*, 2016a).

Fig. 3.1. (a) flowchart of the simulation processes and (b) configuration of the friction model with a front view.

The DLC film is obtained via a melt-quenching procedure that is commonly employed to obtain amorphous structures. The procedure is comprised of four steps. Firstly, a crystalline diamond block with periodic conditions along all the x , y and z -directions is generated in a canonical NVT ensemble at 300 K. The temperature of the block rapidly increases from 300 K up to be above the melting point of crystalline diamond. The high temperature can easily melt the crystalline diamond block. Secondly, the temperature of the block is kept constant for about 20 ps to make the liquid carbon thermostatically equilibrated. Thirdly, the temperature decreases to 300 K with a rate of 1000 K/ps which allows proper relaxations of the amorphous structure. Finally, the residual stress in the

block is eliminated by relaxing its amorphous structure in an isothermal–isobaric NPT ensemble at 300 K. More details of the procedure can refer to previous studies (Sha *et al.*, 2013; Bai *et al.*, 2016a; Bai *et al.*, 2016b).

3.1.2. Simulation methods

As discussed in Chapter 2, the LAMMPS is used to conduct the MD simulation (Plimpton, 1995). The interactions between carbon atoms in the simulation are described by the AIREBO potential (Stuart *et al.*, 2000). Particularly, the long-range dispersive interactions are neglected, since the diamond tip is easily bonded with the DLC film and thus the short-range interactions determine the friction and wear behaviors of the film and its sp^3 - sp^2 transitions (Ma *et al.*, 2011). The time step of the simulation is set as 1 fs, and their molecular visualizations are conducted by using the software OVITO (Stukowski, 2009).

Prior to the friction simulation, a load F_n (2.9, 29, 145, 203, 246.5 or 290 nN) is maintained on the diamond tip to make it in contact with the DLC film and the contact is to be equilibrated within 30 ps. Following the contact equilibration, the diamond tip starts to slide with a velocity v_s (1, 2, 4 or 8 Å/ps) to realize the friction simulation and the sliding lasts about 160 ps. The surface roughness of the DLC film is generated by tailoring its morphology based on the combination of two sine functions that are $z = A\sin(2\pi x/T)$ and $z = A\sin(2\pi y/T)$ (Hu and Martini, 2015), where A is the amplitude and T is the period. In the simulation, T is always set as 10 Å and A is changed to obtain various surface morphologies which correspond to the root mean square roughness R_q of 0.707, 1.414, 2.122, 3.537 and 4.952 Å, respectively. In particular, the v_s is set as 1 Å/ps in the cases

with different F_n , and the F_n is kept as 246.5 nN in the cases with various v_s . The F_n and v_s are set as 246.5 nN and 1 Å/ps in the cases with different surface roughness, respectively.

Table 3.1. Variables in the simulation and their values.

Variables	Values
F_n (nN)	2.9, 29, 145, 203, 246.5, 290
v_s (Å/ps)	1, 2, 4, 8
R_q (Å)	0.707, 1.414, 2.122, 3.537, 4.952

In the simulation, the friction force F_f is evaluated by calculating the tangential forces of the diamond tip in the x -direction. The temperature of atoms is calculated according to its correlation with their kinetic energies (Rapaport, 2004). Hybridizations states of carbon atoms in the DLC film are characterized by calculating their coordination number which represents the number of the nearest neighbors within a cutoff length of 2.0 Å corresponding to the position of first minimum in the radial distribution function of amorphous carbon systems described by the AIREBO potential (Chen *et al.*, 2015). The fourfold, threefold and twofold carbon atoms are regarded as sp^3 , sp^2 and sp bonded, respectively (Sha *et al.*, 2013).

The number of worn atoms N in MD simulation has been only evaluated in few studies (Zhong *et al.*, 2013; Hu and Martini, 2015). According to the fact that the wear of materials commonly refers to the loss of their volume or mass at the macroscale, Zhong *et al.* (2013) defined the worn atoms as those removed from substrates. Such definition is improper to characterize the wear at the nanoscale, since the nanowear includes not only the removed

materials but also all erosions or sideways displacements of atoms from their original position (Stachowiak and Batchelor, 2013). In particular, this definition is inaccurate to calculate the number of worn atoms at a small load, because in this case these worn atoms are still bonded to the substrate instead of removed from it.

Recently, Hu *et al.* (2015) qualified worn atoms by evaluating their displacements. Such qualification can avoid many limitations of the wear definition discussed above. Therefore, this qualification is employed in this study.

For a mild wear which is determined by atom-by-atom attritions (Bhaskaran *et al.*, 2010), a worn atom can be conveniently defined as the one whose bonds with its nearest neighbors break during the friction process. Such breaks can be caused when the displacement of the atom is larger than two-bond length. Since the maximum length of a C-C bond in the DLC films is about 2 Å which corresponds to the first minimum in their radial distribution functions, the length of 4 Å can be chosen as the displacement criteria to estimate the worn atoms. This criterion is also useful to estimate the severe wear of materials that is determined by their plastic deformations. Previous studies defined the worn atoms as those removed from the wear track (Zhong *et al.*, 2013; Xu *et al.*, 2015). It is evident that these atoms have displacements larger than 4 Å. Therefore, the present criteria can provide more information of wear than the method employed in the literature (Xu *et al.*, 2015; Zhong *et al.*, 2013).

It should be noticed that the atom displacements larger than 4 Å may also be caused by the elastic deformation of DLC films under the indentation of the diamond tip. Such deformation can cause errors in the calculation of the worn atoms. In order to eliminate these errors, the calculation of the worn atoms is conducted after the completion of the

wear process. In this case, the elastic deformation of the DLC films has recovered and hardly influences such calculation.

3.2. Results and discussions

3.2.1. Contact interface

Fig. 3.2a shows the effect of F_n on the number of bonds n_b at the contact interface between the diamond tip and the DLC film prior to the sliding of the diamond tip. The n_b increases with the F_n . It is noticed that the increase rate of the n_b is high at a small F_n but decreases at a large F_n . The variation of this increase rate is due to the presence of the interfacial adhesion, which keeps consistent with observations in the models of JKR and DMT (Szlufarska *et al.*, 2008). Moreover, it should be noticed that when the F_n approaches to zero, the n_b is nonzero. This nonzero n_b indicates the existence of bonds at the contact interface even at the zero F_n , agreeing well with results in the literature (Mo *et al.*, 2009; Szlufarska *et al.*, 2008).

The sliding of the diamond tip highly influences the n_b . Fig. 3.2b shows that the n_b increases largely with the F_n and the increase rate always keeps high. Moreover, the n_b also becomes large during the sliding regardless of the F_n . Therefore, it is demonstrated that the sliding significantly changes the contact configuration between the diamond tip and the DLC film.

The contact configurations (Fig. 3.3) prior to the sliding of the diamond tip show that the large n_b at a large F_n is caused by the penetration of the diamond tip into the DLC film. These bonds distribute symmetrically around the diamond tip.

Fig. 3.2. Number of bonds n_b at the contact interface with different loads F_n (a) before and (b) during the sliding.

During the sliding of the diamond tip, a large number of bonds are formed at the contact interface, and these bonds distribute asymmetrically around the diamond tip. Such asymmetrical distribution highly depends on the F_n . At a small F_n , a tail formed by the C atoms of the DLC film follows the diamond tip. However, at a large F_n , a chip is formed in front of the diamond tip due to its penetration into the DLC film. The different distributions demonstrate the presence of diverse tribological behaviors. The tail indicates the occurrence of adhesive friction and wear, while the chip formation shows the

occurrence of abrasive friction and wear. It is found that the chip attaches to the diamond tip and highly increases the n_b , which is responsible for the high increase rate of n_b during the sliding (Fig. 3.2b).

Fig. 3.3. Evolution of the contact between the diamond tip and the DLC film with the load of (a) 2.9 nN and (b) 290 nN when the sliding distance L increases from 0 Å to 100 Å.

3.2.2. Load effect

The relation of F_f with F_n is present in Fig. 3.4a. The F_f increases as a nonlinear function of F_n instead of its linear function as observed in the literature (Mo *et al.*, 2009). This may be due to the fact that the present F_n (about 290 nN) is larger than that (about 100 nN) in the literature (Mo *et al.*, 2009). The F_f at such a small F_n only exhibits a linear

proportion instead of a nonlinear function. Moreover, the F_f at the zero F_n is still quite high. This high F_f is due to the nonzero n_b in this case, which keeps consistent with results in the previous study (Mo *et al.*, 2009).

The F_f also increases with the n_b (Fig. 3.4b). Due to the friction transition from adhesive to abrasive, the increase of F_f may be different from the Bowden-Tabor model which shows a linear dependence of adhesive F_f on n_b . Since the adhesive friction occurs at a small F_n in the present study (Fig. 3.3a), the proportional constant c between F_f and n_b can be calibrated at a small F_n . The function $F_f = cn_b$ of the Bowden-Tabor model is plotted as the dotted line in Fig. 3.4b. It is evident that at a large F_n the value on this line is higher than the F_f in the MD simulation, indicating that the Bowden-Tabor model is inapplicable for the abrasive friction of the DLC film.

To explore more details of the inapplicability of the Bowden-Tabor model, comparison between this model and the MD simulation is further conducted through the friction process, as shown in Fig. 3.4c. At a small F_n , the Bowden-Tabor model keeps consistent with the MD simulation through the whole friction process. At a large F_n , the consistence is present during the running-in period (the distance $L < 50 \text{ \AA}$), but F_f in the MD simulation decreases in the following sliding. It is noticed that the disappearance of the consistence is initiated by the formation of the chip in front of the diamond tip.

The friction reduction after the formation of chip can be elucidated by analyzing the microstructures at the contact interface (Fig. 3.5). At a small F_n , the sliding of the diamond tip only moves few atoms of the DLC film. Therefore, the sliding happens at the contact interface and the F_f is proportional to the interfacial adhesion strength which is linearly related to n_b . As a result, the F_f exhibits a linear dependence on the n_b .

Fig. 3.4. (a) Load F_n dependence of friction force F_f and (b) its correlation with the number of bonds n_b at the contact interface; (c) comparison of the MD simulation (solid line) and the Bowden-Tabor model (dashed or dotted line). The prediction of this model is also plotted as the dotted line in (b).

At a large F_n , however, the diamond tip moves many C atoms of the DLC film in front of or beneath the tip. These moving C atoms actually form the transfer layer, which attaches to the diamond tip and isolates it from the film. As a result, the sliding occurs as a relative movement between the transfer layer and the film.

Fig. 3.5. Contours of atom displacement with the load of (a) 2.9 nN and (b) 290 nN during stable friction. The large atoms belong to the diamond tip, and the small atoms are those of the DLC film.

Since the sliding happens as the internal friction of the DLC film, the F_f in this case is determined by the rheological properties of this film instead of the n_b . The rheological properties of amorphous solids highly depend on their microstructures and temperature (Alexander, 1998; Chattoraj *et al.*, 2010). The microstructures of the DLC film can be

characterized by the fraction of sp^2 atoms f_1 , as shown in Fig. 3.6a. The f_1 highly increases with the F_n .

Fig. 3.6b further shows that the friction temperature T_f is largely raised at a large F_n . The large f_1 of the DLC film commonly indicates its small elastic modulus (Savvides and Bell, 1993), and the high T_f of such film can further soften its microstructure and degrade its mechanical properties (Ferrari *et al.*, 1999). As a result, the DLC film with a large F_n is easy to shear and thus its F_f is highly reduced.

It has been discussed that the Bowden-Tabor model can only predict the F_f in the running-in period which is the stage before the formation of the transfer layer (Fig. 3.4c). This indicates that even in a same friction process the friction mechanism also evolves. The validation of the Bowden-Tabor model is due to the low T_f and a small f_1 in the running-in period. In this case, the bonds between the diamond tip and the DLC film hardly cause the collective movement of film atoms to form transfer layer. As a result, the sliding of the diamond tip happens at the contact interface and thus the F_f is linearly proportional to the n_b .

The invalidation of the Bowden-Tabor model for the abrasive friction in this study is different from results in the literature (Eder *et al.*, 2015). It has been reported that this model can well predict the abrasive friction of iron at the nanoscale. This validation of the model may be due to the weak interfacial adhesion because of van der Waals interactions at contact interfaces (Eder *et al.*, 2015). This weak adhesion hardly induces the formation of transfer layers, and thus the sliding still happens at the contact interface.

The significance of the transfer layer on the friction reduction of DLC films keeps consistent with many experimental studies (Bai *et al.*, 2011; Wang *et al.*, 2013). It is found

that such layer is commonly sp^2 -dominant and exhibits easy-shear properties. Since this layer can efficiently prevent the direct contact between the film and its counterpart, the sliding actually happens as the relative movement of the transfer layer and the film, leading to the friction reduction.

Fig. 3.6. (a) Evolution of the fraction of sp^2 atoms f_1 in the DLC film with sliding distance L , and (b) the dependence of average friction temperature T_f on the load F_n .

The present study demonstrates that the increase of F_n can change the friction mechanisms. At a small F_n , F_f linearly depends on n_b . At a large F_n , such linear dependence is absent due to the formation of the transfer layer which promotes the sliding inside the DLC film.

In the previous simulation studies of nanotribology (Mo *et al.*, 2009; Kim and Kim, 2009; Eder *et al.*, 2015), the number of contact bonds as well as the real contact area are commonly responsible to the determination of the F_f . In the experimental studies of macroscale tribology of DLC films (Erdemir and Donnet, 2006; Liu *et al.*, 1996b), it is found that their friction reduction at a large F_n is due to their high fraction of sp^2 atoms. Present study shows that both of these friction mechanisms are addressed together in the nanotribology of DLC films.

The load F_n influences not only the friction force F_f of the DLC film but also its wear volume which is represented by the number of worn atoms N , as shown in Fig. 3.7a. A large F_n significantly increases the N . In particular, the increase rate of N is the wear rate k . At a large F_n , the k is large in the running-in period but decreases after the formation of the transfer layer. The change of the k keeps consistent with the variation of the F_f (Fig. 3.4c). Therefore, it can be seen that the layer can efficiently reduce both the F_f and k . After the formation of the transfer layer, the k stabilizes.

The wear performance of DLC films can be further studied by comparing their stable k at different F_n (Fig. 3.7b). The k increases as a quadratic function of the F_n , which is different from their linear relation in literature (Hu and Martini, 2015). The difference is attributed to that the small F_n in the previous study determines that the wear is dominated by adhesion.

Since wear is essentially caused by the friction, the relation between k and F_f is commonly significant to understand the tribological mechanisms of the DLC film. Fig. 3.8a shows that the k quadratically depends on the F_f . This dependence can be explained from the point of energy dissipation (Singer, 1994; Hu *et al.*, 2013). When the F_f is small, the friction energy is mostly dissipated by phonon vibrations and heat diffusions and thus only a few amount of such energy is left to cause worn atoms.

Fig. 3.7. (a) Evolution of the number of worn atoms N in DLC films with the sliding distance L , and (b) the dependence of the wear rate k on load F_n .

When the F_f is large, a large amount of friction energy is dissipated by the formation of worn atoms. Moreover, the friction energy dissipated by heat diffusions causes high friction temperature which softens the DLC film by inducing its structural transformations and thus reduces its wear resistances. As a result, the k increases faster than a linear function of F_f .

The wear highly depends on the interfacial adhesion strength which is proportional to n_b . This dependence is also the fundamental for Archard law to predict the macroscale wear (Archard, 1953). The comparison between the Archard law and the present simulation is significant to demonstrate that whether this macroscale law still prevails at the nanoscale, as shown in Fig. 3.8b. The Archard law that is initially developed to predict the adhesive wear can employ the calculation of $V = c_1 AL$, where V is the wear volume, c is the proportional constant, A is the contact area and L is the sliding distance. By differentiating the V to x and correlating A with n_b , the wear rate k_1 in the Archard law can be obtained with the form of $k_1 = c_2 n_b$. The constant c_2 can be calibrated by using the results with a small load F_n of 0.29 nN, since at such F_n the wear is purely adhesive wear.

The difference between the Archard law and the present simulation is denoted as Δk . It can be seen that Δk is almost zero when the n_b is smaller than a critical value of 100. However, the Δk highly increases when the $n_b > 100$. This critical n_b corresponds to a F_n of 90 nN (Fig. 3.2c). Therefore, it is demonstrated that the wear with $F_n < 90$ nN is adhesive and can be determined by Archard law. However, the wear with $F_n > 90$ nN highly increases and is contributed by both the adhesion and abrasion.

Fig. 3.8. (a) Dependence of the wear rate k of DLC films on their friction forces F_f ; (b) comparison between MD simulation and the Archard law in terms of the relation of k with the number of contact bonds n_b ; (c) the sliding depth h dependence of the difference between MD simulation and the Archard law.

The abrasive wear can be further evaluated by relating Δk with the sliding depth h , as shown in Fig. 3.8c. The Δk increases as a quadratic function of the h . This keeps consistent with the calculation of abrasive wear at the macroscale (Bhushan, 2013a) and thus indicates the validation of macroscale abrasive law at the nanoscale.

The wear analysis above shows that the nanoscale wear can still be evaluated by using the macroscale wear laws. The adhesive wear rate has a changed expression of $k_1 = c_2 n_b$, and the abrasive wear rate can be denoted by $k_2 = c_3 h^2$. Therefore, the total wear rate at the nanoscale can be obtained as $k = c_2 n_b + c_3 h^2$, where c_2 and c_3 are proportional constants.

The load-induced transition of wear keeps consistent with experimental results in the literature (Ma *et al.*, 2003; Zhang *et al.*, 2008; Charitidis, 2010). It has been reported that mechanisms of nanoscale wear highly depend on the load. At a small load, the DLC film mainly experiences the elastic deformation, and the wear mechanisms are dominated by the adhesion (Yoon *et al.*, 2005). When the load is larger than a critical value, the DLC film undergoes a mixed elastic-plastic deformation, and in this case the wear is dominated by both the adhesion and the ploughing (Liu and Bhushan, 2002).

The critical load in the present study is about 90 nN which can cause an average contact stress of about 50 GPa. This stress is within the hardness range of DLC films. Therefore, it is demonstrated that the critical load at which transition of wear happens corresponds to the surface hardness of the DLC film (Bhushan and Kulkarni, 1996). The literature predicted that microcomponents under a light load may experience ultralow friction and near-zero wear (Bhushan and Kulkarni, 1996). The prediction is absent in the present study. This is because tests in the literature are commonly conducted in the ambient

conditions. As a result, the interfacial adhesion under a small load is highly reduced because of interface passivations by air molecules.

In particular, the previous study shows that the mechanical properties of materials contribute less to their adhesive wear and friction (Zhang *et al.*, 2008). This agrees well with the validation of the Bowden-Tabor model and the Archard law at a small F_n in this study.

3.2.3. Velocity effect

Besides the load F_n , the velocity v_s can also influence the tribological behaviors of DLC films, as shown in Fig. 3.9a. The friction force F_f decreases with v_s . This decrease keeps consistent with the macroscale and nanoscale experiment observations in the literature (Hauert, 2004; Erdemir and Donnet, 2006; Tambe and Bhushan, 2005c; Tambe and Bhushan, 2005a).

Fig. 3.9b shows that the n_b also decreases with the v_s . The decrease of the n_b is attributed to that with a high v_s large resistant forces are generated by the DLC film to resist the penetration of the diamond tip. As a result, the sliding depth h decreases with the high v_s and causes the decrease of the n_b , thus resulting in the friction reduction.

The v_s can also influence the relation between F_f and n_b , as shown in Fig. 3.9c. The F_f increases with the n_b , which is similar to the observations for the cases with different F_n . However, a nonlinear relation exists between the n_b and the F_f . The increase rate of the F_f is high for a small n_b but decreases for a large n_b . The change of the increase rate of the F_f is due to the structural responses of the DLC film to the v_s .

Fig. 3.9. Effect of sliding velocities v_s on (a) the friction force F_f , (b) the number of bonds n_b at the contact interface and (c) the relation between the F_f and the n_b .

The high v_s represents a high strain rate. At such rate, the DLC film exhibits high elastic modulus, because the film has insufficient time to release the external stress by experiencing the structural transformation. As a result, the film exhibits more rigid behaviors with the high v_s and shows a high increase rate of the F_f .

The v_s significantly influences the wear behaviors of DLC films, as shown in Fig. 3.10a. The wear rate k of the film decreases with the v_s . This decrease of the k keeps consistent with the decrease of the h . The varied wear behavior closely relates with n_b , as shown in Fig. 3.10b. The k increases as a nonlinear function of the n_b , i.e., the increase rate of the k is high for small n_b while becomes small for large n_b . This nonlinear dependence of k on the n_b is also attributed to the structural responses of the DLC film to different v_s .

The effect of v_s on the tribological behaviors of DLC films has been studied in the literature (Liu and Bhushan, 2002; Tambe and Bhushan, 2005c). The friction reduction is observed at a large v_s and caused by the formation of a graphitic transfer layer with easy-shear properties that are due to the phase transformation of DLC films (Kim and Kim, 2009; Tambe and Bhushan, 2005a). This friction reduction mechanism is verified in the present study. It is found that the high v_s can induce a high T_f which causes a high level of graphitization of the transfer layer. The high graphitization level is beneficial for the occurrence of shear.

The present study also shows that the high velocity can reduce the friction and wear by inducing a smaller sliding depth of the diamond tip and thus reducing the formation of bonds between the tip and the DLC film. This friction reduction mechanism is seldom reported in the literature (Tambe and Bhushan, 2005c; Tambe and Bhushan, 2005a; Tao and Bhushan, 2007; Kim and Kim, 2009). This may be because the velocity in these studies

which commonly employ atomic force microscope to conduct friction tests is quite small. As a result, the reduction of the sliding depth caused by the small velocity is negligible and hardly measured.

Fig. 3.10. (a) Effect of sliding velocities v_s on the wear rate k and (b) its relation with the bond number n_b at the contact interface.

3.2.4. Surface roughness effect

The surface roughness is another significant factor to determine the tribological behaviors of materials. Its effect on the friction force F_f and wear rate k of DLC films is

given in Fig. 3.11a-b. With the increase of the root mean square roughness R_q , the F_f increases monotonically while the k firstly decreases to a minimum value and then increases. The presence of the minimum k indicates that the nanotribology is different from the macrotribology in which a high surface roughness commonly causes large F_f and k .

The surface roughness can also influence the adhesion strength at the contact interface by influencing the real contact area (Jacobs *et al.*, 2013; Ryan *et al.*, 2014). Fig. 3.11c shows that n_b firstly decreases to a minimum value and then increases. The decrease of n_b at a small R_q indicates the decrease of the adhesion strength. The increase of n_b at a large R_q is attributed to that the surface asperities in this case easily yield during the friction process and become chips attaching to the diamond tip.

The varied trend of n_b is similar to that of the k . This demonstrates that the increase of surface roughness can induce transitions of wear from adhesive to abrasive. This demonstration keeps consistent with results in the literature (Zhang and Tang, 2013; Gnecco *et al.*, 2002; d'Acunto, 2004). These studies reported that the increase of the surface roughness can highly suppress the adhesive wear but promote the abrasive wear. Hu *et al.* (2015) even proposed an equation to combine both the adhesive and abrasive wear in term of R_q , that is $V = b_1(F_n + b_2)LR_q^{-1} + b_3(F_n + b_4)LR_q$, where V is the wear volume, b_1 , b_2 , b_3 and b_4 are constants. This equation shows that V and k surely have a minimum value when the surface roughness increases, thus validating the results in the present study.

However, the physical mechanisms for the presence of the minimum k still lack detailed explanations. Since such minimum k appears for both the DLC film in the present

study and other materials in the literature (Hu and Martini, 2015), it is evident that the mechanisms responsible for this appearance should be attributed to common properties of materials.

It is found that the presence of the minimum k can be interpreted by the dependence of wear performances of materials on their mechanical modulus. The adhesive wear of materials is dominated by their shear modulus (Bera, 2013) while their abrasive wear closely correlates with their Young's modulus (Harrison *et al.*, 1979). For homogeneous materials, their Young's modulus is larger than their shear modulus due to the relation between these modulus in isotropic Hooke's law (Shames, 1997). As a result, when the roughness-induced transition of wear from adhesive to abrasive happens, materials become difficult to be worn due to their high Young's modulus. In this case, the decrease of the adhesive wear plus a slight increase of the abrasive wear induce the presence of the minimum k .

For DLC films, their Young's modulus is much higher than their shear modulus. This is because the structures of these films are sensitive to their shear deformations (Gogotsi *et al.*, 1998; Gilman, 1995; Car, 1996; Gogotsi *et al.*, 1999). Bai *et al.* (2016) reported that the shear strains can highly promote the propagation of sp^2 clusters in DLC films and thus degrade their mechanical properties. Therefore, the higher Young's modulus of these films further ensures the presence of their minimum k .

The increase of the k with a large R_q is due to the fact that the wear in this case is dominated by the abrasive wear. The asperities of the rough surface of DLC films become worn atoms under the sliding of the diamond tip, thus highly increasing the k .

Fig. 3.11. Effect of surface roughness of the DLC film on (a) its friction force F_f , (b) wear rate k and (c) number of bonds n_b at the contact interface.

It is noticed that the F_f always increases even when the minimum k is present. The increase of F_f is also due to the high Young's modulus of the DLC film. This high modulus can ensure that the surface asperities of the film can largely resist the sliding of the diamond tip and thus increase the F_f .

The effect of surface roughness has been widely studied. The macroscale surface roughness can increase the friction and wear due to the interlocking between the surface asperities (Erdemir and Donnet, 2006). At the nanoscale, a large surface roughness can also cause the increase of the friction and wear due to the occurrence of ploughing (Ruan and Bhushan, 1994; Bhushan, 2005; Gupta *et al.*, 1994). These observations keep consistent with the large increase of F_f and k for a large R_q in this study.

The minimum k caused by the surface roughness is never reported in the experimental studies. This is due to the fact that the surface roughness corresponding to the minimum k is hardly obtained during the fabrication of DLC films in experiment (Peng *et al.*, 2001; Moseler *et al.*, 2005). However, the presence of the minimum k still demonstrates the non-monotonic effect of the surface roughness and may provide a guidance for the wear resistance improvement of DLC films by tailoring their morphologies.

3.3. Summary

The nanotribological behaviors of DLC films are studied by MD simulation. The friction mechanisms of the film highly depend on the load. At a small load, the friction is determined by the adhesion force and thus keeps consistent with the Bowden-Tabor model. However, at a large load, the friction is reduced by the formation of graphitic transfer layer and deviate from the Bowden-Tabor model. Such reduction is due to the fact that the

transfer layer is easy to shear because of the high fraction of sp^2 atoms and the high friction temperature. The wear mechanisms of the DLC film also exhibit the load dependence. At a small load, the film wear is almost pure adhesion and thus follows the Archard law. At a large load, the wear is contributed by both the adhesion and abrasion, which keeps consistent with the experimental results in the literature. The effects of the velocity and surface roughness of the DLC film are also investigated. It is found that the high velocity can reduce the friction force and wear rate by reducing the number of bonds formed between the tip and the film. The large surface roughness can increase the friction force but cause a minimum wear rate by causing the transition of wear from adhesive to abrasive.

Chapter 4. Tribological behaviors of DLC films under three-body contact

The tribological behaviors of DLC films are highly influenced by third particles which may be formed during the wear process or come from the environment. Such influence is hardly studied in experiment due to the fact the difficulty to observe the movement of the third particle and the evolution of contact interfaces between the DLC films. This chapter investigates the effects of the third particle by considering its shape and size, the load and velocity. The simulation results are helpful for the understanding of the tribological mechanisms of the DLC films under a three-body contact condition.

4.1. Modelling

4.1.1. Atomistic configuration

The simulation system consists of two relatively sliding DLC films and a particle located at the interface between them (Fig. 4.1). The relative sliding is realized by setting the upper and lower film with a velocity of $0.5v_s$ and $-0.5v_s$ along the x -direction, respectively. During the sliding, a load is applied by maintaining a force F_n to the upper film along the y -direction. The periodic boundary conditions of the system are set along its x and z -directions.

The particle has the diamond crystalline structure and is set as a rigid body to avoid its wear during the simulation. The spherical, cubic and cuboidal particles are generated to study the effect of their shapes. The spherical particle has a radius r of 12 Å. The cube and cuboid particles have dimensions of $20 \times 20 \times 20$ Å³ and $40 \times 20 \times 20$ Å³, respectively. A small spherical particle with a r of 10 Å is also generated to study its size effect.

The DLC films in the simulation are obtained by the melt-quenching procedure discussed in Chapter 3 and have dimensions of $120 \times 25 \times 60 \text{ \AA}^3$. Each of the films is defined into three different layers from the contact interface to subsurface along the y -direction: Newtonian, thermostatic and rigid layers. The Newtonian layer with a thickness of $18 \text{ \AA}$ is in contact with the diamond ball and contains atoms that are free to move under the forces of their neighbors. The thermostat layer with a thickness of $3 \text{ \AA}$ keeps a constant temperature of 300 K to dissipate the friction energy. The rigid layer with a thickness of $4 \text{ \AA}$ can help to maintain velocity. Moreover, the rigid layer in the upper film is set to take F_n along the y -direction while that in the lower film is prohibited to move along the same direction. More details of the simulation model can refer to our previous studies (Bai *et al.*, 2015; Bai *et al.*, 2016a).

Fig. 4.1. Atomic configuration of the simulation model with (a) the front view and (b) the side view. The model consists of two relative sliding DLC films with a third particle located between them.

4.1.2. Simulation methods

The atomic interactions are described by the Tersoff potential due to its efficiency in modelling large systems (Stuart *et al.*, 2000). The time step of the simulation is set as 1 fs, and their molecular visualizations are conducted via the software OVITO (Stukowski, 2009).

Prior to the friction simulation, a load F_n (7.8, 39.2, 78.4, 117.6 and 196 nN) is applied to the upper DLC film to cause contact between the particle and the films. The contact is equilibrated within in 30 ps. After the equilibration period, the films start to relatively slide and the relative velocity v_s is set as 2, 5, 7 and 10 Å/ps, respectively. In the cases with different F_n , v_s is kept as 2 Å/ps. The F_n is set as 196 nN for the cases with various v_s . In the cases with different shapes and sizes of particles, the F_n and v_s are set as 196 nN and 2 Å/ps, respectively. The total sliding distance is always kept as 300 Å. Hence, the sliding tracks overlap in each simulation due to the periodic condition in the x -direction. The overlapping hardly changes the wear rate and the friction force, thus indicating that this study actually investigates the phenomenon in the running-in period of wear tests in experiments.

Table 4.1. Variables in the simulation and their values.

Variables	Values
F_n (nN)	7.8, 39.2, 78.4, 117.6, 196
v_s (Å/ps)	2, 5, 7, 10
r	10, 12

The friction force F_f is calculated by summing up the forces of atoms in the rigid layer of the upper DLC film along the x -direction. The number of worn atoms N is simply calculated by evaluating their displacements based on the criteria discussed in Chapter 3 (Hu and Martini, 2015). The wear rate k is calculated as $k = N / L$, where N is the number of worn atoms and L is the sliding distance. The average k of two DLC films is employed to indicate their wear performance. The hybridization states of C atoms are also evaluated by calculating their coordination number, as discussed in Chapter 3 (Bai *et al.*, 2016b). The temperature of atoms is calculated according to its correlation with their kinetic energies (Rapaport, 2004).

4.2. Results and Discussions

4.2.1. Contact interface

The load effect is considered in the cases with a spherical particle. The sliding configuration in Fig. 4.2 shows that many covalent bonds are formed at the interface between the particle and the DLC films, indicating that the sticky DLC networks attach to the spherical particle. These bonds cause the strong interfacial adhesion and thus influence the movement of the particle that can be evaluated by calculating its mass-center velocity. It is found that with such strong adhesion the spherical particles undergo pure rolling in the friction process. This is consistent with observations in the literature (Sun *et al.*, 2013a). The sliding configuration demonstrates that the friction and wear of the DLC films with a rolling third particle may closely relate with adhesion.

Fig. 4.2. Atomic configuration of the friction process with a spherical particle.

4.2.2. Load effect

When the load F_n increases, the F_f of the DLC films increases (Fig. 4.3a). The increase of F_f is because a large F_n can penetrate the particle into the films and thus increase the interfacial adhesion strength. This can be verified by the increase of the number of bonds n_b at the contact interface with the F_n (Fig. 4.3b). The n_b is the total number of bonds formed between the particle and the films, due to the fact that all these bonds contribute to the interfacial adhesion.

Recent theoretical studies showed that at the nanoscale F_f is linearly proportional to n_b which represents the real contact area, indicating the validation of the macroscale Bowden-Tabor model at the nanoscale (Mo *et al.*, 2009; Eder *et al.*, 2015). The configuration in Fig. 4.2 has shown that the friction and wear highly depend on the interfacial adhesion due to the pure rolling of the particle. Therefore, the F_f in the three-body contact condition should also be closely related with n_b . In this case the relation between the F_f and n_b in the three-body contact condition is firstly studied, as shown in Fig. 4.3c. It can be seen that this relation can be regarded as linear with a small n_b but becomes nonlinear when the n_b is large. Such relation evolution indicates that at a small load F_n the friction is simply

determined by the interfacial adhesion strength while at a large F_n the friction is dominated by both the adhesion and other factors.

At a large F_n , the spherical particle highly penetrates into DLC films, which can be verified by the increase of the sliding depth of the spherical particle (Fig. 4.4a). As a result, the large deformations of the films can be caused by the spherical particle and highly resist their sliding, thus increasing the F_f . This keeps consistent with results in the literature (Lee *et al.*, 2009). It has been reported that the rolling friction can be highly generated by the energy dissipation involved in the deformation of materials (Miura *et al.*, 2003). Sun *et al.* (2013a) further found that the ploughing is a significant factor in determining the three-body friction and wear within the elastic-plastic regime. Bhushan *et al.* (2004) also reported that the three-body friction is caused by both the adhesion and plastic deformation which represents the ploughing. Therefore, it is evident that the nonlinear relation between the F_f and n_b at a large F_n is caused by the plastic deformation of the films.

Moreover, it is noticed that the F_f is still high when $F_n = 0$. The high F_f is due to the presence of interfacial adhesion at the zero F_n and indicates that the F_f in the three-body contact condition has a direct proportion with the n_b instead of F_n . This keeps consistent with observations in the previous studies under the two-body contact condition (Mo *et al.*, 2009; Eder *et al.*, 2015).

The load F_n also significantly influences the wear performance of DLC films, as shown in Fig. 4.4b. The wear rate k increases with the F_n . Since wear induced by adhesion is proportional to the real contact area that can be represented by n_b , the relation between the k and n_b is meaningful in the investigation of adhesive wear. Fig. 4.4c shows that the relation can be regarded as linear at a small n_b but becomes nonlinear when the n_b is large.

The linear relation is due to the fact that the wear at a small F_n is determined by the interfacial adhesion while the nonlinear relation is attributed to the plastic deformation of the films when the F_n is large.

It is noticed that the k is nonzero when $F_n = 0$. Such nonzero k is different from results in the literature. Zhang *et al.* (1998) reported that a negligible wear can be obtained at a small load that only induces elastic deformation of material surface. This neglected wear should be due to the von der Waals interactions at the sliding interface (Zhang and Tanaka, 1998). In the present study, however, the interfacial forces caused by the strong covalent C-C bonds are quite high and thus can induce worn atoms even when $F_n = 0$.

The contribution of the deformation of DLC films to their wear can be examined by analyzing the sliding depth h of the particle. Fig. 4.4a shows that at the maximum F_n the h approaches to 5 Å which is higher than the displacement criteria for the definition of worn atoms. Because the surface of the films deforms locally, many atoms are worn by such huge deformation even without the sliding. This keeps consistent with the worn atoms caused by plastic deformation in the literature (Hu and Martini, 2015; Bhushan and Nosonovsky, 2004; Lee *et al.*, 2009).

It is noticed that the wear of DLC films caused by their deformations is neglected when the F_n is small. In this case, the wear is determined by adhesion and can be predicted according to the proportion between k and n_b . This proportion is commonly obtained in the two-body contact condition (Archard, 1953). Validation of this proportion indicates that it is the essence of the adhesion wear regardless of in the two-body or three-body contact conditions.

Fig. 4.3. Effect of loads F_n of the DLC film on (a) its friction force F_f , (b) the number of contact bonds n_b and (c) the relation F_f between n_b .

Fig. 4.4. Effect of loads F_n of the DLC film on (a) its wear rate k , (b) the sliding depth of the spherical particle h and (c) the relation between k and h .

4.2.3. Velocity effect

Besides the load, the velocity v_s also highly influences the tribological behaviors of DLC films, as given in Fig. 4.5a. The friction force F_f increases with the v_s . This is different from the observations in the two-body contact conditions. It has been observed that the F_f commonly decreases with the v_s due to the fact that a high v_s can largely increase the friction temperature and reduce the n_b (Bai *et al.*, 2016a). However, in the present study the n_b almost keeps constant when the v_s varies (Fig. 4.5b). This constant n_b seems to conflict with the increase of F_f , indicating the existence of a unique friction mechanism.

The friction mechanism can be understood by analyzing the friction configurations, as shown in Fig. 4.6. When the v_s increases, although the n_b is constant, many networks of DLC films attach to the particle. These networks can highly resist the sliding of the film and thus largely increase the F_f . The attaching of these networks to the particle is due to the structural response of the DLC films to v_s . With a high v_s which indicates a high strain rate, the micro-cracks in the DLC films have insufficient time to be initiated and propagate, thus increasing their yield strains. This keeps consistent with the mechanical theory of solids (Hutchinson, 1977) and has also been proved by our tensile simulations of the DLC films. As a result, more networks can attach to the third particle at a high v_s , leading to the increase of F_f .

The wear performances of DLC films are also influenced by the v_s , as shown in Fig. 4.7a. The wear rate k decreases with the v_s . This trend agrees with the decrease of the sliding depth h at a high v_s . The decrease of the h indicates the suppressed deformation of the films and thus contributes to the decrease of k by highly reducing ploughing.

Fig. 4.5. Effect of velocities v_s of the DLC film on (a) its friction force F_f and (b) the number of contact bonds n_b .

Fig. 4.6. Atomic configuration with different velocities v_s : (a) $2 \text{ \AA}/\text{ps}$ and (b) $10 \text{ \AA}/\text{ps}$.

Effect of v_s on the adhesive wear also contributes to the reduction of k . Fig. 4.8 shows that at a high v_s many DLC networks attach to the spherical particle. The relative sliding between the films largely deform their networks. When the strain energy is high enough to break the bonds between these networks and the spherical particle, majority of them return to the films while only few atoms are worn and still attach to the particle.

Fig. 4.7. Effect of velocities v_s of the DLC film on (a) its wear rate k and (b) the sliding depth h of the spherical particle.

The return of the networks is determined by their flexibility and the instability of their atoms attached to the spherical particle. The flexibility of the DLC networks can be

characterized by the fraction of sp^2 atoms. This fraction can be represented by the total number of new sp^2 atoms Δn_{sp^2} in the friction process. A higher Δn_{sp^2} indicates a larger fraction of sp^2 atoms in the film. Fig. 4.9a shows that the Δn_{sp^2} increases with the v_s , i.e., the film exhibit more flexible behavior at a high v_s .

On the other hand, the instability of the network atoms attached to the spherical particle can be simply characterized by their temperature which can be regarded as the friction temperature T_f . The atoms with a high T_f are active and easily influenced by external forces. Fig. 4.8b shows that the T_f highly increases with the v_s .

Fig. 4.8. Formation process of worn atoms at a high velocity v_s of 10 Å/ps. The dark-red color in the figure highlights the networks attached to the third particle.

The combination of the flexibility of the DLC networks and the high T_f can raise an interpretation of a new wear mechanism. When the films relatively slide, their flexible networks can largely attach to the spherical particle (Fig. 4.8a). These networks deform during the sliding (Fig. 4.8b). As a result, such networks can highly draw the atoms bonded to the particle and make them tend to return to the film. Moreover, the tendency is further enhanced by the high T_f , since it can highly improve the possibility of the breaks for the bonds formed between these atoms and the particle. Therefore, the high v_s can reduce the wear rate of the films by improving their flexibility and the friction temperature.

Fig. 4.9. Effect of velocities v_s of the DLC film on its (a) number of new sp^2 atoms Δn_{sp^2} and (b) friction temperature T_f .

The tribological mechanisms of DLC films with different v_s in this study are quite different from results under the two-body contact condition in the literature (Bai *et al.*, 2016a; Erdemir and Donnet, 2006; Liu *et al.*, 1996b; Liu *et al.*, 1996a). It has been reported that the high v_s can reduce the friction and wear of the films by improving their level of graphitization and promoting the formation of a transfer layer which is easy to shear and capable of isolating the films from their counterparts.

The present study shows that although DLC networks attaching to the third particle are actually the transfer layer, the friction reduction by such layer is neglected. This is attributed to that the friction reduction by the layer is caused by their shear deformation due to their easy-shear properties. However, in this study their shear deformations hardly occur because the pure rolling of the spherical particle mainly causes tensile deformation of the networks.

Therefore, the present study generally shows that the wear reduction at the high v_s in the three-body contact conditions is caused not by the formation of transfer layer but by suppressing the ploughing and improving the flexibility of the DLC networks and the high friction temperature.

4.2.4. Particle effect

The effect of the particle size is considered by changing the radius of the spherical particle, as shown in Table 4.2. The friction force F_f increases with a small-sized particle. Such increase is attributed to that under the same load the small-sized particle can cause a high contact stress and thus largely penetrate into the DLC films. Such penetration can largely cause the deformation of the films and thus increase the F_f . This keeps consistent with results in the literature which stated that the ploughing is significant in determining the three-body friction at the nanoscale (Sun *et al.*, 2013a; Sun *et al.*, 2013b). The large deformation of the films with the small-sized particle also increases their wear rate.

The large F_f and k of DLC films with a small-sized particle is different from observations in the previous studies (Qi *et al.*, 2014; Qi *et al.*, 2010; Qi *et al.*, 2011a; Bai *et al.*, 2013). Qi *et al.* (2010) reported that small-sized sand particles can reduce the friction

and wear of the films mainly by reducing the contact stress. This is because in their studies a large quantity of sand particles were located at the interfaces between the DLC films. The small size of such particles could make them form a relatively flat layer between the films and thus reduce the contact stress. The present study demonstrates that a small number of particles surely exhibit a different abrasive behavior and may severely damage the film and influence their tribological behaviors.

Table 4.2. Effect of particle radius r on the friction and wear of DLC films.

	F_f (nN)	k ($\text{\AA}^{-1}$)
$r = 10 \text{ \AA}$	204	2.67
$r = 12 \text{ \AA}$	181	1.92

The particle shape can also influence the tribological behaviors of DLC films. Fig. 4.10 shows that the cubic particle also purely rolls when the films relatively slide. However, the cuboid particle hardly rolls and is initially attached to the lower film. Such cuboid particle highly ploughs the upper film. This can be proved by the chip formation in front of the cuboid particle. Moreover, the chip exerts a high force to the cuboid particle. When this chip becomes large, this force plus the adhesion force from the upper film can cause the movement of the cuboid particle. As a result, such particle is in turn attached to the upper film and ploughs the lower film. It can be seen that the shape of particles highly influences their movement modes which influence tribological mechanisms of DLC films. This keeps consistent with observations in the previous study which stated that the nanoparticle exhibits an optimum shape to realize its rolling (Anantheshwara *et al.*, 2012).

Fig. 4.11a shows that the cuboid particle causes a high F_f while the spherical and cubic particles cause a low F_f . The dependence of F_f on the particle shape is due to the transition of the friction mechanisms. For the cuboid particle, the ploughing is present and highly increases the F_f . For the spherical and cubic particles, the friction is determined by rolling and the F_f is caused by the adhesion instead of the ploughing. The variance of the F_f for cubic particle is due to the varied interfacial adhesion strength when the particle rolls. Therefore, it can be seen that the presence of ploughing is a significant reason for the high friction in the three-body contact condition.

Fig. 4.10. Atomic configuration with (a) cubic and (b) cuboidal particles during the friction process.

The shape of the third particle also highly influences the wear performance of DLC films (Fig. 4.11b). It is evident that the k with the cuboid particle is much higher than those with the cubic and spherical particles. The high k for the cuboid particle is attributed to the occurrence of ploughing. However, the adhesive wear in the cases with cubic and spherical particles is much lower due to the adhesive wear which is highly reduced by the flexibility of the DLC networks.

Fig. 4.11. Effect of the shape of the third particle on (a) the friction and (b) wear of DLC films.

The effect of the particle shape indicates that the presence of ploughing can highly increase the friction and wear of DLC films. Moreover, such effect demonstrates that the rolling wear rate of the films in the third-body contact condition is lower than their sliding wear rate. This is consistent with results in the previous study (Sun *et al.*, 2013a; Fang *et al.*, 2009). It has reported that the ploughing dominates the three-body wear at the nanoscale (Sun *et al.*, 2013a). Experimental results also found that grooving movement of particles shows a higher contribution to wear volume of workpiece than their rolling mode (Fang *et al.*, 2009). The ploughing caused by the cuboidal particle actually reflects the

properties of the two-body abrasion which cannot be well explained by the mechanisms for spherical and cubic particles. Therefore, it is evident that the shape of the particle can directly determine its movement mode and the friction and wear mechanisms of the DLC films (Anantheshwara *et al.*, 2012).

4.3. Summary

The tribological behaviors of DLC films with a third particle at their contact interface are investigated via MD simulation. The influence factors such as the load F_n , velocity v_s , shape of the particle and its size are considered. It has been found that the friction force F_f and wear rate k of the film are determined by adhesion at a small F_n but dominated by both adhesion and ploughing at a large F_n . This can be verified by examining the relation of the F_f and k with the number of bonds n_b at the contact interface.

With the increase of v_s , the F_f increases and k decreases while the n_b almost keeps constant. This is because with a large v_s the DLC networks exhibit a large strain before their yielding and thus many networks can attach to the third particle to resist the relative sliding of the DLC films. These attached networks highly increase the F_f . The decrease of k at a large v_s is caused by the decrease of the sliding depth and the flexibility of the DLC networks. The small-sized particle can increase the F_f and k by enhancing ploughing.

The shape of the third particle highly influences its movement mode and thus changes the friction and wear of the DLC films. It is found that the spherical and cubic particles purely roll without sliding. However, the cuboidal particle highly increases the F_f and k by purely sliding and ploughing the films, indicating that the cuboidal particle can induce the transition of tribological mechanisms from three-body rolling to two-body sliding.

Chapter 5. Influence of the hydrogen atmosphere on tribological behaviors of DLC films

DLC films exhibit a low friction in a H₂ atmosphere. Such low friction may be caused by the diffusion of H atoms into the subsurface of these films, due to the fact that such diffusion can largely reduce their shear strength and thus cause their friction reduction. This chapter investigates the effect of the H₂ atmosphere on the tribological behaviors of the DLC films. The effects of the H atom diffusions on the contact-interface evolutions are examined, and the mechanisms of the friction reductions are discussed in detail.

5.1. Modelling

The simulation model consists of two DLC films and a random distribution of hydrogen atoms at their interface, which is located at the x - z plane of the Cartesian coordinate system x - y - z . The upper film slides against the lower film along the x -direction with a velocity v_s . The addition of H atoms instead of H₂ molecules at the contact interface of these films ensures that their relative sliding after the complicated tribochemical reactions from H₂ molecules to H atoms in experiment can be directly simulated. Both the films are obtained by the melting-quenching procedure and have dimensions of $47.4 \times 38.5 \times 15.8 \text{ \AA}^3$.

The periodic boundary conditions are set in the x and z -directions. In the y -direction, both the upper and lower DLC films are divided into three layers with different functions. The upmost one of the upper film is defined as a rigid body to keep its structure undeformed. The velocity v_s is applied to such layer to conduct the sliding of the upper film, and such layer also take the load F_n along the y -direction. The lowest layer of the lower film is also

defined as a rigid body but with fixed locations. The other layers consist of the Newtonian atoms whose movements are determined by the interactions of neighbors according to Newton's equation of motion. The layers adjacent to each rigid one in the both films have a constant temperature of 300 K to dissipate the friction energy generated during the friction process. The rest films and the H atoms are contained into the Newtonian layer.

Fig. 5.1. Schematic of the simulation model.

The atomic interactions are described by AIREBO potential (Stuart *et al.*, 2000). Its long-range repulsive forces are ignored because such forces cause the happening of gas-lubricated friction instead of solid-contact friction by largely raising the distances between H and C atoms. The time step of the simulation is set as 0.5 fs, and each simulation lasts

250 ps. Visualization of the simulation is realized by the software OVITO (Stukowski, 2010).

The friction force F_f is calculated by summing up the tangential forces of atoms in the upper rigid layer. The microstructural evolution of the friction system is studied by dividing it into multiple strips along the y-direction. For each strip, the quantities including the number of H atoms, the average temperature and the fractions of sp^3 hybridized C atoms are evaluated. The sp^3 fraction is defined as the ratio of the number of the sp^3 C atoms in such strip to the number of all the C atoms in it. The hybridization states of carbon atoms are calculated by evaluating their coordination numbers. Such coordination numbers are obtained by calculating the number of nearest atoms within a cutoff of 2.0 Å for C-C pairs and 1.5 Å for C-H pairs (Chen *et al.*, 2015).

The effects of the H density ρ_H on F_f are studied in three different conditions. The ρ_H with a unit of atom number per area of the contact interface increases from 0, 10.6 to 27.6 nm^{-2} . In the reference case, the F_n and the v_s are set as 100 MPa and 1 Å/ps, respectively. Such two parameters separately increase in the high-velocity case ($F_n = 100$ MPa and $v_s = 5$ Å/ps) and in the high-load case ($F_n = 1$ GPa and $v_s = 1$ Å/ps).

5.2. Results and discussions

5.2.1. Friction forces and atomic configuration

Fig. 5.2 shows the effect of ρ_H on the F_f under different conditions. The sliding can increase the F_f , and its maximum value can be obtained and followed by a sharp drop. The increase of the F_f is due to the high adhesive force caused by the C-C covalent bonds across the interface between DLC films. Such adhesive force can induce the shear deformations

of these films during their relative sliding. The sharp drop after the maximum of the F_f indicates the breakings of interfacial C-C covalent bonds. Afterwards, the F_f stabilizes and become larger with the presence of stick-slip patterns. The averagely stabilized F_f is about 250 nN for both $F_n = 0.9$ nN and $F_n = 9$ nN when $v_s = 1$ Å/ps and $\rho_H = 0$. Such stabilized F_f is close to those in the previous studies (Schall *et al.*, 2009; Ma *et al.*, 2014; Mao *et al.*, 2010), which helps to validate the accuracy of this simulation model.

The presence of H atoms highly reduces the F_f both before and after its stabilization (Fig. 5.2a). Moreover, the H atoms also delay the F_f stabilization. Such stabilization is reached at the time of about 40 ps for $\rho_H = 0$ but is realized at 60 and 80 ps for $\rho_H = 10.6$ and 27.6 nm⁻², respectively.

At a large F_n (Fig. 5.2b), the F_f before its stabilization increases for $\rho_H = 0$ and 10.6 nm⁻² but is almost unchanged for $\rho_H = 27.6$ nm⁻². After the F_f stabilization, the magnitude of the stick-slip patterns slightly increases for $\rho_H = 10.6$ and 27.6 nm⁻² while is constant for $\rho_H = 0$. This slight increase reveals that the effect of the H atoms on the F_f reduction tends to be weakened at a large F_n .

With the increase of v_s , the F_f significantly decreases either before or after its stabilization (Fig. 5.2c). Such decrease should be attributed to the high friction temperature T_f induced by the high v_s . In particular, the stabilized F_f for $\rho_H = 27.6$ nm⁻² is only slightly smaller than those for $\rho_H = 0$ and 10.6 nm⁻². This indicates that the effect of the H atoms on the F_f reduction is largely eliminated with a high v_s .

Fig. 5.2. Effect of H atoms on friction forces with various velocities and loads: (a) $v_s = 1 \text{ \AA/ps}$, $F_n = 100 \text{ MPa}$, (b) $v_s = 1 \text{ \AA/ps}$, $F_n = 1 \text{ GPa}$ and (c) $v_s = 5 \text{ \AA/ps}$, $F_n = 100 \text{ MPa}$.

Atomistic configurations of DLC films is helpful for the understanding of the mechanisms of the friction reduction caused by H atoms, as shown in Fig. 5.3. The film deformation is highlighted by defining an inner straight red marker before the sliding commencement. For $\rho_H = 0$, the inclined marker indicates that the films are under shear deformations and no sliding occurs at their contact interface. However, for $\rho_H = 10.6$ and 27.6 nm^{-2} , the marker is interrupted at the interface, thus revealing the presence of the sliding at such interface. This presence of the sliding indicates that the H atoms can significantly decrease the interfacial adhesion strengths between the films. Such decrease is due to the fact that the H atoms largely reduce the chemical activity of the films by passivating the dangling bonds of C atoms on the film surfaces (Paulmier *et al.*, 1993; Erdemir, 2004).

Atomistic configurations of DLC films with different ρ_H after the F_f stabilization are shown in Fig. 5.4. Such films are merged together, indicating the disappearance of their interface. The H atoms originally at the interface become widely distributed, thus revealing the occurrence of their diffusions.

The interfacial phenomenon of DLC films after the F_f stabilization is analyzed by defining an inner straight marker during the sliding. After a short simulation time, each marker has a mediate segment becoming inclined. Such inclined segment indicates the region in which the sliding occurs. The sliding region for $\rho_H = 0 \text{ nm}^{-2}$ has a large width w , and the increase of the ρ_H causes the decrease of the w . It is evident that the H atoms are only distributed inside the sliding region. Therefore, the decrease of the w implies that the H atoms can degrade the mechanical properties of the DLC films. Moreover, the width of the H-distributed region w_H determines the degradation effect, i.e., a smaller w_H

represents a denser distribution of the H atoms in the sliding region and thus indicates the significant degradation of the mechanical strength of the DLC films. The w_H depends on the testing parameters including the F_n and v_s , which will be discussed later.

The degradation of mechanical properties of DLC films by H atoms is consistent with results in the previous studies. Fontaine *et al.* (2004) stated that H atoms in DLC films can significantly increase their viscoplastic behaviors which indicate a small shear resistance and thus a low friction force. Sanchez-Lopez *et al.* (2001) found that such viscoplastic behaviors of the films are essential to their superlow friction in a vacuum environment.

The atomistic configurations are capable of interpreting the evolution of the F_f . For $\rho_H = 0$, before the F_f stabilization, the C-C bonds across the contact interface of DLC films connect them and induce their shear deformations during the sliding, thus increasing the F_f . Breakings of such bonds are subsequently induced, and the mechanical mixing promotes the atom diffusions across the interface, resulting in the mergence of upper and lower DLC films. This merged structure is most stable for the sliding and thus the F_f is stabilized.

The F_f stabilization is largely delayed by the presence of H atoms. This is because such atoms can passivate the dangling C bonds at the interface between DLC films and significantly reduce the number of C-C bonds across such interface. This reduction is much more significant for a high ρ_H , due the fact that a large number of the H atoms almost isolate the DLC films and suppress the formation of C-C bonds across the contact interface (Hayashi *et al.*, 2011). Such suppression highly reduces the mechanical mixing of the interface and thus delay the stabilization of the F_f . This keeps consistent with the results in Fig. 5.2.

Fig. 5.3. Atomistic configuration of the interfacial evolution before the friction stabilization for $v_s = 1 \text{ \AA/ps}$ and $F_n = 100 \text{ MPa}$. A thin straight slab is highlighted in red color as a marker to indicate the material deformations caused by sliding.

It should be noted that in Figs. 2a and 2b the F_f increases after its stabilization. This is attributed to that the merge of DLC films makes them thoroughly connected and thus induces a higher adhesion strength between them (Gao *et al.*, 2002). The decrease of the F_f after its stabilization in Fig. 5.2c may be due to the high T_f .

The stick-slip pattern of the F_f after its stabilization is attributed to the periodic deformation-yield of DLC films in their sliding regions. The period and the magnitude of

such pattern decrease with ρ_H . This is because the H-passivations highly decrease the mechanical strengths of these films.

Fig. 5.4. Atomistic configuration of the interfacial evolution after the friction stabilization for $v_s = 1 \text{ \AA/ps}$ and $F_n = 100 \text{ MPa}$. A similar marker is defined to show the material deformation as in Fig. 5.3.

The discussions above can help to roughly understand the mechanisms of the F_f reduction caused by environmental H atoms. Before the stabilization of F_f , its reduction is attributed to that the H-passivation of the dangling bonds at the contact interface between DLC films can highly reduce their adhesion strengths. However, the reduction mechanism

of F_f after its stabilization is different. In this case, the F_f reduction is due to the fact that the H atoms can soften the films in their merged regions. The H-passivations make C atoms less bonded with their neighbor C atoms, thus significantly degrading the carbon networks of the DLC films and their mechanical properties (Fontaine *et al.*, 2004). The degraded films are easy to shear and thus exhibit a low F_f .

5.2.2. Friction temperatures and element diffusions

The T_f can highly change the microstructures of materials and their mechanical strength and thus is significant in the analysis of tribological phenomena. Fig. 5.5 shows that the evolution of T_f of the DLC films is divided into two stages by the F_f stabilization. Before such stabilization, a low T_f is observed, due to the fact that the sliding only causes elastic deformations of these films for $\rho_H = 0$ is zero or induces the relative sliding between H atoms for $\rho_H = 10.6$ and 27.6 nm^{-2} . After the F_f stabilization, the T_f increases and changes periodically. Such periodic changes are due to the stick-slip friction patterns which induce periodic storages of strain energy and its release (Bai *et al.*, 2015). Each release of the strain energy can cause a temperature rise. The maximum T_f is meaningful (Bai *et al.*, 2015), since it largely induces the graphitization of the DLC films and promotes H-atom diffusions into these films. For convenience, the T_f discussed below refers to its maximum value.

Fig. 5.5. Effect of H atoms on the friction temperature with various velocities and loads: (a) $v_s = 1 \text{ Å/ps}$, $F_n = 100 \text{ MPa}$, (b) $v_s = 1 \text{ Å/ps}$, $F_n = 1 \text{ GPa}$ and (c) $v_s = 5 \text{ Å/ps}$, $F_n = 100 \text{ MPa}$.

The presence of H atoms can significantly reduce the T_f , which is due to the F_f reduction. The T_f closely relates with the F_f , i.e., a large T_f always follows a large F_f . This is attributed to that the large F_f significantly deform the DLC films and thus cause a large amount of energies stored and released.

Fig. 5.5b shows that the F_n hardly influences the patterns and values of the T_f . This keeps consistent with the slight effect of the F_n on the F_f (Fig. 5.2b). Fig. 5.5c further depicts that a high v_s significantly increases the T_f without large variations. This increase is due to the fact that more energies are generated and subsequently thermally dissipated by the DLC films (Bai *et al.*, 2011). It can be seen that the small F_f is observed the large v_s . The fact that this high T_f corresponds to the small F_f is different from the trend that a large T_f always follows a large F_f discussed above, thus indicating existences of a complicated tribological mechanisms that cannot be interpreted only by the T_f .

Such complicated tribological mechanisms may be interpreted by the diffusion of H atoms. This is attributed to the phenomenon that the H-atom diffusions highly degrade the mechanical properties of DLC films (Fig. 5.4). Therefore, the evolution of the w_H with various F_n and v_s needs to be investigated (Fig. 5.6).

It can be seen that the sliding can increase the w_H . For the reference case (Fig. 5.6a), the w_H is almost same for the different ρ_H . Therefore, the passivation level of C atoms in the H-distributed region is high for a high ρ_H . Such high passivation level is beneficial for the F_f reduction.

Fig. 5.6. Evolution of the width of H-distributed regions with simulation time for various sliding velocities and loads: (a) $v_s = 1 \text{ Å/ps}$, $F_n = 100 \text{ MPa}$, (b) $v_s = 1 \text{ Å/ps}$, $F_n = 1 \text{ GPa}$ and (c) $v_s = 5 \text{ Å/ps}$, $F_n = 100 \text{ MPa}$.

With the increase of the F_n , the w_H for $\rho_H = 10.6$ and 27.6 nm^{-2} slightly increases compared with that in the reference case (Fig. 5.6b). This increase of the w_H slightly reduces the passivation level of C atoms and tends to raise the F_f , and keeps consistent with the slight increase of its amplitudes (Fig. 5.2b). Hence, the H-atom diffusions into DLC films well interpret their friction behaviors in the reference case and the high-load case.

The v_s can highly increase the w_H for $\rho_H = 10.6$ and 27.6 nm^{-2} (Fig. 5.6c). The w_H for $\rho_H = 10.6 \text{ nm}^{-2}$ sharply increases after the F_f stabilization. This is because the T_f at a high v_s is quite high and significantly promotes the diffusions of H atoms. Such high T_f also makes w_H with $\rho_H = 10.6 \text{ nm}^{-2}$ always larger than that with $\rho_H = 27.6 \text{ nm}^{-2}$. Since the H-passivations cause a significant reduction of the F_f , the H-atom diffusions can highly suppress this reduction. However, the small F_f is observed for the high v_s . This reveals that the friction of DLC films in the high-velocity case may be dominated by other mechanisms rather than the H-atom diffusions.

5.2.3. Graphitization and atom density

The friction mechanisms of DLC films can also be interpreted by their graphitization. The graphitization represents the transitions of C atoms from sp^3 to sp^2 bonding states. Therefore, it is convenient to denote the graphitization level of the films the fraction of sp^3 bonded atoms f_2 . A small f_2 indicates a high graphitization level.

Fig. 5.7 shows that f_2 is small in the sliding region of DLC films and is large at their outmost regions. This is attributed to that the T_f is highest in their sliding region and gradiently decreases along the direction from such region to the subsurface of these films, thus causing the lowest temperature at their outmost regions. Since a high T_f can increase

the graphitization level of the DLC films, the temperature gradient along the y -direction determines a gradient f_2 . It is noted that the region with low f_2 has a width about 40 Å (from $y = 20$ Å to $y = 60$ Å) which is larger than that of the sliding region about 20 Å (Fig. 5.4). Such large width of the low- f_2 region is attributed to that the gradient temperature is much higher than the phase-transition point (about 900 K) for the graphitization of DLC films (Liu *et al.*, 1996a).

In particular, Fig. 5.7a shows that the f_2 with various ρ_H fluctuates around a same value, indicating the independence of f_2 on ρ_H . With the increase of the F_n , the f_2 is almost unchanged, thus keeping consistent with the unchanged T_f (Fig. 5.5b). It is noted that the increase of the v_s only slightly decreases the f_2 . This is due to the fact that the T_f at a small v_s is already high enough to induce a high graphitization level of DLC films. As a result, the high T_f induced by the large v_s is difficult to highly raise the graphitization level. This agrees well with other theoretical works (Ma *et al.*, 2014).

The independence of f_2 on ρ_H can be observed in all the test conditions. This indicates that the graphitization level of the DLC films cannot explain their friction behaviors under the effect of H atoms. This independence is different from results in the literature which stated that the H atoms tend to be bonded with sp^3 C atoms and increase the f_2 (Donnet and Erdemir, 2007). In fact, the independence of f_2 on ρ_H is attributed to that the shear deformation easily promotes the transition of C atoms from sp^3 to sp^2 bonding (Car, 1996; Chacham and Kleinman, 2000). Moreover, under shear deformations of DLC films, the H atoms tend to be bonded with sp^2 atoms to form π bonds that are beneficial to the occurrence of such shear deformations. This is verified by analyzing the coordination number of C atoms bonded with H atoms.

Fig. 5.7. Effect of H atoms on the fraction of sp^3 atoms f_2 for various velocities and loads: (a) $v_s = 1 \text{ Å/ps}$, $F_n = 100 \text{ MPa}$, (b) $v_s = 1 \text{ Å/ps}$, $F_n = 1 \text{ GPa}$ and (c) $v_s = 5 \text{ Å/ps}$, $F_n = 100 \text{ MPa}$.

In fact, for amorphous solids, their nanoscale friction behaviors closely relate with their rheological properties (Bai *et al.*, 2015). Such rheological properties can be characterized by calculating the atom density in the sliding regions. A small atom density represents a packless network which is easy to shear and exhibits a low friction force. For the DLC films, with the presence of the H atoms, the H-passivations of C atoms can make them less bonded with their nearest C atoms. Hence, the carbon networks of the films in the H-distributed region would be damaged and become packless. The density of C atoms ρ_C can help to roughly describe such networks, i.e., a higher ρ_C commonly represents a denser networks. The distribution of ρ_C through the DLC films (Fig. 5.8) shows that the ρ_C is generally low in their sliding regions due to the high friction temperature T_f and the graphitization and increases gradually from the interface to their subsurfaces due to the decrease of T_f .

The ρ_C in the sliding region is highly dependent on the ρ_H . This dependence can be exemplified by the reference case. With the increase of ρ_H , the ρ_C significantly decreases in the sliding region. This is due to the fact that the H atoms are distributed in this region and thus expand its volume, leading to a small ρ_C . As a result, DLC films become packless and their networks are highly degraded. Their mechanical properties are significantly weakened and their easy-shear properties are obtained, thereby leading to a low F_f . This is consistent with the dependence of F_f on ρ_H discussed before. Besides, the width of the region with the small ρ_C is quite small and almost similar for $\rho_H = 10.6$ and 27.6 nm^{-2} . This corresponds to their similar evolution of the w_H with sliding.

Fig. 5.8. Effect of H atoms on the density of C atoms for different velocities and loads: (a) $v_s = 1 \text{ Å/ps}$, $F_n = 100 \text{ MPa}$, (b) $v_s = 1 \text{ Å/ps}$, $F_n = 1 \text{ GPa}$ and (c) $v_s = 5 \text{ Å/ps}$, $F_n = 100 \text{ MPa}$.

When the F_n increases, it can slightly increase the ρ_c through the DLC films, since a high pressure can induce a denser structure. The width of the region with the small ρ_c increases, due to the diffusion of H atoms promoted by the high F_n .

When the v_s increases, the ρ_c in the sliding region highly decreases for the DLC films with different ρ_H . This is attributed to that the high T_f in this case can increase the volume of the films by their thermal expansions as well as their graphitization. The ρ_c in the sliding region is low and the width of the region with such low ρ_c becomes large. The large width keeps consistent with the significant diffusions of H atoms at the high T_f . Both the low ρ_c and the large width contribute to the low F_f observed.

Combination of the analysis of T_f , the diffusions of H atoms, and the distribution of ρ_c in the DLC films as well as their graphitization can help to clear their tribological mechanisms. The F_f is highly reduced when the ρ_c is small in the sliding region. Such small ρ_c can be obtained by H-passivations of C atoms in the films and their thermal expansions as well as graphitization, depending on the T_f . The low T_f hardly induces an evident diffusion of H atoms and thus they are mainly distributed in a narrow region. The H-passivations highly reduce the ρ_c in this region and thus lead to a low F_f . On the contrary, the high T_f can highly promote the diffusion of H atoms into the films and also thermally expand such films and slightly increase their graphitization level. The ρ_c is significantly reduced by the thermal expansions and graphitization with the assistance of H-passivations, leading to the reduction of the F_f .

Such tribological mechanisms for the stable F_f are also applicable for the explanation of F_f before its stabilization. In this case, the H atoms are distributed at the interface between DLC films. In the H-distributed region, only a few C atoms exist. As a result, the strong interactions inside such region are absent and the low F_f is obtained.

It should be noticed that the higher ρ_H can always reduce the F_f whatever the T_f . In experiment, this higher ρ_H can be obtained by increasing the pressure of environmental H_2 gas. Donnet *et al.* found that the high friction of hydrogenated DLC films in high vacuum could be highly reduced by introducing at least 1 kPa of H_2 gas in the test chamber (Donnet *et al.*, 2001). The friction reduction was attributed to the formation of carbonaceous transfer layers during these tests. Fontaine *et al.* (2001) reported that the intermediate and high H_2 pressures could provide the healing effect on the transfer layers to reduce the friction force of DLC films. This is because these layers with a high fraction of H atoms exhibit low shear strength that is attributed to the weak Van der Waals interaction between flexible hydrocarbon chains along the sliding direction. Erdemir *et al.* (2014) further verified the high fraction of H atoms in the transfer layer and the existence of H-passivations of C atoms by using element distribution technique. In the present simulation, the films in the sliding region where sliding happens can be regarded as the transfer layer observed in the experiment. The atomic configurations in Fig. 5.4 demonstrate that the environmental H atoms can highly degrade mechanical properties of DLC films by passivating their C atoms. This degradation of the mechanical properties is highly related with the low ρ_C in the sliding region as shown in Fig. 5.8, since the hydrocarbon materials with low ρ_C exhibit coarse networks. Therefore, it can be concluded that the simulation results correspond well to those of experiments.

The effect of high temperature on the friction force of DLC films in H₂ environment has been reported in literature. Donnet *et al.* (2001) found that a relatively high test temperature can thermally assist diffusion of environmental H atoms into the carbonaceous network, resulting in the reduction of friction force of the DLC films. In the present study, it is demonstrated that this reduction is caused not only by the diffusions of H atoms but also by the expansion of the films as well as their graphitization.

In experiment, the effect of test parameters on the friction behaviors of DLC films in H₂ environment has been rarely reported. Most of relevant studies focused on the effect of the H₂ pressure. The present study indicates that for an appointed pressure of H₂, a large applied load can lead to an increase of the friction force by reducing the density of H atoms in the sliding region via promoting their diffusion. Moreover, the high sliding velocity may help to reduce the friction force by causing high friction temperature to accelerate the diffusions of H atoms and reducing the density of C atoms in the sliding regions. These phenomena caused by high applied load and high sliding velocity need the experimental verification in future.

For the friction mechanisms of DLC films, the present study further suggests that the ρ_C at the sliding interface may be a suitable parameter to accurately characterize the friction behavior. This is because the small ρ_C can represent the coarse networks of the films as well as their good viscoplastic behavior. Both such coarse networks and viscoplastic behavior demonstrate the easy shear properties of the films and thus their low friction force. As a result, application of the ρ_C to indicate the friction behavior of the DLC films is not only suitable in H₂ environment but also applicable in other environment.

It should be noticed that in the present simulation the H atoms are only added into the interface prior to the sliding. On the contrary, in experiment the surfaces of DLC films are always exposed to H₂ atmosphere; the H atoms can be continuously absorbed on such surfaces during the sliding after the tribochemical reaction from H₂ molecules to H atoms. According to the present simulation, the sliding can promote the diffusion of continuously absorbed H atoms into DLC films and thus improve the H-passivation level of C atoms, resulting in the low friction force. This force will be much lower than the one obtained in the present simulation and even exhibit superlow as reported in literature (Donnet *et al.*, 2001; Fontaine *et al.*, 2004; Fontaine *et al.*, 2001).

In general, although the simplification of experiment tests is implemented in the present simulation, the conclusions obtained are meaningful and capable of improving the understanding of the friction mechanism of DLC films and extending their applications.

5.3. Summary

The effect of environmental H atoms on the tribological behaviors of DLC films is investigated via MD simulation. The friction force F_f increases with the commencement of sliding and becomes stable after a sharp drop. The stabilization of the F_f is accompanied with the disappearance of the interface between films and the formation of their mixing region. The H atoms can highly reduce the F_f . Its reduction before its stabilization is attributed to that the H atoms can passivate the dangling C bonds at the interface between films and thus highly reduce the adhesion force at such interface. After the stabilization of F_f , its reduction is due to the fact that the H atoms can soften the DLC films in their mixing region by passivating C atoms to make them less bonded with their neighboring C atoms.

Such passivations can significantly degrade the networks of films and weaken their mechanical properties, thus inducing their easy-shear properties.

Further study indicates that the reduction of F_f after its stabilization results from the H-passivation and thermal expansion of DLC films as well as their graphitization, depending on the friction temperature T_f . At low T_f , the H atoms are distributed in a narrow region in which the sliding occurs. This region has small densities of C atoms and can be easily sheared. At high T_f , it not only induces the significant diffusion of the H atoms but also thermally expands the DLC films and slightly increase the level of their graphitization. Such thermal expansions can induce a wide region with low densities of C atoms under the assistance of H-passivations and graphitization, ensuring the low F_f . The mechanisms of friction reduction in the present study provide a new understanding for the superlow friction of DLC films in H_2 atmosphere.

Chapter 6. Influence of the graphene lubrication on tribological behaviors of DLC films

Sensitivity of the tribological behaviors of DLC films to their compositions can be efficiently eliminated by using other lubricants. Graphene exhibits excellent lubrication properties and superior chemical inertness and thus can lubricant materials with different compositions. Because of the nanoscale thickness of the graphene, its lubrication performance for the DLC film has been seldom studied in experiment. This chapter investigates such lubrication performance by considering the effect of hydrogenations of the DLC film, layer number of the graphene, its flake-size and defects.

6.1. Modeling

The modeling system is comprised of a crystalline diamond tip scratching the surface of a DLC film (Fig. 6.1). The scratch is realized by setting the diamond tip with a lateral velocity v_s and a normal velocity v_n and pinning the bottom of the film to avoid its free movement. The surface of the film is passivated by H atoms. Moreover, the film is fully covered by graphene that is located between the film and the diamond tip to isolate their direct contact.

The periodic boundary conditions are applied in the x and y -directions of the modelling system. The DLC film is generated via the melt-quenching and has dimensions of 66.31 Å, 63.81 Å and 16 Å along the x , y and z -directions, respectively. The bottom of the film is pinned by fixing positions of the atoms in its lowest layer with a thickness of about 3 Å in the z -direction. The rest atoms in the film and all atoms in the graphene can move freely under the interactions of their neighboring atoms. The diamond tip that is a half-sphere

with a radius of $10 \text{ \AA}$ is located in the middle of the graphene in the y -direction. The diamond tip is set as a rigid body to keep its geometry unchanged during the scratch tests.

Fig. 6.1. Illustration of the atomistic model with (a) the front view and (b) the top view. In the model, a diamond tip scratches a DLC film which is passivated by H atoms and fully covered by graphene.

The interactions between atoms are the AIREBO potential (Stuart *et al.*, 2000). This potential is able to determine the transition of force between C atoms from van der Waals interaction to covalent bond, and thus help to realistically describe the lubrication of graphene for DLC films. The molecular visualization of the simulation is realized by the

software OVITO (Stukowski, 2010). The simulation step is set as 0.5 fs and each scratch test lasts for 40 ps.

Prior to the scratch test, a minor loading force along the z -direction is applied to the diamond tip to allow it to come in contact with the DLC film. To conduct the scratch tests, the lateral velocity v_s and normal velocity v_n of the diamond tip are set as 1 Å/ps and 0.3 Å/ps, respectively. The total lateral sliding distance L of the diamond tip and its maximum indentation depth h are 36 Å and 11 Å, respectively. During the scratch test, the system is evaluated by constant NVE integrations to update positions and velocities of atoms. The temperature of the system is constantly kept at 300 K by recalling the velocities of atoms. The force undertaken by the diamond tip along the x and z -directions is calculated as friction force F_f and normal force F_n , respectively.

The effects of factors including the layer number of the graphene, its boundary condition and the presence of defects on the F_f and F_n are studied. The boundary condition of the graphene includes the pinned boundary and the free boundary. The pinned boundary is accomplished by fixing the positions of the boundary atoms of the graphene and is useful to study the behavior of a large-sized graphene that is commonly pinned to the surface of a substrate (Klemenž *et al.*, 2014). However, the free boundary indicates that the atoms at the boundary of the graphene are free to move according to the forces of their surroundings. Such free boundary helps to simulate the behaviors of graphene flakes that can move freely during their friction. To distinguish the graphene with different boundary conditions, the layer number of the free-boundary graphene is denoted as m_g , while the layer number of the pinned-boundary graphene is denoted as m_p . The defects (or porosities) of the graphene are generated by randomly deleting its atoms with a fraction η of 2%, 5% and 10%,

respectively. The bond formation across the contact interfaces is evaluated based on a cutoff of 2.0 Å. This cutoff corresponds to the first minimum in the radial distribution function of carbon materials and indicates the maximum length for C-C covalent bonds. Therefore, a bond is defined to be formed between two C atoms when their distance is smaller than 2.0 Å.

The non-hydrogenated DLC film with H-passivation on its surface is used to represent the hydrogenated DLC film to save computational time, since friction of the graphene is mainly influenced by the H atoms on the surface of the film. In the following section, the non-hydrogenated DLC film without the H-passivation is simply denoted as DLC film and the one with the H-passivation is denoted as DLC-H film.

6.2. Results and discussions

6.2.1. Friction force

When the graphene is absent ($m_g = 0$), the diamond tip directly scratches the DLC film. The friction force F_f almost increases simultaneously with the commencement of the scratch (Fig. 6.2a). This increase is attributed to that dangling bonds on the surfaces of both the diamond tip and the DLC film can form covalent bonds across their contact interface. These covalent bonds are sufficiently strong to cause the high interfacial adhesion. Moreover, the F_f increases linearly during the scratching. This linear increase is due to the penetration of the diamond tip into the DLC film. This high F_f can be significantly reduced by graphene.

When the single-layer graphene is present ($m_g = 1$), the F_f is superlow at $h < 3.5$ Å. The F_f increases rapidly at a large h . For the bilayer graphene ($m_g = 2$), the F_f remains

superlow until the h of 5 Å. When $h > 5$ Å, the F_f with $m_g = 2$ is much lower than that for $m_g = 1$ and $m_g = 0$. Therefore, the graphene with more layers exhibits a much lower F_f and better lubrication performance, which is consistent with results in the literature (Berman *et al.*, 2014).

The superlow F_f indicates the superlubrication of the graphene. This superlubrication is attributed to the chemical inertness of the graphene that can ensure van der Waals interactions instead of covalent bonds at the interface between the diamond tip and the DLC film. As a result, the interfacial adhesion is highly reduced and the sliding at the interface easily happens, thus leading to the significant decrease of F_f .

The lubrication behavior of graphene highly depends on its boundary condition. Fig. 6.2a shows that the pinned-boundary graphene exhibits F_f much higher than that for the free-boundary graphene. This high F_f demonstrates that a large size of the graphene may degrade its lubrication performance.

The H-passivation of the DLC film can highly influence its friction behavior. Fig. 6.2b shows that the DLC-H film without graphene shows a much lower F_f than that of the DLC film (Fig. 6.2a). This lower F_f evidently shows the dependence of the friction behavior of the DLC and DLC-H films on their compositions. The DLC-H film exhibits a superlow F_f at $h < 1.5$ Å. This superlow F_f is due to the fact that the H atoms passivate all dangling bonds on the film surface and suppress the formation of covalent bonds between the DLC-H film and the diamond tip. The increase of the F_f at $h > 1.5$ Å is due to the failure of such suppression. In this case, the penetration of the tip into the film removes the H atoms on the film surface. As a result, the covalent bonds between the film and the diamond tip can be formed and significantly increase their interfacial adhesion and thus the F_f .

The high F_f of the DLC-H film at the large h can be highly reduced by the graphene (Fig. 6.2b). It is observed that a larger m_g causes a lower F_f . Similar observation is also made earlier for the case of the DLC film (Fig. 6.2a). Moreover, with the same m_g , the F_f of the DLC-H film is slightly lower than that of the DLC film, which may be due to the interactions between the H atoms and the graphene.

In general, Fig. 6.2 shows that both the DLC and DLC-H films exhibit low F_f with the presence of graphene. Therefore, it can be concluded that these films can be significantly lubricated by the graphene and the dependence of their friction behaviors on compositions can also be efficiently eliminated.

The lubrication of the graphene can be further understood by investigating the evolution of its structure. Such evolution is studied here by exemplifying the scratch process for the DLC film with a single-layer graphene, as presented in Fig. 6.3. At a small h of 2 Å, the graphene becomes curved. It is observed that no covalent bonds are formed at the contact interfaces between the graphene and the diamond tip and between the graphene and the DLC film. As a result, contact forces at these interfaces are mainly contributed by van der Waals interactions.

However, with the increase of the h from 2 Å to 3.5 Å, the covalent bonds are formed at each of the contact interfaces. The formation of such covalent bonds indicates the occurrence of tribochemical reactions of the graphene. The relation of these tribochemical reactions to the F_f in Fig. 6.2a shows that these covalent bonds highly raise the friction force and are responsible for the disappearance of the superlow F_f . The further increase of the h induces damages to the graphene structure.

Fig. 6.2. Effect of graphene on the friction force F_f of (a) the DLC film and (b) the DLC-H film.

The superlow F_f before the tribochemical reactions (Fig. 6.2a) is nonzero and mainly caused by the curvature of the graphene (Fig. 6.3a) that is also called the puckering effect (Li *et al.*, 2010). The pucker formed in front of the diamond tip can resist its lateral movement and thus generate friction. The F_f increases with the indentation depth h and is quite close to those in previous studies (Ye and Martini, 2014; Yoon *et al.*, 2015), thus validating the code in the present study. In addition, it is noticed that the boundary condition of the graphene can highly influence such F_f , due to the effect of such condition

on the movement of the graphene. The free boundary allows the graphene to move freely following the lateral sliding of the diamond tip, thus significantly suppressing the formation of pucker. However, the pinned boundary of the graphene can largely hinder its movement and is beneficial to the formation of its pucker.

Fig. 6.3. Atomic configuration of the simulation system with single-layer graphene at an indentation depth h of (a) 2 Å, (b) 3.5 Å and (c) 6 Å, respectively. The bonds are generated with a cutoff of 1.9 Å which corresponds to the first minimum in the radial distribution function of carbon materials.

The effect of the boundary condition of graphene on its puckering effect can be demonstrated by its cross-sectional profile, as shown in Fig. 6.4. The profile is almost symmetric around the indentation location for the free-boundary graphene, but becomes asymmetric with the formation of a high pucker in front of the indentation location for the pinned-boundary graphene. In fact, when the h is small, this puckering effect is observed in all the simulation with graphene.

Fig. 6.4. Cross-sectional images of atom position in graphene.

The puckering effect of the graphene is responsible for the superlow F_f at small h but is unable to explain the high F_f at the large h . The configuration (Fig. 6.3b) indicates that such high F_f is most probably caused by tribochemical reactions of the graphene. This indication can be validated by investigating the number of covalent bonds between the graphene and the DLC film n_1 and between the graphene and the diamond tip n_2 , as shown in Fig. 6.5. Both the n_1 and n_2 simultaneously increase with the F_f (Fig. 6.2a). The simultaneous increase is observed in the simulation with the graphene regardless of its boundary conditions.

Fig. 6.5c further shows that after the tribochemical reactions of the graphene its structure keeps pristine but with changed bond angles. Therefore, it is evident that the DLC film and the diamond tip form covalent bonds with the graphene before its rupture. This configuration can help to understand the damage process of the graphene (Fig. 6.3c).

Fig. 6.5. The number of bonds between the single-layer graphene and DLC film n_1 and between this graphene and the diamond tip n_2 when the graphene is set with (a) free boundary and (b) pinned boundary; (c) configuration of the bond between the graphene and the DLC film.

A small indentation depth h only causes a concave of the graphene. The increase of the h induces the tribochemical reactions of the graphene by causing the formation of the covalent bonds between it and the diamond tip and between it and the DLC film. Such bond formation promotes the transition of C atoms in graphene from sp^2 to sp^3 hybridized bonding. As a result, the symmetries of these atoms are broken and distribution of their bonds changes from planar to tetrahedral. These changes highly degrade the mechanical strength of the graphene. As a result, with the further increase of the h , the graphene can be easily torn by the diamond tip.

The chemical reactions of the graphene are useful to explain the effect of its pinned boundary condition on its lubrication behavior (Fig. 6.2a). For the pinned-boundary graphene, its F_f increases highly at a small h of about 2 Å. Such increase is due to the fact that the high stress caused by the high pucker can make atoms in the graphene chemically active by inducing its structural instabilities (Sharma *et al.*, 2001; Chung, 2006). As a result, these active atoms in the graphene can easily form bonds with those in the diamond tip and the DLC film, thus significantly increasing the F_f .

Therefore, it is demonstrated that the superlubrication of the graphene is terminated by its tribochemical reactions. This demonstration has been seldom reported. In the literature (Ye and Martini, 2014), the repulsive potential is commonly used to describe atomic interactions between graphene and substrate and between graphene and tip. As a result, the formation of covalent bonds is prevented at the contact interfaces.

The excellent superlubrication of the bilayer graphene may be due to the fact that the interlayer van der Waals interactions between the graphene layers highly minimize their puckering effects and thus reduce their friction (Berman *et al.*, 2014). Furthermore, Fig.

6.5 shows that a minimized pucker can release the stress of atoms in graphene under the indentation and thus reduce the possibility for the occurrence of tribochemical reactions. This can be verified by investigating the bond formation in the simulation of the bilayer graphene, as shown in Fig. 6.6a. The bonds between the graphene and the diamond tip and between the graphene and the DLC film are formed at the h of about 4 Å which is much larger than that for the film with the single-layer graphene. Therefore, the bilayer graphene exhibits better chemical inertness than the single-layer graphene.

It is noticed that the formation of covalent bonds between the graphene layers commences at a large h of about 5.5 Å. Since the corresponding F_f shown in Fig. 6.2a highly increases at the same h , the superlubrication for the h between 4.0 to 5.5 Å should be dominated by a different mechanism instead of the puckering effect of the graphene. Fig. 6.6b shows that at the h of 5.0 Å the contact force between the graphene layers is still dominated by von der Waals interactions. In this case, the lateral sliding during scratching occurs as the relative movement of concaves of the graphene layers (Lee *et al.*, 2010; Smolyanitsky *et al.*, 2012). When $h > 5.5$ Å, the covalent bonds are formed between the graphene layers. The further increase of the h damages the structures of these graphene layers and thus highly increases the F_f .

The above discussion of the tribochemical reactions of graphene is also applicable to explain its lubrication improvement by H passivation of the DLC film. With the increase of h , many covalent bonds are formed between the tip and the graphene, while less bonds are formed between the graphene and the DLC film due to its H-passivation. As a result, the number of bonds at the sliding interface is reduced, leading to the decrease of the F_f .

Fig. 6.6. (a) The bond number between graphene and the DLC film n_1 , between graphene and the diamond tip n_2 and between graphene layers n_3 and (b) the configuration of the system with bilayer graphene at the h of 5 Å.

6.2.2. Load capacity

The evolution of F_f with F_n is significant to evaluate the lubrication performance of graphene, as shown in Fig. 6.7. The direct scratch of the diamond tip against the DLC film ($m_g = 0$) causes F_f to be almost linearly proportional to the F_n . This linear proportion is significantly influenced by the presence of the graphene. Under an appointed F_n the F_f is highly reduced with a large m_g , thereby indicating that the graphene can efficiently

lubricate the DLC film even in extreme conditions. This is attributed to the formation of covalent bonds between the graphene and the diamond tip and between the graphene and the DLC film only in the contact area. As a result, the van der Waals interactions still exist at the contact interfaces outside this area. Hence, a larger m_g induces stronger interactions, which can lower the adhesion force and thus the friction force.

Moreover, when the graphene is present, the superlow F_f is observed at small F_n . Such superlow F_f corresponds to the van der Waals interactions at the contact interfaces between graphene, the diamond tip and the DLC film. A threshold F_n at which the F_f starts to increase determines the commencement of the formation of covalent bonds at the contact interfaces. Such threshold F_n increases with the m_g , due to the better chemical inertness of the graphene with more layers.

This threshold F_n also shows the limitation for superlubrication of the graphene. The threshold F_n for $m_g = 1$ causes an average contact stress of about 90 GPa which is lower than the ideal rupture stress of the graphene (Klemenzen *et al.*, 2014; Meng *et al.*, 2014). The lower contact stress indicates that the superlubrication of the graphene disappears and its structure is damaged far before its rupture. This indication is consistent with results in Fig. 6.5c where the graphene is torn by the diamond tip, but is different from the observation in the literature (Klemenzen *et al.*, 2014; Sandoz-Rosado *et al.*, 2012). In these studies, the Lennard-Jones potential is employed to model the interactions at the contact interfaces between graphene and tip and between graphene and substrate. This potential leads to that the structure damage of the graphene is only caused by its out-of-plane deformation.

Although the contact stress that initiates the disappearance of superlubrication of graphene is lower than its ideal rupture stress, such contact stress is still much higher than

those reported in the experimental studies (Machado and Cavalca, 2015; Kulchytsky-Zhyhailo and Bajkowski, 2012; Wang and Zhou, 2014). Therefore, the excellent lubrication of graphene can be realized in experiments, which agrees well with experimental observations (Berman *et al.*, 2014; Berman *et al.*, 2013a; Berman *et al.*, 2013b).

It can be seen that the lubrication of graphene is highly influenced by its boundary condition (Fig. 6.7a). When its boundary is pinned, the threshold F_n initiating the increase of the F_f decreases, and at a large h such F_f can almost reach the value for the absence of the graphene. The decrease of the threshold F_n is due to the effect of pinned boundary of the graphene on the formation of pucker in front of the diamond tip. The high F_f is caused by the ruptured graphene. At the large h , the diamond tip contacts with the DLC film by crossing the ruptured graphene. As a result, the sliding of such tip is hindered by not only the DLC film but also the ruptured graphene that is unable move laterally due to its pinned boundary condition. Both the decrease of the threshold F_n and the increase of the F_f demonstrate that the graphene with a large size is unsuitable to be solid lubricants.

Besides the friction force F_f , the scratching can also influence the normal force F_n . Under the maximum h that is constant in all the simulation, the DLC film without graphene undertakes a quite large F_n . This F_n is significantly reduced with the presence of the graphene, i.e., a larger layer number of graphene m_g commonly causes a lower F_n .

The effect of the graphene on the F_n can be interpreted by the contact configurations (Fig. 6.2a). After the initial equilibrium procedure before scratch tests, the presence of the graphene can highly increase the distance between the diamond tip and the DLC film by replacing covalent bonds between them with van der Waals interactions. Since the covalent

bonds are commonly much stiffer than the van der Waals interactions, under a same h , the increase of F_n caused by the van der Waals is lower than that caused by the covalent bonds.

Fig. 6.7. Evolution of the friction force F_f with the normal force F_n for (a) the DLC film and (b) the DLC-H film.

The H-passivations of the DLC film can influence the dependence of F_f on the F_n (Fig. 6.7b). When graphene is absent, such passivations can evidently reduce the increase of the F_f . The reduction is due to the fact that these passivations can suppress the formation of

covalent bonds between the diamond tip and the DLC film, resulting in a low adhesion force between them and thus the low F_f .

The superlow F_f observed in Fig. 6.2a is nearly absent in Fig. 6.7. This is due to the weak van der Waals interactions between H atoms and C atoms. These weak interactions only cause a small F_n at a small indentation depth h at which the superlow F_f is present, i.e., the superlow F_f is actually obtained at a quite small F_n .

When the graphene is present, the H-passivation of DLC film has a negligible effect on the threshold F_n for the increase of F_f but slightly reduces its increase. Such reduction is due to that the H-passivation can degrade C-C networks at the interface between the DLC film and the diamond tip and make lateral sliding easily happen at such interfaces (Erdemir *et al.*, 2014).

6.2.3. Effect of defects in graphene

The excellent lubrication of graphene significantly relies on its perfect structure which guarantees its properties such as good chemical inertness and supreme mechanical strength. However, in the fabrication of graphene, its defects are commonly present and can highly degrade these properties and may influence its lubrication behavior. The porosity is a typical defect of the graphene and thus can be exemplified to investigate the effect of defects on its lubrication.

Fig. 6.8a shows that the graphene with defects becomes uneven and easily forms covalent bonds with the diamond tip and the DLC film during the equilibrium procedure, indicating the strong chemical activities of the graphene. Such chemical activities are induced by the symmetry breaks of C atoms in graphene by its defects. The C atoms

adjacent to these defects cannot form π bonds and the unsaturated bonds of such atoms dangle outside the plane of the graphene, thus increasing the chemical activities of the graphene. These dangling bonds can be easily saturated by those dangling bonds of the tip and the film.

Fig. 6.8b shows that the graphene with a larger fraction of defects η exhibits a higher F_f at a small h . This indicates that the defects of the graphene highly degrade its lubrication performance. This degradation is mainly due to the fact that these defects can largely decrease the mechanical strength of the graphene (Tserpes and Vatistas, 2015) and promote the formation of covalent bonds between the graphene with the diamond tip and between the graphene and the DLC film. As a result, the diamond tip can easily tear the graphene with the degraded mechanical strength even at a small h , thus leading to the increase of F_f . With the increase of the fraction of defects in graphene, more covalent bonds are formed, thus causing a higher F_f even at a small h .

At a large h , F_f is almost same regardless of the fraction of defects in graphene. This is because at the large h the structure of the graphene has been significantly damaged. The scratching actually happens as the diamond tip directly scratching the DLC film regardless of the presence of the graphene.

Fig. 6.8. (a) The contact configuration of the system with 10% defects in graphene, (b) the effect of the defects of graphene on the friction force F_f and (c) its dependence on the normal force F_n for the DLC film when single graphene layer is used.

The presence of defects in the graphene can also influence the dependence of F_f on F_n , as shown in Fig. 6.8c. For $F_n < 250$ N, a larger fraction of defects can induce a higher F_f , due to the formation of more covalent bonds at the sliding interfaces. However, this F_f is still lower than that for the DLC film without the graphene in Fig. 6.7a. This is attributed to that the F_n is not large enough to highly damage the structure of graphene and thus the graphene can still isolate the diamond tip and the film. Hence, the graphene with defects can still lubricate the film at a small F_n .

Moreover, Fig. 6.8c shows that when the F_n is larger than 250 N, the F_f for graphene with different fractions of defects almost reaches the F_f of the DLC film without graphene (Fig. 6.6a). This is because the diamond tip directly scratches the film after the thorough damage of the graphene structure.

In general, graphene can significantly reduce the friction of the DLC films regardless of the presence of their H-passivations and eliminate their composition dependence of friction behavior. Moreover, the chemical inertness of the graphene indicates that it may help to control the environment sensitivities of friction behaviors of the DLC films. The reduction of such sensitivities by graphene will be further studied in the future.

6.3. Summary

The lubrication of graphene for DLC films scratched by a diamond tip is simulated by MD simulation. The effect of factors including layer number of graphene, its boundary conditions and defects on the friction behavior of the film is studied. The graphene can lubricate the film with and without H-passivations by preventing the formation of covalent bonds between it and the diamond tip. Under a small normal force F_n , superlow friction

force F_f is present and dominated by the puckering effect of the graphene. However, under a large F_n , the F_f highly increases, due to the tribochemical reactions of the graphene that cause the formation of covalent bonds between the graphene and the diamond tip and between the graphene and the DLC film, respectively. These bonds help the diamond tip to easily tear the graphene during the scratching.

The increase of layer number of graphene can significantly improve its lubrication performance, since the graphene with more layers is capable of keeping its chemical inertness at a much larger F_n . The presence of defects in graphene can degrade its lubrication performance, due to the fact that these defects can degrade its mechanical strength and increase its chemical activities. The pinned-boundary condition of the graphene can degrade its superlubrication and increase the F_f . It is suggested that the graphene with a large size is unsuitable to be solid lubricants. In general, both the DLC film with and without H-passivations exhibit lower F_f under the lubrication of the graphene. Therefore, it is concluded that the graphene can highly reduce the friction force of the DLC films and thus eliminate their composition independence of friction behaviors.

Chapter 7. Conclusions and recommendations

This chapter presents main conclusions and contributions based on the works conducted during this PhD study and also gives recommendations for future works.

7.1. Conclusions and contributions

MD simulation is conducted to investigate tribological behaviors of DLC films at the nanoscale. The effects of contact conditions including two-body and three-body on the friction force and wear performances of the films are considered. The effect of environmental H atoms is studied to explore the superlow-friction mechanisms of the films in H₂ atmosphere. Moreover, the lubrication of graphene for the films is evaluated to reduce the composition dependence of their friction behaviors. The main conclusions and contributions are listed as follows.

For the DLC film under the two-body contact conditions, its wear rate increases with the load which can induce a transition of wear from adhesive to abrasive. The friction force of the film follows the Bowden-Tabor model at a small load, but deviates from the model at a large load due to the formation of transfer layers. Since the formation of these layers is commonly regarded as the main factor inducing the low friction of the DLC film at the macroscale, the present work demonstrates that these macroscale friction mechanisms are still valid at the nanoscale. The high velocity can reduce the friction force and wear rate of the film by reducing sliding depth of the diamond tip and number of bonds at the contact interface. With the increase of surface roughness, abrasive wear is highly promoted, leading to that the friction force of the film increases while its wear rate firstly decreases

and then increases. A minimum wear rate is thereby observed, which is attributed to competitions between the adhesive and abrasive wear.

For the DLC film under three-body contact conditions, its friction and wear are determined by adhesion at a small load but dominated by both adhesion and ploughing at a large load. A high velocity can increase the friction of the film but reduce its wear, due to the response of its carbon networks to a high strain rate indicated by such velocity. The shape of the particle highly influences its movement mode and thus changes the friction and wear of the film. It is found that a small-sized particle can increase the friction and wear of the film by enhancing ploughing.

The environmental H atoms can significantly reduce friction force of the DLC films, and the reduction mechanisms depend on the friction temperature. At low friction temperatures, H atoms are concentrated near the contact interfaces, and their passivations highly reduce the interfacial adhesion, resulting in low friction forces. However, high friction temperature induces significant diffusions of H atoms and thermal expansions of the DLC film and also increases its graphitization level. As a result, a wide region with easy-shear properties is formed at the high friction temperature, thus inducing low friction forces. Therefore, it can be concluded that besides the passivation of the H atoms their diffusions are also responsible for the low friction of DLC films in the H₂ environment.

The graphene can efficiently lubricate the DLC film, and its lubrication performance can be improved by the increase of its layer number but degraded by its defects and the increase of its size. The friction mechanisms of the graphene during its lubrication highly depend on the normal force. Under a small normal force, superlow friction force that represents the superlubrication of the graphene is obtained due to its puckering effect.

Under a large normal force, the friction force increases due to the tribochemical reactions of the graphene. Such reactions happen before the rupture of graphene, which indicates the limitations of the superlubrication of the graphene in a realistic situation.

7.2. Recommendations

It has been discussed that the tribological behaviors of the DLC films can be influenced by many factors such as testing parameters and environment. Such influences highly complicate the tribological mechanisms of these films and induce the instability of their friction and wear and degrade their reliabilities. Future works are recommended here to understand such complicated mechanisms of the DLC films at the nanoscale.

Firstly, the effect of doping elements on the tribological behaviors of DLC films should be investigated. The films in this PhD study are pure and intact, thus exhibiting relatively simple tribological mechanisms. Experimentally, different elements such as titanium, silicon and silver have been doped into the DLC films to improve their mechanical properties. These films with doping elements may exhibit a nanocrystalline structure. Such structure can possess different mechanical strengths as compared to the carbon matrix and highly influence the graphitization of the films and thus the generation of wear debris. Moreover, during the friction process, the high friction temperature and mechanical mixing can cause the diffusions of the doping elements. These diffusions would largely change the properties at the contact interfaces and thus influence the mechanical properties in the subsurface of the DLC films.

Secondly, it is of significance to investigate the effect of active gas on the tribological behaviors of DLC films. The active gases such as oxygen and water vapor can induce

tribochemical reactions at the contact interface between the films and their counterparts. The experimental studies have demonstrated that such reactions can highly influence the formation of transfer layers and their shear properties and thus change the friction mechanisms of the DLC films. Simulation of these tribochemical reactions can help to uncover the mechanisms underlying the experimental observations.

Thirdly, the effects of multiple particles on the tribological behavior of DLC films should be considered. When the multiple particles are present, the tribological mechanisms of the films are influenced not only by the interactions between films and particles but also by the interactions between the particles. Such interactions highly depend on the particle size, shape and mechanical properties. These interactions can cause the particle fragmentations which highly influence the contact stress of the DLC films and their wear mechanisms.

Finally, the lubrication of other low-dimensional materials may also help to reduce the sensitivity of the DLC films to their compositions and the test environment. The low-dimensional materials such as carbon nanotube (CNT) and fullerene can work as lubricants of the films and are capable of reducing their friction and wear. Moreover, these materials have excellent chemical inertness and can highly reduce the chemical sensitivities of the DLC films, leading to the stabilization of their friction and wear.

References

- Aghdam A and Khonsari M. 2011. On the correlation between wear and entropy in dry sliding contact. *Wear* 270: 781-790.
- Akamine S, Barrett R and Quate C. 1990. Improved atomic force microscope images using microcantilevers with sharp tips. *Appl Phys Lett* 57: 316-318.
- Alexander S. 1998. Amorphous solids: their structure, lattice dynamics and elasticity. *Physics reports* 296: 65-236.
- Amiri M and Khonsari MM. 2010. On the thermodynamics of friction and wear—A review. *Entropy* 12: 1021-1049.
- Anantheshwara K, Lockwood A, Mishra RK, Inkson B and Bobji M. 2012. Dynamical evolution of wear particles in nanocontacts. *Tribology Letters* 45: 229-235.
- Andersson J, Erck R and Erdemir A. 2003a. Friction of diamond-like carbon films in different atmospheres. *Wear* 254: 1070-1075.
- Andersson J, Erck R and Erdemir A. 2003b. Frictional behavior of diamondlike carbon films in vacuum and under varying water vapor pressure. *Surface and Coatings Technology* 163: 535-540.
- Archard J. 1953. Contact and rubbing of flat surfaces. *J Appl Phys* 24: 981-988.
- Archard J. 1980. Wear theory and mechanisms. *Wear Control Handbook* 58.
- Bai L, Qi J, Lu Z, Zhang G, Wang L, Wang Y, Wu Z and Yan P. 2013. Theoretical Study on Tribological Mechanism of Solid Lubricating Films in a Sand–Dust Environment. *Tribology Letters* 49: 545-551.
- Bai L, Sha Z-D, Srikanth N, Pei Q-X, Wang X, Srolovitz DJ and Zhou K. 2015. Friction between silicon and diamond at the nanoscale. *Journal of Physics D: Applied Physics* 48: 255303.
- Bai L, Srikanth N, Wu H, Liu F, Liu B and Zhou K. 2016a. Effect of environmental hydrogen atoms on the tribological behaviors of diamond-like carbon films. *Tribology International* 99: 258-266.
- Bai L, Srikanth N, Wu H, Liu Y, Liu B and Zhou K. 2016b. Investigation on tensile behaviors of diamond-like carbon films. *J Non-Cryst Solids* 443: 8-16.
- Bai L, Zhang G, Lu Z, Wu Z, Wang Y, Wang L and Yan P. 2011. Tribological mechanism of hydrogenated amorphous carbon film against pairs: a physical description. *J Appl Phys* 110: 033521.

- Bai S, Onodera T, Nagumo R, Miura R, Suzuki A, Tsuboi H, Hatakeyama N, Takaba H, Kubo M and Miyamoto A. 2012. Friction reduction mechanism of hydrogen-and fluorine-terminated diamond-like carbon films investigated by molecular dynamics and quantum chemical calculation. *The Journal of Physical Chemistry C* 116: 12559-12565.
- Bera B. 2013. Adhesive wear theory of micromechanical surface contact. *Int J Comput Eng Res* 3: 73-78.
- Berman D, Erdemir A and Sumant AV. 2013a. Few layer graphene to reduce wear and friction on sliding steel surfaces. *Carbon* 54: 454-459.
- Berman D, Erdemir A and Sumant AV. 2013b. Reduced wear and friction enabled by graphene layers on sliding steel surfaces in dry nitrogen. *Carbon* 59: 167-175.
- Berman D, Erdemir A and Sumant AV. 2014. Graphene: a new emerging lubricant. *Materials Today* 17: 31-42.
- Bhaskaran H, Gotsmann B, Sebastian A, Drechsler U, Lantz MA, Despont M, Jaroenapibal P, Carpick RW, Chen Y and Sridharan K. 2010. Ultralow nanoscale wear through atom-by-atom attrition in silicon-containing diamond-like carbon. *Nature nanotechnology* 5: 181-185.
- Bhushan B. 1980. Stick-slip induced noise generation in water-lubricated compliant rubber bearings. *Journal of lubrication technology* 102: 201-210.
- Bhushan B 1998. *Handbook of micro/nano tribology*. CRC press, Boca Raton.
- Bhushan B. 1999. Nanoscale tribophysics and tribomechanics. *Wear* 225: 465-492.
- Bhushan B 2000. *Modern tribology handbook*, two volume set. CRC press, Boca Raton.
- Bhushan B. 2005. Nanotribology and nanomechanics. *Wear* 259: 1507-1531.
- Bhushan B 2012. *Fundamentals of tribology and bridging the gap between the macro-and micro/nanoscales*. n. 10: Springer Science & Business Media, Berlin.
- Bhushan B 2013a. *Introduction to tribology*. John Wiley & Sons, New York.
- Bhushan B. 2013b. Wear and mechanical characterisation on micro-to picoscales using AFM. *International materials reviews*.
- Bhushan B, Davis RE and Kolar HR. 1985. Metallurgical re-examination of wear modes II: Adhesive and abrasive. *Thin Solid Films* 123: 113-126.
- Bhushan B, Israelachvili JN and Landman U. 1995. Nanotribology: friction, wear and lubrication at the atomic scale. *Nature* 374: 607-616.
- Bhushan B and Kulkarni AV. 1996. Effect of normal load on microscale friction

measurements. *Thin Solid Films* 278: 49-56.

Bhushan B and Kwak KJ. 2007. Velocity dependence of nanoscale wear in atomic force microscopy. *Appl Phys Lett* 91: 163113.

Bhushan B and Nosonovsky M. 2004. Comprehensive model for scale effects in friction due to adhesion and two-and three-body deformation (plowing). *Acta materialia* 52: 2461-2474.

Bhushan B and Sundararajan S. 1998. Micro/nanoscale friction and wear mechanisms of thin films using atomic force and friction force microscopy. *Acta Materialia* 46: 3793-3804.

Bisson E 1969. Various modes of wear and their controlling factors. *Evaluation of Wear Testing*: ASTM International.

Bowden F and Tabor D. 1942. Mechanism of metallic friction. *Nature* 150: 197-199.

Bowden FP and Tabor D 1973. *Friction: an introduction to tribology*. RE Krieger Publishing Company, Florida.

Braun O and Naumovets A. 2006. Nanotribology: Microscopic mechanisms of friction. *Surface Science Reports* 60: 79-158.

Brenner DW, Shenderova OA, Harrison JA, Stuart SJ, Ni B and Sinnott SB. 2002. A second-generation reactive empirical bond order (REBO) potential energy expression for hydrocarbons. *Journal of Physics: Condensed Matter* 14: 783.

Bull S. 1995. Tribology of carbon coatings: DLC, diamond and beyond. *Diamond and related materials* 4: 827-836.

Car R. 1996. A microscopic model for surface-induced diamond-to-graphite transitions. *Nature* 379: 8.

Chacham H and Kleinman L. 2000. Instabilities in diamond under high shear stress. *Phys Rev Lett* 85: 4904.

Charitidis C. 2010. Nanomechanical and nanotribological properties of carbon-based thin films: a review. *International Journal of Refractory Metals and Hard Materials* 28: 51-70.

Chattoraj J, Caroli C and Lemaître A. 2010. Universal additive effect of temperature on the rheology of amorphous solids. *Phys Rev Lett* 105: 266001.

Chen Y-N, Ma T-B, Chen Z, Hu Y-Z and Wang H. 2015. Combined Effects of Structural Transformation and Hydrogen Passivation on the Frictional Behaviors of Hydrogenated Amorphous Carbon Films. *The Journal of Physical Chemistry C* 119: 16148-16155.

Cho M. 2009. The role of transfer film and back transfer behavior on the tribological performance of polyoxymethylene in sliding. *Journal of Mechanical science and*

Technology 23: 2291-2298.

Chung K-H and Kim D-E. 2003. Fundamental investigation of micro wear rate using an atomic force microscope. *Tribology Letters* 15: 135-144.

Chung PW. 2006. Theoretical prediction of stress-induced phase transformations of the second kind in graphene. *Physical Review B* 73: 075433.

Coulomb CA 1821. *Theorie des machines simples: en ayant egard au frottement de leurs parties et a la roideur des cordages*. Bachelier.

Czichos H and Habig K-H 2010. *Tribologie-Handbuch: Tribometrie, Tribomaterialien, Tribotechnik*. Springer-Verlag, Berlin.

D'acunto M. 2004. Theoretical approach for the quantification of wear mechanisms on the nanoscale. *Nanotechnology* 15: 795.

De Barros' Bouchet M, Martin J, Le-Mogne T and Vacher B. 2005. Boundary lubrication mechanisms of carbon coatings by MoDTC and ZDDP additives. *Tribology International* 38: 257-264.

Dong Y, Li Q and Martini A. 2013a. Molecular dynamics simulation of atomic friction: A review and guide. *Journal of Vacuum Science & Technology A: Vacuum, Surfaces, and Films* 31: 030801-030801-030824.

Dong Y, Li Q and Martini A. 2013b. Molecular dynamics simulation of atomic friction: A review and guide. *Journal of Vacuum Science & Technology A* 31: 030801.

Dong Y, Vadakkepatt A and Martini A. 2011. Analytical models for atomic friction. *Tribology Letters* 44: 367-386.

Donnet C. 1998. Recent progress on the tribology of doped diamond-like and carbon alloy coatings: a review. *Surface and Coatings Technology* 100: 180-186.

Donnet C and Erdemir A 2007. *Tribology of diamond-like carbon films: fundamentals and applications*. Springer Science & Business Media, Berlin.

Donnet C, Fontaine J, Grill A and Le Mogne T. 2001. The role of hydrogen on the friction mechanism of diamond-like carbon films. *Tribology Letters* 9: 137-142.

Dowson D 1979. *History of tribology*. Addison-Wesley Longman Limited, Toronto.

Eder S, Feldbauer G, Bianchi D, Cihak-Bayr U, Betz G and Vernes A. 2015. Applicability of macroscopic wear and friction laws on the atomic length scale. *Physical review letters* 115: 025502.

Enke K, Dimigen H and Hübsch H. 1980. Frictional properties of diamondlike carbon layers. *Appl Phys Lett* 36: 291-292.

- Erdemir A. 2004. Genesis of superlow friction and wear in diamondlike carbon films. *Tribology International* 37: 1005-1012.
- Erdemir A and Donnet C. 2006. Tribology of diamond-like carbon films: recent progress and future prospects. *Journal of Physics D: Applied Physics* 39: R311.
- Erdemir A, Eryilmaz O and Kim S. 2014. Effect of tribochemistry on lubricity of DLC films in hydrogen. *Surface and Coatings Technology* 257: 241-246.
- Erdemir A, Eryilmaz O, Nilufer I and Fenske G. 2000. Synthesis of superlow-friction carbon films from highly hydrogenated methane plasmas. *Surface and Coatings Technology* 133: 448-454.
- Family F, Hentschel H and Braiman Y. 2000. Friction at the nanoscale. *The Journal of Physical Chemistry B* 104: 3984-3987.
- Fang L, Zhao J, Li B and Sun K. 2009. Movement patterns of ellipsoidal particle in abrasive flow machining. *Journal of Materials Processing Technology* 209: 6048-6056.
- Ferrari A, Kleinsorge B, Morrison N, Hart A, Stolojan V and Robertson J. 1999. Stress reduction and bond stability during thermal annealing of tetrahedral amorphous carbon. *J Appl Phys* 85: 7191-7197.
- Filleter T, Mcchesney JL, Bostwick A, Rotenberg E, Emtsev K, Seyller T, Horn K and Bennewitz R. 2009. Friction and dissipation in epitaxial graphene films. *Phys Rev Lett* 102: 086102.
- Fontaine J, Belin M, Le Mogne T and Grill A. 2004. How to restore superlow friction of DLC: the healing effect of hydrogen gas. *Tribology International* 37: 869-877.
- Fontaine J, Donnet C, Grill A and Lemogne T. 2001. Tribochemistry between hydrogen and diamond-like carbon films. *Surface and Coatings Technology* 146: 286-291.
- Fontaine J, Loubet J, Mogne TL and Grill A. 2004. Superlow friction of diamond-like carbon films: a relation to viscoplastic properties. *Tribology Letters* 17: 709-714.
- Fouvry S, Liskiewicz T, Kapsa P, Hannel S and Sauger E. 2003. An energy description of wear mechanisms and its applications to oscillating sliding contacts. *Wear* 255: 287-298.
- Fujisawa S, Sugawara Y, Ito S, Mishima S, Okada T and Morita S. 1993. The two-dimensional stick-slip phenomenon with atomic resolution. *Nanotechnology* 4: 138.
- Gao G, Mikulski PT and Harrison JA. 2002. Molecular-scale tribology of amorphous carbon coatings: effects of film thickness, adhesion, and long-range interactions. *J Am Chem Soc* 124: 7202-7209.
- Gilman JJ. 1995. Mechanism of shear-induced metallization. *Czech J Phys* 45: 913-919.

- Gnecco E, Bennewitz R and Meyer E. 2002. Abrasive wear on the atomic scale. *Phys Rev Lett* 88: 215501.
- Gogotsi YG, Kailer A and Nickel KG. 1998. Pressure-induced phase transformations in diamond. *J Appl Phys* 84: 1299-1304.
- Gogotsi YG, Kailer A and Nickel KG. 1999. Materials: transformation of diamond to graphite. *Nature* 401: 663-664.
- Gotsmann B and Lantz MA. 2008. Atomistic wear in a single asperity sliding contact. *Phys Rev Lett* 101: 125501.
- Grill A. 1997. Tribology of diamondlike carbon and related materials: an updated review. *Surface and Coatings Technology* 94: 507-513.
- Gupta B, Malshe A, Bhushan B and Subramaniam VV. 1994. Friction and wear properties of chemomechanically polished diamond films. *Journal of tribology* 116: 445-453.
- Harrison A, Huggett R and Handley R. 1979. A correlation between abrasion resistance and other properties of some acrylic resins used in dentistry. *Journal of biomedical materials research* 13: 23-34.
- Harrison JA, Schall JD, Knippenberg MT, Gao G and Mikulski PT. 2008. Elucidating atomic-scale friction using molecular dynamics and specialized analysis techniques. *Journal of Physics: Condensed Matter* 20: 354009.
- Hauert R. 2004. An overview on the tribological behavior of diamond-like carbon in technical and medical applications. *Tribology International* 37: 991-1003.
- Hayashi K, Tezuka K, Ozawa N, Shimazaki T, Adachi K and Kubo M. 2011. Tribochemical reaction dynamics simulation of hydrogen on a diamond-like carbon surface based on tight-binding quantum chemical molecular dynamics. *The Journal of Physical Chemistry C* 115: 22981-22986.
- Hod O. 2012. Interlayer commensurability and superlubricity in rigid layered materials. *Physical Review B* 86: 075444.
- Holm R 2013. *Electric contacts: theory and application*. Springer Science & Business Media, Berlin.
- Holmberg K and Mathews A. 1994. Coatings tribology: a concept, critical aspects and future directions. *Thin Solid Films* 253: 173-178.
- Hu X and Martini A. 2015. Atomistic simulation of the effect of roughness on nanoscale wear. *Computational Materials Science* 102: 208-212.
- Hu Y-Z, Ma T-B and Wang H. 2013. Energy dissipation in atomic-scale friction. *Friction* 1: 24-40.

- Hutchinson, J.W. and Neale, K. W. 1977. Influence of strain-rate sensitivity on necking under uniaxial tension. *Acta Metallurgica* 25: 839-846.
- Irmer G and Dorner-Reisel A. 2005. Micro-Raman Studies on DLC coatings. *Advanced Engineering Materials* 7: 694-705.
- Jacobs TD, Ryan KE, Keating PL, Grierson DS, Lefever JA, Turner KT, Harrison JA and Carpick RW. 2013. The effect of atomic-scale roughness on the adhesion of nanoscale asperities: A combined simulation and experimental investigation. *Tribology Letters* 50: 81-93.
- Jost P. 1976. Economic impact of tribology. *Proc Mechanical Failures Prevention Group*: 117-139.
- Khrushchov M. 1974. Principles of abrasive wear. *Wear* 28: 69-88.
- Kim H-J and Kim D-E. 2009. Nano-scale friction: a review. *International Journal of Precision Engineering and Manufacturing* 10: 141-151.
- Kim H, Lince J, Eryilmaz O and Erdemir A. 2006. Environmental effects on the friction of hydrogenated DLC films. *Tribology Letters* 21: 51-56.
- Kimock FM and Knapp BJ. 1993. Commercial applications of ion beam deposited diamond-like carbon (DLC) coatings. *Surface and Coatings Technology* 56: 273-279.
- Klemenzt A, Pastewka L, Balakrishna SG, Caron A, Bennewitz R and Moseler M. 2014. Atomic Scale Mechanisms of Friction Reduction and Wear Protection by Graphene. *Nano letters* 14: 7145-7152.
- Kulchitsky-Zhyhailo R and Bajkowski A. 2012. Analytical and numerical methods of solution of three-dimensional problem of elasticity for functionally graded coated half-space. *International Journal of Mechanical Sciences* 54: 105-112.
- Kunze T, Posselt M, Gemming S, Seifert G, Konicek AR, Carpick RW, Pastewka L and Moseler M. 2014. Wear, plasticity, and rehybridization in tetrahedral amorphous carbon. *Tribology Letters* 53: 119-126.
- Lee C, Li Q, Kalb W, Liu X-Z, Berger H, Carpick RW and Hone J. 2010. Frictional characteristics of atomically thin sheets. *Science* 328: 76-80.
- Lee W, Cho K and Jang H. 2009. Molecular dynamics simulation of rolling friction using nanosize spheres. *Tribology Letters* 33: 37-43.
- Li J 2005. Basic molecular dynamics. *Handbook of Materials Modeling*: Springer, p. 565-588.
- Li Q, Lee C, Carpick RW and Hone J. 2010. Substrate effect on thickness-dependent friction on graphene. *physica status solidi (b)* 247: 2909-2914.

- Lin E-Q, Niu L-S, Shi H-J and Duan Z. 2012. Molecular dynamics simulation of nano-scale interfacial friction characteristic for different tribopair systems. *Applied Surface Science* 258: 2022-2028.
- Ling F, Bryant M and Doelling K. 2002. On irreversible thermodynamics for wear prediction. *Wear* 253: 1165-1172.
- Liu H and Bhushan B. 2002. Investigation of nanotribological properties of self-assembled monolayers with alkyl and biphenyl spacer chains. *Ultramicroscopy* 91: 185-202.
- Liu J, Grierson D, Moldovan N, Notbohm J, Li S, Jaroenapibal P, O'connor S, Sumant A, Neelakantan N and Carlisle J. 2010. Preventing nanoscale wear of atomic force microscopy tips through the use of monolithic ultrananocrystalline diamond probes. *Small* 6: 1140-1149.
- Liu X, Pu J, Wang L and Xue Q. 2013. Novel DLC/ionic liquid/graphene nanocomposite coatings towards high-vacuum related space applications. *Journal of Materials Chemistry A* 1: 3797-3809.
- Liu X, Wang L, Lu Z and Xue Q. 2012. Vacuum tribological performance of DLC-based solid-liquid lubricating coatings: influence of sliding mating materials. *Wear* 292: 124-134.
- Liu X, Wang L and Xue Q. 2011a. DLC-based solid-liquid synergetic lubricating coatings for improving tribological behavior of boundary lubricated surfaces under high vacuum condition. *Wear* 271: 889-898.
- Liu X, Wang L and Xue Q. 2011b. A novel carbon-based solid-liquid duplex lubricating coating with super-high tribological performance for space applications. *Surface and Coatings Technology* 205: 2738-2746.
- Liu Y, Erdemir A and Meletis E. 1996a. An investigation of the relationship between graphitization and frictional behavior of DLC coatings. *Surface and Coatings Technology* 86: 564-568.
- Liu Y, Erdemir A and Meletis E. 1996b. A study of the wear mechanism of diamond-like carbon films. *Surface and Coatings Technology* 82: 48-56.
- Liu Y and Meletis E. 1997. Evidence of graphitization of diamond-like carbon films during sliding wear. *Journal of Materials Science* 32: 3491-3495.
- Ma T-B, Hu Y-Z and Wang H. 2009. Molecular dynamics simulation of shear-induced graphitization of amorphous carbon films. *Carbon* 47: 1953-1957.
- Ma T-B, Hu Y-Z, Xu L, Wang L-F and Wang H. 2011. Shear-induced lamellar ordering and interfacial sliding in amorphous carbon films: A superlow friction regime. *Chem Phys Lett* 514: 325-329.
- Ma T-B, Wang L-F, Hu Y-Z, Li X and Wang H. 2014. A shear localization mechanism for

lubricity of amorphous carbon materials. Scientific reports 4.

Ma X-G, Komvopoulos K, Wan D, Bogy D and Kim Y-S. 2003. Effects of film thickness and contact load on nanotribological properties of sputtered amorphous carbon thin films. *Wear* 254: 1010-1018.

Machado TH and Cavalca KL. 2015. Modeling of hydrodynamic bearing wear in rotor-bearing systems. *Mechanics Research Communications*: 15-23.

Mao T, Wang H and Hu Y 2010. Friction between Diamond-Like Carbon (DLC) Films—a Molecular Dynamics Study. *Advanced Tribology*: Springer, p. 554-555.

Mate CM, McClelland GM, Erlandsson R and Chiang S 1987. Atomic-scale friction of a tungsten tip on a graphite surface. *Scanning Tunneling Microscopy*: Springer, p. 226-229.

Meng X, Li M, Xing Y and Bai Z. 2014. A MECHANICAL MODEL FOR SELF-ASSEMBLED GRAPHENE AROUND NANOTUBE. *International Journal of Applied Mechanics* 06: 1450036.

Miura K, Kamiya S and Sasaki N. 2003. C 60 molecular bearings. *Phys Rev Lett* 90: 055509.

Miyake S, Saito T, Yasuda Y, Okamoto Y and Kano M. 2004. Improvement of boundary lubrication properties of diamond-like carbon (DLC) films due to metal addition. *Tribology International* 37: 751-761.

Mo Y, Turner KT and Szlufarska I. 2009. Friction laws at the nanoscale. *Nature* 457: 1116-1119.

Moore M. 1974. A review of two-body abrasive wear. *Wear* 27: 1-17.

Moseler M, Gumbsch P, Casiraghi C, Ferrari AC and Robertson J. 2005. The ultrasmoothness of diamond-like carbon surfaces. *Science* 309: 1545-1548.

Myers N. 1962. Characterization of surface roughness. *Wear* 5: 182-189.

Nair RP and Zou M. 2008. Surface-nano-texturing by aluminum-induced crystallization of amorphous silicon. *Surface and Coatings Technology* 203: 675-679.

Paulmier D, Zaidi H, Nery H, Le Huu T and Mathia T. 1993. Tribological behaviour of diamond-like coatings: effect of active gases in atomic and molecular states. *Surface and Coatings Technology* 62: 570-576.

Peng X, Barber Z and Clyne T. 2001. Surface roughness of diamond-like carbon films prepared using various techniques. *Surface and Coatings Technology* 138: 23-32.

Pham DC, Na K, Yang S, Kim J and Yoon E-S. 2010. Nanotribological properties of silicon nano-pillars coated by a Z-DOL lubricating film. *Journal of mechanical science and*

technology 24: 59-65.

Plimpton S. 1995. Fast parallel algorithms for short-range molecular dynamics. *Journal of computational physics* 117: 1-19.

Plimpton S, Crozier P and Thompson A. 2007. LAMMPS-large-scale atomic/molecular massively parallel simulator. Sandia National Laboratories 18.

Podgornik B, Hren D and Vižintin J. 2005. Low-friction behaviour of boundary-lubricated diamond-like carbon coatings containing tungsten. *Thin Solid Films* 476: 92-100.

Podgornik B, Jacobson S and Hogmark S. 2003. Influence of EP and AW additives on the tribological behaviour of hard low friction coatings. *Surface and Coatings Technology* 165: 168-175.

Podgornik B, Jacobson S and Hogmark S. 2005. Influence of EP additive concentration on the tribological behaviour of DLC-coated steel surfaces. *Surface and Coatings Technology* 191: 357-366.

Qi J, Liu H, Luo Y, Zhang D and Wang Y. 2014. Influences of added sand-dust particles on the tribological performance of graphite-like coating under solid-liquid lubrication. *Tribology International* 71: 69-81.

Qi J, Wang L, Wang Y, Pu J, Yan F and Xue Q. 2011a. The tribological performance of selected solid lubricant films in sand-dust environments. *Wear* 271: 899-910.

Qi J, Wang L, Yan F and Xue Q. 2010. Ultra-high tribological performance of magnetron sputtered aC: H films in sand-dust environment. *Tribology letters* 38: 195-205.

Qi J, Wang L, Yan F and Xue Q. 2011b. Comparative study of microstructure and tribological behavior of TiC/a-C: H and a-C: H coatings in a sand-dust environment. *Surface and Interface Analysis* 43: 836-846.

Rabinowicz E. 1965. *Friction and wear of materials*. John Wiley & Sons, New York.

Rabinowicz E, Dunn L and Russell P. 1961. A study of abrasive wear under three-body conditions. *Wear* 4: 345-355.

Ramalho A and Miranda J. 2006. The relationship between wear and dissipated energy in sliding systems. *Wear* 260: 361-367.

Rapaport DC 2004. *The art of molecular dynamics simulation*. Cambridge university press, Cambridge. .

Reynolds JF, Smith DMS, Lambin EF, Turner B, Mortimore M, Batterbury SP, Downing TE, Dowlatabadi H, Fernández RJ and Herrick JE. 2007. Global desertification: building a science for dryland development. *Science* 316: 847-851.

- Rigney D and Hirth J. 1979. Plastic deformation and sliding friction of metals. *Wear* 53: 345-370.
- Robertson J. 2001. Ultrathin carbon coatings for magnetic storage technology. *Thin Solid Films* 383: 81-88.
- Rowe G. 1960. Some observations on the frictional behaviour of boron nitride and of graphite. *Wear* 3: 274-285.
- Ruan JA and Bhushan B. 1994. Frictional behavior of highly oriented pyrolytic graphite. *Journal of Applied Physics* 76: 8117-8120.
- Ryan KE, Keating PL, Jacobs TD, Grierson DS, Turner KT, Carpick RW and Harrison JA. 2014. Simulated adhesion between realistic hydrocarbon materials: effects of composition, roughness, and contact point. *Langmuir* 30: 2028-2037.
- Sanchez-Lopez J, Donnet C, Loubet J, Belin M, Grill A, Patel V and Jahnes C. 2001. Tribological and mechanical properties of diamond-like carbon prepared by high-density plasma. *Diam Relat Mater* 10: 1063-1069.
- Sandoz-Rosado EJ, Tertuliano OA and Terrell EJ. 2012. An atomistic study of the abrasive wear and failure of graphene sheets when used as a solid lubricant and a comparison to diamond-like-carbon coatings. *Carbon* 50: 4078-4084.
- Savvides N and Bell T. 1993. Hardness and elastic modulus of diamond and diamond-like carbon films. *Thin Solid Films* 228: 289-292.
- Schall JD, Gao G and Harrison JA. 2009. Effects of Adhesion and Transfer Film Formation on the Tribology of Self-Mated DLC Contacts†. *The Journal of Physical Chemistry C* 114: 5321-5330.
- Sha Z-D, Sorkin V, Branicio PS, Pei Q-X, Zhang Y-W and Srolovitz DJ. 2013. Large-scale molecular dynamics simulations of wear in diamond-like carbon at the nanoscale. *Appl Phys Lett* 103: 073118.
- Sha Z, Branicio P, Pei Q, Sorkin V and Zhang Y. 2013. A modified Tersoff potential for pure and hydrogenated diamond-like carbon. *Computational Materials Science* 67: 146-150.
- Shames IH 1997. Elastic and inelastic stress analysis. CRC Press, Boca Raton.
- Sharma SM, Karmakar S, Sikka S, Teredesai PV, Sood A, Govindaraj A and Rao C. 2001. Pressure-induced phase transformation and structural resilience of single-wall carbon nanotube bundles. *Physical Review B* 63: 205417.
- Sin H, Saka N and Suh N. 1979. Abrasive wear mechanisms and the grit size effect. *Wear* 55: 163-190.

- Singer I. 1994. Friction and energy dissipation at the atomic scale: A review. *Journal of Vacuum Science & Technology A* 12: 2605-2616.
- Smolyanitsky A, Killgore J and Tewary V. 2012. Effect of elastic deformation on frictional properties of few-layer graphene. *Physical Review B* 85: 035412.
- Stachowiak G and Batchelor AW 2013. *Engineering tribology*. Butterworth-Heinemann, Oxford.
- Stuart SJ, Tutein AB and Harrison JA. 2000. A reactive potential for hydrocarbons with intermolecular interactions. *The Journal of chemical physics* 112: 6472-6486.
- Stukowski A. 2009. Visualization and analysis of atomistic simulation data with OVITO—the Open Visualization Tool. *Modelling and Simulation in Materials Science and Engineering* 18: 015012.
- Stukowski A. 2010. Visualization and analysis of atomistic simulation data with OVITO—the Open Visualization Tool. *Modelling and Simulation in Materials Science and Engineering* 18: 015012.
- Suh NP. 1973. The delamination theory of wear. *Wear* 25: 111-124.
- Suh NP. 1977. An overview of the delamination theory of wear. *Wear* 44: 1-16.
- Sun J, Fang L, Han J, Han Y, Chen H and Sun K. 2013a. Abrasive wear of nanoscale single crystal silicon. *Wear* 307: 119-126.
- Sun K, Fang L, Yan Z and Sun J. 2013b. Atomistic scale tribological behaviors in nano-grained and single crystal copper systems. *Wear* 303: 191-201.
- Szlufarska I, Chandross M and Carpick RW. 2008. Recent advances in single-asperity nanotribology. *Journal of Physics D: Applied Physics* 41: 123001.
- Tagawa M, Ikemura M, Nakayama Y and Ohmae N. 2004. Effect of water adsorption on microtribological properties of hydrogenated diamond-like carbon films. *Tribology Letters* 17: 575-580.
- Tambe N and Bhushan B. 2005a. Nanowear mapping: a novel atomic force microscopy based approach for studying nanoscale wear at high sliding velocities. *Tribology Letters* 20: 83-90.
- Tambe NS and Bhushan B. 2004. Scale dependence of micro/nano-friction and adhesion of MEMS/NEMS materials, coatings and lubricants. *Nanotechnology* 15: 1561.
- Tambe NS and Bhushan B. 2005b. Friction model for the velocity dependence of nanoscale friction. *Nanotechnology* 16: 2309.
- Tambe NS and Bhushan B. 2005c. Nanoscale friction-induced phase transformation of

- diamond-like carbon. *Scripta materialia* 52: 751-755.
- Tao Z and Bhushan B. 2007. Velocity dependence and rest time effect on nanoscale friction of ultrathin films at high sliding velocities. *Journal of Vacuum Science & Technology A* 25: 1267-1274.
- Tersoff J. 1988. New empirical approach for the structure and energy of covalent systems. *Physical Review B* 37: 6991.
- Tersoff J. 1989. Modeling solid-state chemistry: Interatomic potentials for multicomponent systems. *Physical Review B* 39: 5566.
- Tserpes K and Vattistas I. 2015. Buckling analysis of pristine and defected graphene. *Mechanics Research Communications* 64: 50-56.
- Vanossi A, Manini N, Urbakh M, Zapperi S and Tosatti E. 2011. Modeling friction: from nano to meso scales. *arXiv preprint arXiv:11123234*.
- Vercammen K, Meneve J, Dekempeneer E, Smeets J, Roberts E and Eiden M. 1999. Study of RF PACVD diamond-like carbon coatings for space mechanism applications. *Surface and Coatings Technology* 120: 612-617.
- Wang L, Bai L, Lu Z, Zhang G and Wu Z. 2013. Influence of load on the tribological behavior of aC films: experiment and calculation coupling. *Tribology Letters* 52: 469-475.
- Wang X and Zhou K. 2014. An inclusion of arbitrary shape in an infinite or semi-infinite isotropic multilayered plate. *International Journal of Applied Mechanics* 6: 1450001.
- Wang Y, Wang J, Zhang G, Wang L and Yan P. 2012. Microstructure and tribology of TiC(Ag)/a-C:H nanocomposite coatings deposited by unbalanced magnetron sputtering. *Surface and Coatings Technology* 206: 3299-3308.
- 2007 IEEE Aerospace Conference, 2007. IEEE, 1-10 p.
- Xu S, Wan Q, Sha Z and Liu Z. 2015. Molecular dynamics simulations of nano-indentation and wear of the γ Ti-Al alloy. *Computational Materials Science* 110: 247-253.
- Yan Y, Geng Y and Hu Z. 2015. Recent advances in AFM tip-based nanomechanical machining. *International Journal of Machine Tools and Manufacture* 99: 1-18.
- Ye Z and Martini A. 2014. Atomistic simulation of the load dependence of nanoscale friction on suspended and supported graphene. *Langmuir* 30: 14707-14711.
- Yoon E-S, Singh RA, Oh H-J and Kong H. 2005. The effect of contact area on nano/micro-scale friction. *Wear* 259: 1424-1431.
- Yoon HM, Jung Y, Jun SC, Kondaraju S and Lee JS. 2015. Molecular dynamics simulations of nanoscale and sub-nanoscale friction behavior between graphene and a silicon tip: analysis of tip apex motion. *Nanoscale* 7: 6295-6303.

Zhang H-S, Endrino JL and Anders A. 2008. Comparative surface and nano-tribological characteristics of nanocomposite diamond-like carbon thin films doped by silver. *Applied Surface Science* 255: 2551-2556.

Zhang L and Tanaka H. 1997. Towards a deeper understanding of wear and friction on the atomic scale—a molecular dynamics analysis. *Wear* 211: 44-53.

Zhang L and Tanaka H. 1998. Atomic scale deformation in silicon monocrystals induced by two-body and three-body contact sliding. *Tribology International* 31: 425-433.

Zhang L and Tang C. 2013. Friction and wear of diamond–silicon nano-systems: Effect of moisture and surface roughness. *Wear* 302: 929-936.

Zhong J, Shakiba R and Adams JB. 2013. Molecular dynamics simulation of severe adhesive wear on a rough aluminum substrate. *Journal of Physics D: Applied Physics* 46: 055307.