Vol 17 No 8, August 2008
1674-1056/2008/17(08)/3035-05

Chinese Physics B

© 2008 Chin. Phys. Soc.
and IOP Publishing Ltd

Modelling of spreading process: effect from hydrogen bonds*

Li Xin(李 欣)[a], Hu Yuan-Zhong(胡元中)[b], and Jiang Lan(姜 澜)[a]

[a] *Department of Mechanical and Automation Engineering, 3rd School Beijing Institute of Technology, Beijing* 100081, *China*

[b] *The State Key Laboratory of Tribology, Tsinghua University, Beijing* 100084, *China*

(Received 19 February 2008; revised manuscript received 2 April 2008)

Lubricant spreading on solid substrates has drawn considerable attention not only for the microscopic wetting theory but also for the dramatic application in head-disk interface of magnetic storage drive systems. Molecular dynamic simulation based on a coarse-grained bead-spring model has been used to study such a spreading process. The spreading profiles indicate that the hydrogen bonds among lubricant molecules and the hydrogen bonds between lubricant molecules and polar atoms of solid substrates will complicate the spreading process in a tremendous degree. The hydrogen bonds among lubricant molecules will strengthen the lubricant combination intensity, which may hinder most molecules from flowing down to the substrates and diffusing along the substrates. And the hydrogen bonds between lubricant molecules and polar atoms of solid substrates will confine the lubricant molecules around polar atoms, which may hinder the molecules from diffusing along the substrates and cause precursor film to vanish.

Keywords: perfluoropolyether, molecular dynamic simulation, thin film lubrication, spreading
PACC: 7115Q, 6810G

1. Introduction

Starting with an initial droplet, liquids form a film on the top of a substrate: this is spreading.[1] In theoretical study, spreading can be classified into three regimes.[2,3] (1) The bulk spreading appears when the film thickness is larger than 1μm, which belongs to the macroscopic spreading. (2) The secondary spreading appears where there exist several molecular layers, which belongs to the microscopic spreading. In this regime, the disjoining pressure gradient is a main driving force. (3) The primary spreading appears when the film thickness is a monolayer or submonolayer. In this regime, the surface diffusion plays a dominating role. In experimental study, Heslot *et al*[4,5] found that there was a foot, corresponding to the precursor film, in the spreading of polydimethylsiloxane droplets and pointed out that the interactions between the lubricant molecules and substrates played a significant role in a spreading process. Cazabat *et al*[6] and Fraysse *et al*[7] studied the spreading behaviour of polydimethylsiloxane terminated with hydroxyl groups and pointed out that the functional endgroups played an important role in the spreading process.

Owing to the important application of perfluoropolyether (PFPE) in magnetic storage drive systems, lubricant spreading on solid substrates drew extensive attention.[8] Novotny[9] investigated the spreading of polyperfluoropropylene oxides on silica substrates and found that surface diffusion coefficient was independent of film thickness when film thickness was below 1 nm. O'Connor *et al*[10,11] studied the spreading of perfluoropolyether on silica substrates under different endgroup functionalities and molecular weights. They observed that the spreading profile of nonfunctional PFPE was smooth while the spreading profile of functional PFPE had a sharp boundary. Ma *et al*[12] studied the spreading of perfluoropolyether on amorphous carbon substrates and found a complex layered structure in the spreading profiles of functional PFPE. Waltman *et al*[13] investigated the interaction between functional PFPE and amorphous carbon substrates by using quantum chemical computations and found that the hydrogen bonds between lubricant endgroups and solid the substrates determined the liquid-solid adhesion.

*Project supported by the Specialized Research Fund for the Doctoral Program of Higher Education of China (Grant No 20060003025), the Science Foundation for Post Doctoral Research from the Ministry of Science and Technology of China (Grant No 20070420017), the 111 Project (Grant No B08043) and the National Natural Science Foundation of China (Grant No 50705009).
†E-mail: lixin02@bit.edu.cn

In this paper, molecular dynamics (MD) simulation[14] based on a coarse-grained bead-spring model is performed to examine the spreading process on solid substrates. Particularly, the hydrogen bonds among lubricant molecules and the hydrogen bonds between lubricant molecules and solid substrates are studied in detail.

2. Simulation model

In a real hard disk drive system, a random copolymer named perfluoropolyether (PFPE) is adopted as lubricant. The chemical structure of PFPE is X-[$(OCF_2CF_2)_p$-$(OCF_2)_q$]-O-X ($p/q \approx 2/3$). For nonfunctional PFPE, the endgroup X is $-CF_3$. And for the functional PFPE, the endgroup X is $-CF_2CH_2OH$.[15]

A coarse-grained bead-spring model is adopted to study the lubricant spreading on solid substrates.[16,17] In that model, a PFPE molecule is composed of a series of rigid beads which are connected freely. Beads are classified into backbone group and endgroup. Those bonded beads interact through a finitely extensible nonlinear elastic (FENE) potential. All the nonbonded beads interact through a truncated-shifted Lennard-Jones (LJ) potential. The endgroups interact with each other through the hydrogen bonds. That interaction among endgroups is described by an additional short-range exponential decay potential as follows:

$$U_{\mathrm{eb-eb}} = \begin{cases} -\varepsilon_{\mathrm{ee}} \exp\left(-\dfrac{r-r_0}{d}\right), & r \geq r_0, \\ \infty, & r < r_0, \end{cases} \tag{1}$$

where d is the characteristic length for the short range interaction, and $\varepsilon_{\mathrm{ee}}$ represents the potential well depth of endgroup–endgroup interaction.

The lubricant molecules interact with the solid substrates in a complex way.[18] The interaction between beads and solid substrates may be classified into the dispersive interaction, which shows the van der Waals interaction, and the functional interaction, which shows the hydrogen bonds interaction. The dispersive interaction is described by a 9–3 LJ potential as shown below:

$$U_{\mathrm{bb-substrate}}(z) = \begin{cases} \varepsilon_{\mathrm{w}} \left[\dfrac{1}{2}\left(\dfrac{\sigma}{z}\right)^9 - \dfrac{3}{2}\left(\dfrac{\sigma}{z}\right)^3\right], & z > 0, \\ \infty, & z < 0, \end{cases} \tag{2}$$

where σ is the LJ diameter of bead, z is the distance between bead and substrate, and ε_{w} represents the well depth of beads-substrate interaction. And we locate one layer of polar atoms at the position of solid surface (z=0) to introduce a functional interaction. The interaction between endgroups of lubricant molecules and polar atoms of solid substrates is described by an additional short-range exponential decay potential as follows:

$$U_{\mathrm{eb-subatom}} = \begin{cases} -\varepsilon_{\mathrm{esa}} \exp\left(-\dfrac{r-r_{cc}}{d}\right), & r \geq r_{\mathrm{cc}}, \\ \infty, & r < r_{\mathrm{cc}}, \end{cases} \tag{3}$$

where d is the characteristic length for the short range interaction, and $\varepsilon_{\mathrm{esa}}$ represents the potential well depth of endgroups–polar atoms interaction.

MD simulation with a canonical ensemble[19,20] is performed with a time step dt of 0.001τ, where$\tau = \sigma(m/\varepsilon)^{0.5}$ and the number of computing steps is 5×10^5. A modified Nose–Hoover chain thermostat[21] is adopted, and the spreading process is examined by using the following Newton's equations of motion:

$$m_i \dot{r}_i = p_i, \quad \text{and} \quad \dot{p}_i = F_i - \zeta(z) p_i, \tag{4}$$

where m_i, r_i and p_i are the mass, the position vector and the momentum of the ith bead respectively, F_i is the force acting on the ith bead, and $\zeta(z)$ represents the thermostat damp for the ith bead and is given as

$$\begin{aligned} \zeta(z) &= \zeta \exp(\sigma - z), \\ \dot{\zeta} &= \frac{1}{Q}\left(\sum_{i=1}^{N} p_i^2/m - g k_{\mathrm{B}} T\right), \end{aligned} \tag{5}$$

where z is the bead-substrate distance, ζ and Q represent the thermostat damp and the thermostat mass respectively, and T is the temperature expressed as $T = 1.0\varepsilon/k_{\mathrm{B}}$ with k_{B} being the Boltzmann constant.

3. Results and discussion

Figure 1 shows the spreading profiles of nonfunctional PFPE on nonpolar solid substrates at time t=100000, 300000, 400000 MD steps. The spreading exhibits a smooth profile with a precursor film, which accords with Tyndall's experimental results.[22] In the spreading process, several forms of molecule motions may occur: (1) molecules at the droplet boundary break away from the other molecules and flow down toward the substrates; (2) molecules in the front of

liquid diffuse along the solid substrates to form a precursor film; (3) molecules above the precursor film fill those cavities created by the precursor film diffusion.

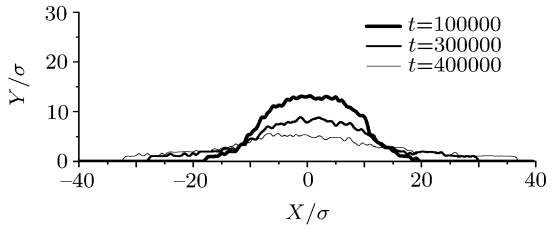


Fig.1. Thickness profiles at time t=100000, 300000, 400000 MD steps, where X is in the direction of spreading, Z is in the direction normal to the surface, with the interaction parameters being ε_{ee}=0, ε_{esa}=0 and ε_{w}=20ε.

Figure 2 shows the spreading profiles of functional PFPE on nonpolar solid substrates at time t=100000, 300000, 400000 MD steps. The spreading exhibits a steep profile with a shoulder and a precursor film. In the spreading process, the molecule motions are basically in a way similar to that of nonfunctional PFPE on nonpolar solid substrates. However, the spreading of functional PFPE exhibits a steeper profile and a slower spreading speed than that of nonfunctional PFPE under the same conditions.

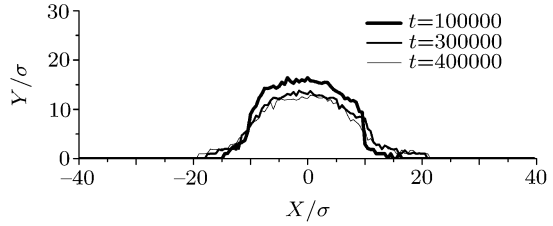


Fig.2. Thickness profiles at time t=100000, 300000, 400000 MD steps, where X is in the direction of spreading, Z is in the direction normal to the surface, with the interaction parameters being ε_{ee}=2ε, ε_{esa}=0 and ε_{w}=20ε.

Functional PFPE is terminated with hydroxyl groups. When those endgroups approach each other, the hydrogen bonds among lubricant molecules may form. The microstructures of PFPE film have validated that they have a dipolymer structure caused by the hydrogen bonds among lubricant molecules.[23] According to the coarse-grained bead-spring model, the hydrogen bonds will be described by the summation of the Lennard–Jones potential and the additional short-range exponential decay potential (Eq.1). Actually, clusters of endgroups are observed in the whole functional PFPE droplets in the spreading process (Fig.3), that is, there exist the hydrogen bonds among lubricant molecules in both the fluid region and the precursor film, which will greatly strengthen the lubricant combination intensity. Affected by the hydrogen bonds in the fluid region, lubricant molecules at the droplet boundary are bound together and can hardly break away from each other to flow down toward the substrates. Affected by the hydrogen bonds in the precursor film, lubricant molecules in the front of liquid are combined with other molecules to move along the substrates jointly, which may hinder surface diffusion and confine the formation of the precursor film.

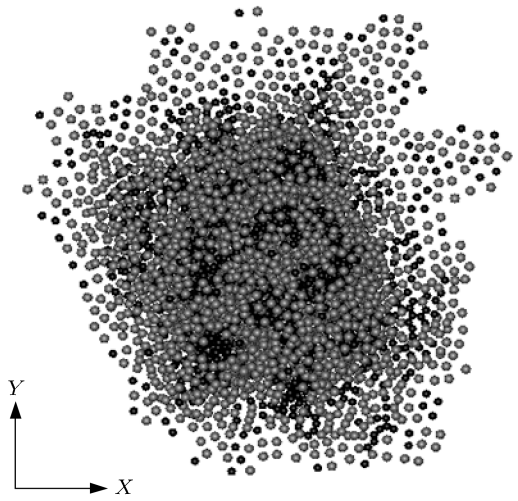


Fig.3. Spreading profile at time t=300000 MD steps, where XY are in the direction of spreading, the silver beads represent backbone groups and black beads refer to functional endgroups.

Figure 4 shows the spreading profiles of functional PFPE on polar solid substrates at time t=100000, 300000, 400000 MD steps. The spreading exhibits an extremely steep profile with a shoulder, which conforms with Ma's experimental results.[12] In the spreading process, the molecule motions may be classified into the same forms as those in nonfunctional PFPE on nonpolar solid substrates. However, the spreading of functional PFPE on polar solid substrates exhibits the steepest profile and the slowest spreading speed among the three instances under the same conditions, without any obvious appearance of precursor film.

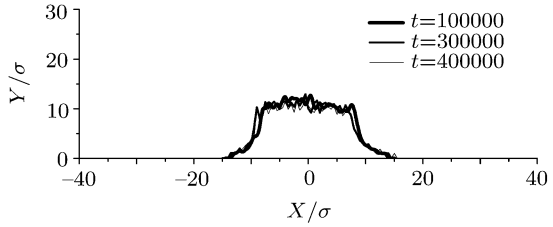


Fig.4. Thickness profiles at time t=100000, 300000, 400000 MD steps, where X is in the direction of spreading, and Z is in the direction normal to the surface, with the interaction parameters being $\varepsilon_{ee}=2\varepsilon$, $\varepsilon_{esa}=50\varepsilon$ and $\varepsilon_{w}=20\varepsilon$.

When the endgroups of lubricant molecules approach the polar solid substrates, the hydrogen bonds between lubricant molecules and polar atoms of solid substrates may form. According to the coarse-grained bead-spring model, the hydrogen bonds will be described by the summation of the 9–3 LJ potential (Eq.2) and the additional short-range exponential decay potential (Eq.3).

In our model, the PFPE molecule is composed of a sequence of rigid beads which are classified into backbone group and endgroup. The interaction between backbone group and substrate is described by the 9–3 LJ potential. And the interaction between endgroup and substrate is the summation of the 9–3 LJ potential and the additional short-range exponential decay potential. At early stages of spreading, when the shoulder profiles have not formed, lots of lubricant molecules are drawn down to the substrates. Here, the additional short-range interaction intensifies the attraction of the substrates for flowing-down lubricant molecules and accelerates these lubricant molecules flowing down. As time goes on, when the shoulder profiles gradually form, lubricant molecules, which are far from substrates, have to flow along the droplet boundary to the substrates. Here, the additional short-range interaction has little effect on the attraction of the substrates for the flowing-down lubricant molecules. However, the additional short-range interaction has a tremendous effect on the attraction of the polar atoms of the substrates for diffusive lubricant molecules. And the hydrogen bonds interaction is so strong that the endgroups of lubricant molecules are combined with polar atoms of solid substrates in a one-to-one way, that is, hydrogen bonds confine endgroups of functional PFPE molecules around the polar atoms of the substrates (Fig.5). Accordingly, the hydrogen bonds between lubricant molecules and polar atoms of solid substrates hinder the molecules from diffusing along the substrates and cause precursor film to vanish. Besides, they hinder the molecules from filling cavities because fewer cavities will be created by surface diffusion.

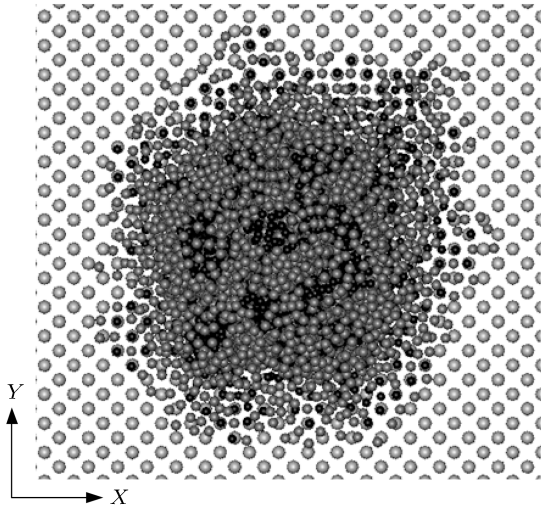


Fig.5. Spreading profile at time t=500000 MD steps, where XY are in the direction of spreading, the silver beads represent backbone groups, black beads refer to functional endgroups and white beads denote polar atoms of solid substrates.

The simulation results of functional PFPE spreading on polar solid substrates correspond to the instances such as functional PFPE on amorphous carbon surfaces.[12] Both simulation results and experimental results show that the spreading exhibits an extremely steep profile with a shoulder. And simulation results explain the experimental phenomenon well. In the surface layer of lubricant films, the hydrogen bonds between lubricant molecules and polar atoms of solid substrates will confine the lubricant molecules around polar atoms, which prevents the precursor film from forming. In the transition layer of lubricant films, lubricant molecules are attracted by substrates and partly break the hydrogen bonds among lubricant molecules to flow down, which help shoulder profiles to form. In the bulk region of lubricant films, the hydrogen bonds among lubricant molecules will strengthen the combination intensity of lubricant and hinder lubricant molecules from flowing down, which helps steep profiles to form.

4. Conclusion

The spreading of PFPE on solid substrates has been examined by using the molecular dynamics simulation. Particularly, the effects from the hydrogen

bonds among lubricant molecules and from the hydrogen bonds between lubricant molecules and polar atoms of solid substrates are studied in detail. The simulation results indicate that the hydrogen bonds among lubricant molecules take effect in both the fluid region and the precursor film. In the fluid region, they hinder lubricant molecules from flowing down to the substrates, while in the precursor film, they hinder lubricant molecules from diffusing along the substrates. And the hydrogen bonds between lubricant molecules and polar atoms of solid substrates will combine lubricant molecules with polar atoms of solid substrates in a one-to-one way, which may hinder the molecules from diffusing along the substrates and cause precursor film to vanish.

References

[1] Voue M and de Coninck J 2000 *Acta Mater* **48** 4405
[2] Teletzke G F, Davis H T and Scriven L E 1987 *Chem. Eng. Comm.* **55** 41
[3] Ivanov I B 1988 *Thin Liquid Films: Fundamentals and Applications* (New York: Dekker) p9
[4] Heslot F, Fraysse N and Cazabat A M 1989 *Nature* **338** 640
[5] Heslot F, Cazabat A M, Levinson P and Fraysse N 1990 *Phys. Rev. Lett.* **65** 599
[6] Cazabat A M, Fraysse N and Heslot F 1991 *Colloids and Surfaces* **52** 1
[7] Fraysse N, Valignat M P, Cazabat A M, Heslot F and Levinson P 1993 *J. Colloid Interface Sci.* **158** 27
[8] Bhushan B 2004 *Springer Handbook of Nanotechnology* (New York: Springer) p861
[9] Novotny V J 1990 *J. Chem. Phys.* **92** 3189
[10] O'Connor T M, Jhon M S, Bauer C L, Yoon B G and Karis T E 1995 *Tribology Letters* **1** 219
[11] O'Connor T M, Back Y R, Jhon M S, Yoon D Y and Karis T E 1996 *J. Appl. Phys.* **79** 5788
[12] Ma X, Gui J, Smoliar L, Grannen K, Marchon B, Bauer C L and Jhon M S 1999 *Phys. Rev.* E **59** 722
[13] Waltman R J, Tyndall G W and Pacansky J 1999 *Langmuir* **15** 6470
[14] Ma T B, Hu Y Z and Wang H 2007 *Acta Phys. Sin.* **56** 480 (in Chinese)
[15] Karis T E, Kim W T and Jhon M S 2005 *Tribology Letters* **18** 27
[16] Li X, Hu Y Z and Wang H 2006 *J. Appl. Phys.* **99** 024905
[17] Guo Q, Li L, Hsia Y and Jhon M S 2005 *J. Appl. Phys.* **97** 10P302
[18] Ma T B, Hu Y Z and Wang H 2006 *Acta Phys. Sin.* **55** 2922 (in chinese)
[19] Ma T B, Hu Y Z, Wang H and Li X 2007 *Phys. Rev.* B **75** 035425
[20] Ma T B, Hu Y Z, Wang H and Li X 2007 *J. Appl. Phys.* **101** 014901
[21] Braun O M and Peyrard M 2001 *Phys. Rev.* E **63** 046110
[22] Tyndall G W and Karis T E 1999 *Tribology Transactions* **42** 463
[23] Li X, Hu Y Z and Wang H 2005 *Acta Phys. Sin.* **54** 3787 (in Chinese)