Vol 15 No 4, April 2006
1009-1963/2006/15(04)/0818-04

Chinese Physics

© 2006 Chin. Phys. Soc.
and IOP Publishing Ltd

Molecular dynamic simulation of lubricant spreading: effect from the substrate and endbead*

Li Xin(李 欣), Hu Yuan-Zhong(胡元中),
Wang Hui(王 慧), and Yang Dong(杨 冬)

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

(Received 24 November 2005; revised manuscript received 26 December 2005)

Molecular dynamic simulations based on a coarse-grained, bead-spring model are adopted to investigate the spreading of both nonfunctional and functional perfluoropolyether (PFPE) on solid substrates. For nonfunctional PFPE, the spreading generally exhibits a smooth profile with a precursor film. The spreading profiles on different substrates are compared, which indicate that the bead-substrate interaction has a significant effect on the spreading behaviour, especially on the formation of the precursor film. For functional PFPE, the spreading generally exhibits a complicated terraced profile. The spreading profiles with different endbeads are compared, which indicate that the endbead-substrate interaction and the endbead–endbead interaction, especially the latter, have a significant effect on the spreading behaviour.

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

1. Introduction

The wetting and spreading of liquid films on solid substrates at the molecular scale has gained considerable attention for the technological applications of lubrication in data storage system.[1] At present, perfluoropolyether (PFPE) is available commercially to serve as the lubricant, which has the chemical structure of X–[$(OCF_2CF_2)_p$–$(OCF_2)_q$]–O–$X(p/q \cong 2/3)$. Here, the endbead X is $-CF_3$ (nonfunctional) for Z or $-CF_2CH_2OH$ (functional) for Zdol.[2] A considerable number of experiments were conducted to investigate the spreading profiles of both nonfunctional and functional PFPE.[3] Yet owing to the limitation of instruments, computer simulations were also performed. For example, quantum chemical computation was adopted to model the interactions between the PFPE and the carbon overcoat.[4] Monte Carlo approach was employed to examine the static structure of PFPE.[5] In this paper, molecular dynamic simulation based on a coarse-grained, bead-spring model is adopted to investigate the spreading of both nonfunctional and functional PFPE on solid substrates. Especially, the spreading profiles of PFPE on different substrates and with different endbeads are compared, this comparison reveals the effects from the substrate and endbead on the spreading behaviour.

2. Model and simulation method

A coarse-grained, bead-spring model developed by Guo[6,7] is used in this study to characterize the nonfunctional and functional PFPE films. In this model, a PFPE molecule is described as a sequence of beads which are bonded by finitely extensible nonlinear elastic potential. All the nonbonded beads interact with each other by Lennard-Jones potential. And all the beads interact with the substrate by 9–3 Lennard-Jones potential. For functional PFPE, the endbeads interact with the substrate or other endbeads by short-range exponential potential. It has to be remarked that the interaction parameters of ε_w, ε_{ew} and ε_{ee} are introduced to describe the bead-substrate interaction, endbead–substrate interaction and endbead–endbead interaction respectively. And the large interaction parameters represent the strong corresponding interactions.

*Project supported by the National Natural Science Foundation of China (Grant No 50390060) and the State Key Development Program for Basic Research of China (Grant No 2003CB716201).
†E-mail: lixin02@mails.tsinghua.edu.cn

Molecular dynamic simulations with the canonical ensemble are performed to investigate the spreading of both nonfunctional and functional PFPE. A modified Nose–Hoover chain thermostat[8] is adopted with Newton's equations of motion:

$$m_i\dot{r}_i = p_i,$$
$$\dot{p}_i = F_i - \zeta(z)p_i, \qquad (1)$$

where m_i, r_i, 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.

$$\zeta(z) = \zeta\exp(\sigma - z),$$
$$\zeta' = \frac{1}{Q}\left(\sum_{i=1}^{N} p_i^2/m - gk_{\mathrm{B}}T\right), \qquad (2)$$

where z is the bead-substrate distance, g is degree of freedom and $\zeta\&Q$ represent the thermostat damp and thermostat mass.

3. Results and discussion

3.1. Spreading of nonfunctional liquid: effect from the substrate

For nonfunctional PFPE, the interaction parameters are selected as $\varepsilon_{\mathrm{ew}} = \varepsilon_{\mathrm{ee}}$=0. Fig.1 shows the spreading profiles of nonfunctional PFPE on different substrates at time t=100000, 300000, 500000 MD steps. The spreading of nonfunctional PFPE generally exhibits a smooth profile with a precursor film, which is in agreement with Tyndall's experimental results.[3] During the spreading process, two types of molecular movements are observed: the molecules at the droplet boundary break away from other molecules and flow down. After reaching the substrate, those molecules take random walk and diffuse along the substrate, which helps to form a precursor film. The overall picture is that the spreading goes with the migration of molecules from the higher to the lower layer, eventually reaches the substrate.

It can be seen that, when the bead–substrate interaction is weak, the migration of molecules is slow owing to the small driving force from the substrate, so the precursor film is hard to form (Fig.1(a)). At small time steps, no molecular layering is found; as time goes by, the first layer of the precursor film becomes visible. On the other hand, when the bead-substrate interaction is strong, the migration of molecules is fast (Fig.1(b)). That is, after reaching the substrate, more and more molecules will break away from the main body of the droplet and diffuse along the substrate to form the precursor film. At small time steps, the first layer has already been visible; and as time goes by, a second layer appears due to the strong bead-substrate interaction (The first and second of the precursor film are not clearly identified in Fig.1). As a whole, the simulation results indicate that the bead-substrate interaction has a significant effect on the spreading behaviour, especially on the formation of the precursor film.

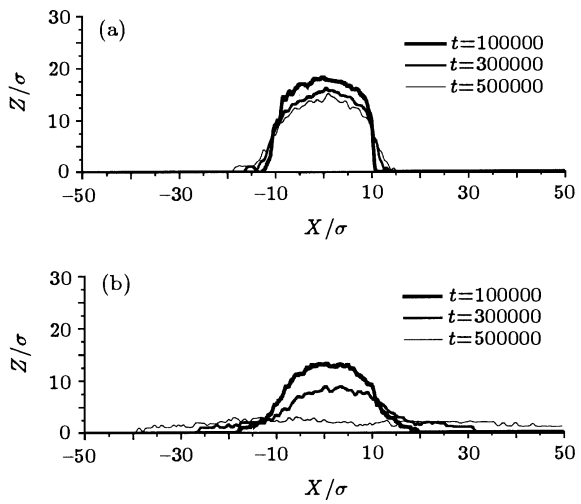


Fig.1. Thickness profiles at time t=100000, 300000, 500000 MD steps, where X is in the direction of spreading, Z is in the direction normal to the surface. The interaction parameters are $\varepsilon_{\mathrm{ew}} = \varepsilon_{\mathrm{ee}}$=0 with (a)$\varepsilon_{\mathrm{w}}$=10; (b)$\varepsilon_{\mathrm{w}}$=20.

3.2. Spreading of functional liquid: effect from the endbead

Figure 2 shows the spreading profiles of functional PFPE with different endbeads at time t=100000, 300000, 500000 MD steps, where the interaction parameters are selected as (a) $\varepsilon_{\mathrm{ew}} = \varepsilon_{\mathrm{ee}}$=2; (b) $\varepsilon_{\mathrm{ew}}$=2, $\varepsilon_{\mathrm{ee}}$=5; (c) $\varepsilon_{\mathrm{ew}}$=100, $\varepsilon_{\mathrm{ee}}$=2. The spreading of functional PFPE generally exhibits complicated terraced profiles, characterized by the formation of a precursor film, a shoulder and a vertical step, which are also consistent with Tyndall's experimental results.[3] It is found from comparison that the spreading of functional PFPE displays different profiles and flux from that of nonfunctional PFPE on the same substrate, which indicates that the endbead–substrate interaction and the endbead–endbead interaction may complicate the spreading process.

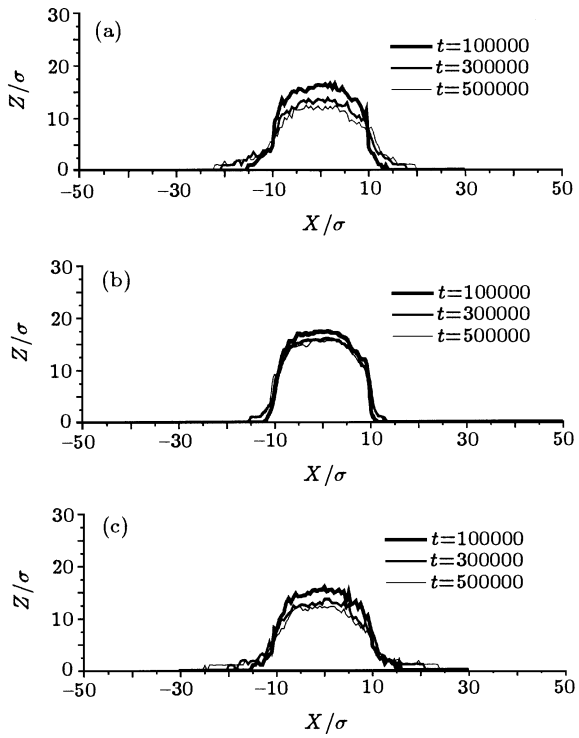


Fig.2. Thickness profiles at time t=100000, 300000, 500000 MD steps, where X is in the direction of PFPE spreading, Z is in the direction normal to the surface. The interaction parameters are (a) $\varepsilon_{ew} = \varepsilon_{ee}$=2; (b) ε_{ew}=2, ε_{ee}=5; (c) ε_{ew}=100, ε_{ee}=2 with ε_{w}=20.

In comparison with the spreading of nonfunctional PFPE (Fig.1(b)), the migration of functional PFPE molecules flowing down is significantly restricted due to the endbead–endbead interaction, which leads to a vertical step profile, while the migration of molecules diffusing along the substrate is strongly slowed down due to the endbead–substrate interaction, which leads to a slower formation of precursor film (Fig.2(a)). In comparison with the spreading of PFPE with weak endbead–endbead interaction (Fig.2(a)), it can be seen from Fig.2(b) that the migration of molecules flowing down is obstructed intensively for the strong endbead–endbead interaction. As the strong endbead–endbead interaction helps functional PFPE molecules to bind tightly and form a biopolymer structure,[9] it is difficult for molecules to escape from the binding of other molecules and diffuse along the substrate. Therefore, the vertical step becomes steeper and the precursor film becomes smoothed out. In comparison with the spreading of PFPE with weak endbead–substrate interaction (Fig.2(a)), the migration of molecules diffusing along the substrate is found to be accelerated to some extent as a result of the strong endbead–substrate interaction (Fig.2(c)). As the strong endbead–substrate interaction helps to enhance the driving force, more molecules can escape from the binding of other molecules and diffuse along the substrate freely to form a fast precursor film. Besides, the fast precursor film provides more cavities for molecules in the higher layer to fill in, which also helps the migration of molecules flowing down and smooth the vertical step. In general, the simulation results indicate that the endbead–substrate interaction and the endbead–endbead interaction have a significant effect on the spreading behaviour. Especially, the endbead–endbead interaction plays the crucial role.

4. Conclusion

Molecular dynamic simulations based on a coarse-grained, bead-spring model are adopted to investigate the spreading of both nonfunctional and functional PFPE on a solid substrate. For nonfunctional PFPE, a smooth profile and a small flux can be obtained for weak bead-substrate interaction, while a smooth profile with a distinct precursor film and a large flux can be obtained for strong bead-substrate interaction. For functional PFPE, a precursor film, a shoulder and a vertical step, as well as a small flux, can be obtained for weak endbead–substrate interaction and endbead–endbead interaction. Besides, a fast precursor film can be obtained for strong endbead–substrate interaction, while a vanishing precursor film, a steeper vertical step and a smallest flux can be obtained for strong endbead–endbead interaction. Our simulation results indicate that the bead-substrate interaction, the endbead–substrate interaction and endbead–endbead interaction jointly determine the spreading behaviour.

References

[1] Ma X, Gui J, Smoliar L, Grannen K, Marchon B, Bauer C L and Jhon MS 1999 *Phys. Rev.* E **59** 722

[2] Guo Q, Izumisawa S, Jhon M S and Hsia Y 2004 *IEEE Trans. Mag.* **40** 3177

[3] Tyndall G W and Karis T E 1999 *Tribol. Trans.* **42** 463

[4] Waltman R J, Tyndall G W and Pacansky J 1999 *Langmuir* **15** 6470

[5] Ma X, Bauer C L, Jhon M S, Gui J and Marchon B 1999 *Phys. Rev.* E **60** 5795

[6] Guo Q, Izumisawa S, Phillips D M and Jhon M S 2003 *J. Appl. Phys.* **93** 8707

[7] Li X, Hu Y Z and Wang H 2006 *J. Appl. Phys.* **99** 024905

[8] Heine D R, Grest G S and Edmund B 2003 *Phys. Rev.* E **68** 061603

[9] Li X, Hu Y Z and Wang H 2005 *Acta Phys. Sin.* **54** 3787 (in Chinese)