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Molecular behaviour in thin film lubrication

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ABSTRACT – The behaviour of lubricant molecules, especially the molecules near the solid surface is very important to the property of the whole tribo-system. However, how do the liquid molecules behave in a nano-confined space, especially in a nano lubricant film? Thin film lubrication (TFL) theory has been invoked to characterize the molecular pattern in lubrication film less than hundred nanometers, which effectively bridged the gap between elastohydrodynamic lubrication (EHL) and boundary lubrication. Unfortunately, to date, the molecular model of TFL which was proposed 20 years ago has not been well proven. Recently a novel method based on surface-enhanced Raman spectroscopy developed in our group allows us to access the molecular behavior in a nano-confined film, along with both the packing and orientation of the liquid molecules in TFL regime. The presentation attempts to systematically review the major developments of TFL, including the state-of-art studies on experimental technologies, researches and applications. Future prospects of relevant researches and applications will be also discussed.

1. INTRODUCTION

A remarkable lubrication regime to solve the transition from boundary lubrication to EHL has been revealed, termed thin film lubrication (TFL) [1-3], which has been systematically investigated since 1990s by a number of researchers, such as Johnston et al. [4], Luo et al. [5,6], Tichy [7], Hartal et al. [8], Matsuoka and Kato [9], Guangteng and Spikes [10] and so on. Luo and Yian [11] suggested a gap-bridging model in terms of description of interlaced change of qualitative lubrication and quantitative parameters in 1989, which can be considered to be the embryo of thin film lubrication model. In the meanwhile, the super thin film lubrication was proposed and developed by Spikes and Johnston et al. [4], describing the situation with lubricating films less than 15nm. Gupta and Sharma et al. [12] succeeded with revealing the microscopic behavior of lubricant films ranging from 1 to 10 nm, by examining various contributions to the disjoining pressure, in which both the van der waals force and the structural force resulted from the molecular orientation and packing have been emphasized. In 1994, the physical model of thin film lubrication (TFL) was respectively proposed by Luo and Wen, as shown in Figure 1, indicating that the combined effect of molecules attached on surfaces and in the thin lubricating film resulting in a distinct lubrication performance. From that time forth, growing interest has been stimulated to reveal the origins and characteristics of thin film lubrication model, bringing numerous advances in both experimental and theoretical studies.

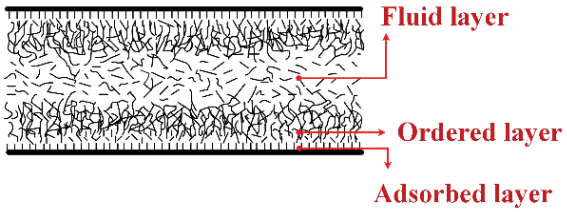

Figure 1 Thin film lubrication model.

2. RESEARCHES AT MOLECULAR LEVEL

The central idea of TFL theory is the surface-and friction-induced molecular ordering and packing. Futher researches have been conducted to explore the molecular behaviours in TFL regime. Xie et al. [13] demonstrated a "freezing" of lubricant in a nanogap. Such freezing can be observed for both polar liquids and nonpolar ones. The freezing process of n-hexadecane with a thickness of around 12 nm, as demonstrated in Figure 2, can be explained by the ordering alignment in the central contact region under the external electric field.

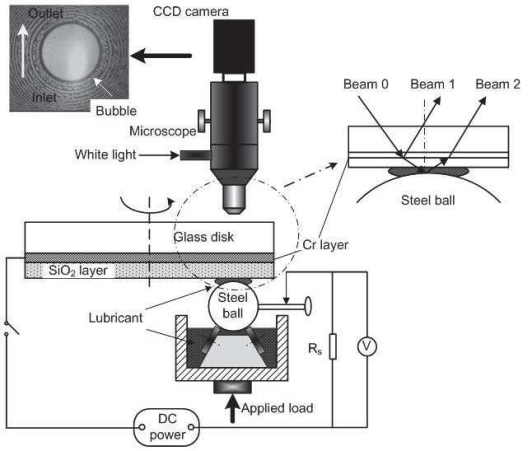

Figure 2 The sketch of the experimental setup for TFL under external electrical field.

During the lubrication process in TFL, in each layer lubricant molecules aligned in various pattern. This result opened up a new view on the investigation of lubricant at molecular level. By employing the in-situ Raman spectroscopy, Zhang et al. [14] and Zhang [15] has successfully detected the molecular structure of both polar and nonpolar lubricant molecules in nano lubrication films, as shown in Figure 3. The orientation

along the rolling direction is found to still exist in the ordered film in nonpolar solvents, but it disappears in polar solvents. Furthermore, Gao et al. [16] explore the molecular structure and orientation of lubricant molecules by trapping different liquid crystals between two solid surfaces. Nematic liquid crystals with different length of molecular side chain from CB family were utilized. It has been indicated that both shearing velocity and the alkyl chain length will affect the orientation of liquid crystal molecules confined in a nanoscale gap.

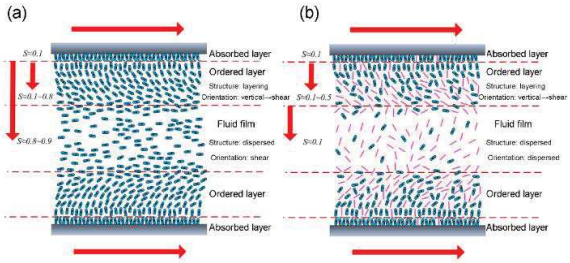

Figure 3 Molecular structures of 5CB in (a) nonpolar solvent (hexadecane) and (b) polar solvent (decanol).

Recently, a method based on surface-enhanced Raman spectroscopy was developed to show both the packing and orientating of liquid molecules in the TFL regime. By trapping liquid crystal molecules between a structured silver surface and a glass surface, a layered structure consisting of an adsorbed layer, an ordered-molecule layer and a fluid layer was finally demonstrated even in a nano gap. It was found that the orientation of the 6CB molecules is determined by the growth direction of the Ag structure in the static state, caused by the vertical adsorption of the 6CB molecules on the silver through C-N bonds. The molecules align vertically near the surfaces but horizontally in the fluid layer. It was indicated that the Ag nanorods would be reoriented to the flow direction by the shearing force, resulting in the 6CB molecules adsorbed on it being aligned perpendicularly to the shearing direction.

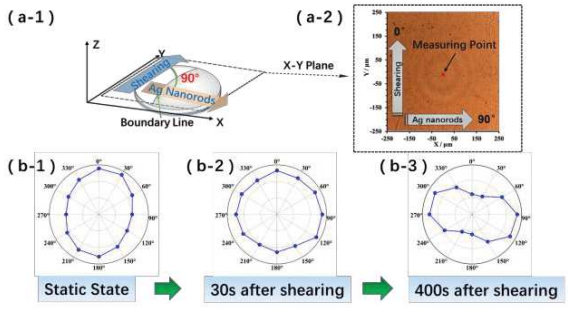

Figure 4 Evolution of the molecular orientation of the absorbed layer on Ag substrate.

3. SUMMARY

A remarkable mode of lubrication has been revealed since two decades ago, termed thin film lubrication (TFL), in which, the lubricant film could be divided into absorbed film, ordered film, and fluid film. Since the establishment of the theory and concept of TFL twenty years ago, it has become a great concern, and attracted the interests of not only tribologists, but also physicists and chemists. Innovative explorations and studies on the TFL have been have been reviewed. We have focused on the researches about molecular behaviours in TFL regime, providing new perspectives for the development and applications of TFL.

REFERENCES

[1] Luo, J. B. (1994). Study on the measurement and experiments of thin film lubrication. Ph.D Thesis. Beijing (China): Tsinghua University.

[2] Luo, J., Wen, S., & Huang, P. (1996). Thin film lubrication. Part I. Study on the transition between EHL and thin film lubrication using a relative optical interference intensity technique. *Wear*, *194*(1-2), 107-115.

[3] Ma, L., & Luo, J. (2016). Thin film lubrication in the past 20 years. *Friction*, *4*(4), 280-302.

[4] Johnston, G. J., Wayte, R., & Spikes, H. A. (1991). The measurement and study of very thin lubricant films in concentrated contacts. *Tribology Transactions*, *34*(2), 187-194.

[5] Luo, J., & Wen, S. (1996). Mechanism and characters of thin film lubrication at nanometer scale. *Science in China Series A-Mathematics*, *39*(12), 1312-1322.

[6] Luo, J. B., Wen, S. Z., Li, K. Y. (1998). The effect of substrate energy on the film thickness at nanometer scale. *Lubrication Science*, 10: 23-29.

[7] Tichy, J. A. (1995). Modeling of thin film lubrication. *Tribology transactions*, *38*(1), 108-118.

[8] Hartl, M. J. I. P. M. R., Krupka, I., Poliscuk, R., Liska, M., Molimard, J., Querry, M., & Vergne, P. (2001). Thin film colorimetric interferometry. *Tribology Transactions*, *44*(2), 270-276.

[9] Matsuoka, H., & Kato, T. (1997). An ultrathin liquid film lubrication theory—calculation method of solvation pressure and its application to the EHL problem. *Journal of Tribology*, *119*(1), 217-226.

[10] Guangteng, G., & Spikes, H. A. (1996). Boundary film formation by lubricant base fluids. *Tribology Transactions*, *39*(2), 448-454.

[11] Luo, J. B., & Yian, C. N. (1989). Fuzzy view point in lubricating theory. *Lubr Eng*, *4*, 1-4.

[12] Gupta, A., & Sharma, M. M. (1992). Stability of thin aqueous films on solid surfaces: I. Ellipsometric measurement of disjoining pressure isotherms for aqueous films bounded by glass and mercury. *Journal of colloid and interface science*, *149*(2), 392-406.

[13] Xie, G., Luo, J., Liu, S., Guo, D., & Zhang, C. (2009). "Freezing" of nanoconfined fluids under an electric field. *Langmuir*, *26*(3), 1445-1448.

[14] Zhang, S., Liu, Y., & Luo, J. (2014). In situ observation of the molecular ordering in the lubricating point contact area. *Journal of Applied Physics*, *116*(1), 014302.

[15] Zhang, S. H., (2014) Experimental Study on Molecular Arrangement of Nanoscale Lubricant

Films. Ph.D. Thesis under supervisor of Luo J B, Beijing (China): Tsinghua University.

[16] Gao, M., Ma, L., & Luo, J. (2016). Effect of alkyl chain length on the orientational behavior of liquid crystals nano-film. *Tribology Letters*, *62*(2), 24.