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Depletion kinetics of perfluoropolyether films with functional end groups using molecular dynamics simulation

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Molecular dynamics simulation coupled with a coarse-grained model is employed to investigate the surface depletion kinetics of functional polyether film under heat treatment. The real-time evolutions of lubricant film desorption and decomposition are examined during rapid heating and isothermal stages. The reaction order of lubricant depletion is evaluated during the rapid heating using a constant heating rate and various coverages. It reveals that a peak in the desorption (decomposition) rate is formed and is independent of the mass (bond) coverage, which gives rise to a first-order, coverage independent depletion kinetics. The rate constants for lubricant desorption and decomposition are thus calculated based on a first-order kinetics-controlled reaction during the isothermal stage. The kinetics of functional lubricant depletion shows that desorption is the main mechanism of lubricant depletion under rapid and isothermal heat treatment and is the major cause of lubricant thermal instability on the surface.

1. Introduction

The surface dynamics of ultrathin oligomeric films is of both theoretical and practical interest because micro- and nano-structured polymers play essential roles in modifying interfacial properties such as adhesion and lubrication. The study of interfacial phenomena assists to address challenging engineering issues which retard the advances in many industrial and biological applications. As an example, the magnetic recording industry utilizes a single monolayer of perfluoropolyether (PFPE) film as topical lubricant to minimize friction and wear between flying heads and rotating disks at the head disk interface (HDI). The presence of molecularly thin PFPE film deposited onto a sputtered carbon overcoat (a-CH_x or a-CN_x) is essential to maintain the long-term stability and reliability of the hard disk drive (HDD). The most commonly used class of PFPE lubricants in HDDs are Fomblins, which are random co-polymers with a linear backbone chain having the chemical structure of

$$X-(OCF_2-CF_2)_p(OCF_2)_q-O-X \quad (p/q\approx 0.8-1.3)$$

The Fomblin backbone can be terminated with a number of different end groups. The most common commercially available ones include non-functional Fomblin *Z* and functional Fomblin Zdol which consist of fluoromethyl ($X = CF_3$) and hydroxyl ($X = CF_2CH_2OH$) end groups, respectively. The Fomblin lubricants are widely chosen due to their excellent properties such as good thermal and chemical inertness, good lubricity, low vapour pressure, and low volatility even at high molecular weights (MWs). Besides the disperse interaction that characterizes the adhesion between non-functional backbone and carbon overcoat, the functional end groups can interact with the polar active sites on carbon overcoat via hydrogen bonding. The additional adhesion provided by the hydroxyl groups (−OH) dominates the adsorption energetics of functional lubricant on the disk surface, which minimizes lubricant loss from the surface, thereby enhancing the magnetic performance and integrity of the HDI.

The areal data density, the number of data bits stored per unit area, has increased during the past decade at an enormous pace. However, the disk drive industry is facing huge challenges to overcome the superparamagnetic limit occurring when small magnetic recording bits (of the order of 10 nm) are used to further increase the areal density [1]. Heat assisted magnetic recording (HAMR) is believed to be a promising technique to alleviate the problem of superparamagnetic effect [2,3]. In a HAMR system, a high anisotropic medium is used, but be written using a combination of heat produced by a laser beam and field produced by a magnetic head. Therefore, a tiny area of the media is heated up to its Curie temperature (∼400 °C) within nanoseconds, making it easier to be overwritten during writing process. However, HAMR can cause severe lubricant depletion on the disk surface due to the high temperature involved during laser heating. The depletion of lubricant

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films is attributed to desorption from and/or decomposition on disk surface at elevated temperatures. It is believed that the commercial PFPEs such as Fomblin Zdol are unsuitable for use in HAMR systems [4]. Many recent experiments [5–12] were devoted to investigate the kinetics and mechanisms of lubricant depletion from solid surfaces. Tyndall and Waltman [5,6] measured the evaporation rates of both polydisperse and monodisperse PFPEs from a CH*x* surface at various temperatures. It was found that the evaporation of PFPEs from amorphous carbon follows non-classic, first-order kinetics. They suggested that the non-classic feature arises from the polydispersity of the lubricant and the heterogeneity of the CH_x surface that a distribution of activation energies would exist for the desorption of Fomblin lubricant. Paserba and Gellman [7–9] reported a series of thermally programmed desorption (TPD) spectra for desorption of n-alkanes, poly(ethylene glycol) dimethyl ethers, and poly(ethylene glycols) from graphite surfaces. The desorption was observed to occur molecularly through a first-order process with desorption energy, ΔE_{des}, that is independent of the coverage but is dependent on the MW. They found, more intriguingly, that ΔE_{des} has a nonlinear relation with chain length and takes the form of $\Delta E_{\text{des}} = A + Bn^{\alpha}$, with the exponent $\alpha \approx 0.5$. Tagawa et al. [10,11] carried out fundamental research on lubricant depletion due to laser heating in thermally assisted magnetic recording. It revealed that lubricant depletion depth and width were much smaller for Ztetraol2000 than Zdol2000. The lubricant bonding ratio was also found to have a significant impact on lubricant depletion, that is, the higher the bonding ratio, the lesser the lubricant is depleted. Additionally, Ma and Liu [12] investigated the lubricant depletion under HAMR conditions through experiments and developed a logarithmic relation between depletion depth and laser heating time. It demonstrated that the lubricant ridge accumulating around the lubricant depletion track takes a considerable percentage of lubricant loss and contributes to lubricant recovery during media cooling process after laser heating. Moreover, it was predicted that almost all lubricant on the disk will be depleted over the lifetime of the drive. On the other hand, numerical research work [13–15] has provided another insight into lubricant depletion instability. Lim et al. [13] investigated the kinetics of laser induced desorption and decomposition of Fomblin Zdol on carbon overcoats. It was shown that under HAMR conditions lubricant films with MW of less than 3000 g/mol are most likely to desorb from rather than decompose on the disk surface during rapid heating, while decomposition is preferred at temperatures (>400 °C) expected in HAMR for higher MW lubricants. Wu [14] described a model for lubricant flow dynamics under a scanning laser beam and studied the mechanisms of lubricant depletion on both glass and aluminium disks. It showed a ridge circumscribing the depletion zone was formed due to thermocapillary stress. For low MW Z-type PFPEs, the evaporation, as well as the thermocapillary stress, is able to cause a significant amount of lubricant depletion from disk surface. However, the evaporation is reduced remarkably and is no longer the dominant depletion mechanism for high MW lubricants. Furthermore, Li et al. [15] studied the evolution and depletion of molecularly thin lubricant when subjected to rapid laser heating via molecular dynamics (MD) simulation. In the studies, it was found that the lubricant film endured severe depletion with increasing heating duration, resulting in aggravated lubricant evaporation and raised ridges around the heating spot. It was also observed that the lubricant depletion is mainly attributed to the non-uniform distribution of surface tension gradient and the non-equilibrium thermocapillary stress.

In contrast with the depletion of small molecules, desorption and decomposition of polymeric molecules is much more complicated and until now has not been fully understood, especially under conditions of rapid laser heating. Lubricant molecule with a long chain can adsorb on a surface in many configurations, all of which will influence the desorption kinetics. The laser induced heating rate used in HAMR is estimated to be in an order of 10^{11}–10^{12} K/s, which further complicates the lubricant depletion kinetics. In addition, experimental measurements of surface dynamics of macromolecules are becoming technically difficult due to ultralow concentrations of surface species and extremely short time scales [16]. As such, in this paper, we make use of MD simulation to study lubricant depletion instability on a solid surface. In experiments, the local temperature T due to laser irradiation is expressed as a linear relation with the laser power P when the magnetic medium fully adsorbs the light of the laser beam [17]. As the lubricant film is only a few nanometres thick, the temperature of Fomblin lubricant is treated to be the same as that of the disk. Therefore, the rapid laser heating used in HAMR systems can be divided into a two-step heating process. A rapid heat treatment to lubricant represents the step where the laser is initiated and the power intensity increases quickly, while an isothermal heat treatment corresponds to a constant laser power after stabilization. Following the two-step heat treatment, the MD simulations will be performed to investigate in real-time the kinetics of lubricant desorption and decomposition on the surface during both rapid heating and isothermal stages.

2. Molecular dynamics simulation and methodology

2.1. Molecular model

The Knudsen number is one of the criteria to determine whether a model is appropriate to describe fluid flow in micro- or nano-applications [18]. In fluid dynamics, the Knudsen number Kn is defined as the ratio of the molecular mean free path λ to a characteristic physical length of interest, i.e., the film thickness h. For thick lubricants used in macro-devices, the Knudsen number is very small due to the large value of h and thus the fluids are considered as continuous mediums. But for ultrathin lubricants in micro- or nano-devices, the fairly large Knudsen number shows that classic continuum mechanics is inadequate to study the free molecular flow of ultrathin films. In the present work, we employ MD simulation method to investigate the behaviours of ultrathin lubricant film and depletion instability for a HAMR system. In the simulations, the lubricant molecule is characterized by a coarse-grained model, which has been widely incorporated into MD simulations to investigate nanostructures and properties of macromolecules in the field of physics, chemistry, materials science, and biomolecules [15,19–26]. Although the coarse-grained model is less informative than a full atomic model, it requires less computational time making it feasible for large polymer systems.

In this work, the coarse-grained model as shown in Fig. 1(a) is constructed to describe the Fomblin lubricant, which simplifies the detailed atomic information but still maintains the essence of the internal molecular structure [25]. The Fomblin lubricant is treated as a pure material and each polymer chain is connected linearly by a number of beads (N_p), which is set as 10 for an MW of about 2000 g/mol. Fig. 1(b) shows the front view of the equilibrated system with lubricant beads $N = 6480$ at $T^* = 1.0$ (see $T^* = k_B T/\varepsilon$ in Section 2.2), which illustrates a bilayer film structure. Since polar interaction plays an essential role in lubricant depletion instability, the lubricant beads are assigned with different functionalities and are categorized into non-functional backbone beads (*bbs*) and functional end beads (*ebs*). Our previous studies [27] revealed that surface roughness has little effect on the intermolecular interactions between the lubricant and the disk surface. As such, to save computation time, the disk surface is modelled as a thermally inert, infinitely long, and infinitely deep flat surface, located at $z = 0$.