Perfluoropolyether Lubricant Interactions With Novel Overcoat via Coarse-Grained Molecular Dynamics

Sesha Hari Vemuri[1], Pil Seung Chung[1], Robert Smith[1], Geun-Young Yeom[2], Young In Jhon[2], Nae-Eung Lee[2], Lorenz T. Biegler[1], and Myung S. Jhon[1,2]

[1]Department of Chemical Engineering and Data Storage Systems Centers, Carnegie Mellon University, Pittsburgh, PA 15213 USA
[2]School of Advanced Materials Science and Engineering, Sungkyunkwan University, Suwon, 440-746 Korea

In this paper, we investigated physiochemical properties of new lubricant candidates for head-disk interface through various perfluoropolyether lubricant films on diamond, diamond-like carbon, and graphene overcoat surfaces via large scale coarse-grained bead-spring molecular dynamics stemming from the atomistic theory. Lubricant film conformations were characterized by investigating perpendicular component of molecular conformation, which determines the thickness of monolayer lubricant film. The distribution of functional endgroups and the mobility were analyzed via self-diffusion process. Here, we illustrate the effects of endgroup structure and carbon-surface structure on the film conformation and the mobility by expanding the multiscale simulation methodology and select candidates for future HDI design.

Index Terms—Graphene, head-disk interface, lubricant film, molecular dynamics, multiscale, perfluoropolyether.

I. INTRODUCTION

INTRODUCING graphene as a novel carbon-overcoat opens a new paradigm for high areal density in hard disk drives (HDDs) by reducing head-media spacing (HMS) to 3.4 nm, which is less than half of the conventional HMS and will provide up to six times the current recording capacity (see Fig. 1) [1]. Along with the development of new lubricant materials, the head-disk interface (HDI) in HDD systems can be achieved via combinations of lubricants and novel architecture of carbon overcoat systems. Hence, we applied a coarse-graining method bridging atomistic and molecular/mesoscale models, which provides the accurate potential energy forms and parameters enabling the novel system designs [2], [3]. By using the force field calculation based on first principles (e.g., ab initio), intramolecular and intermolecular interaction energies of various perfluoropolyethers (PFPEs) were estimated [4], [5] for inputs to molecular dynamics.

In this paper, we investigated and compared physiochemical properties of various perfluoropolyether lubricant films on diamond, diamond-like carbon (DLC), and graphene via large scale coarse-grained, bead-spring molecular dynamics (CGMD) based on the endgroup-surface potential energy parameters determined from atomistic theory. Intermolecular force fields between PFPEs and carbon overcoats were estimated from the equilibrium geometries of truncated PFPEs (endgroup) and the segments of the overcoat materials. By using CGMD, lubricant film conformations were characterized by anisotropic radius of gyration where the perpendicular component determines the thickness of the lubricant film. The mobility of PFPE molecules was investigated via self-diffusion. The focus of this multiscale combinatorial problems is
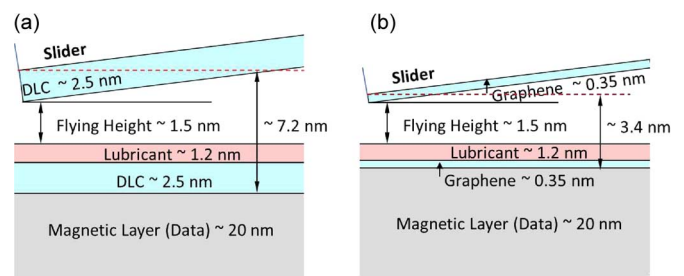

Fig. 1. HMS of head-disk interface with (a) DLC and (b) graphene overcoats.

on: 1) observing the effects of endgroup's chemical structure on the film conformation and the mobility; 2) structural effects of carbon surface, which may provide selection criteria for materials in future HDIs; and 3) expanding the feasibility of multiscale simulation methodology, which we have developed thus far. Here, we found the relationships of endgroup-endgroup and endgroup-surface interactions on the agglomeration and the PFPE mobility. By examining the properties as a function of endgroup-surface functionality, one could tailor PFPE film-surface interactions by tuning the overcoat surface.

II. COARSE-GRAINED MOLECULAR DYNAMICS

In our previous research [6]–[8], PFPE molecules were characterized via a coarse-grained, bead-spring model, which simplifies the detailed atomistic structures by categorizing groups of atoms with uniform bead size for backbone and endgroup based on the dimension of the oligomer. This approach, nevertheless, retains the essence of molecular structure and chain flexibility. To implement the atomistic level theory in our previous MD models, we applied a coarse-graining procedure linking atomistic potentials and molecular/mesoscale simulations combining the parameters obtained from quantum mechanical calculation, as illustrated in Fig. 2. Our reduced order model (ROM) [9], [10] was introduced to optimize the force field parameters for the coarse-grained level models
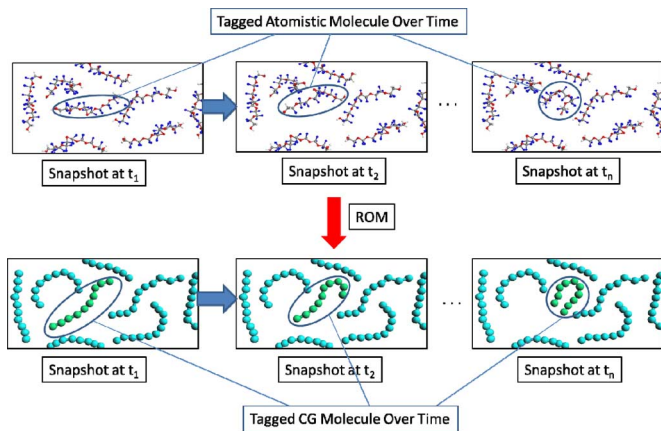
Fig. 2. Illustration of coarse-graining procedure by using ROM for PFPE molecular systems.

TABLE I
BONDING PARAMETERS (FENE) FOR COARSE-GRAINED MD MODEL, WHERE
k AND R_0 REPRESENT THE STRETCHING BOND CONSTANT $(kcal/mol \cdot Å)$
AND THE EQUILIBRIUM BOND LENGTH $(Å)$ (BOND1: BACKBONE-BACKBONE
AND BOND2: BACKBONE-ENDGROUP)

	k	R_0
Bond1	−43.7	2.524
Bond2	−58.3	2.332

allowing for lubricant oligomer chain dynamics and flexibility compatible to the fully atomistic simulations.

The method focuses on transferring the distribution of structural parameters from the atomistic to the coarse-grained model. The procedure involves performing an atomistic MD simulation of a bulk PFPE system and calculating the equilibrium probability distributions. A Boltzmann distribution for bond lengths is fit to the distribution determined from the MD simulation by varying the parameters of the bonded potential

$$P(r) \propto \exp\left(-U_r(r)/k_B T\right). \quad (1)$$

Here, P is the probability distribution, U_r is the bond potential, k_B is Boltzmann constant, and T is absolute temperature. Intramolecular (bonding) parameters for coarse-grained model are listed in Table I.

An ideal flat and smooth surface was used to model the carbon overcoat with the dissipative dynamics by Langevin equation. The force field was constructed by the Lennard Jones (LJ) and finitely extensible nonlinear elastic (FENE) model for the intramolecular interaction and connected beads [11]. Short-range exponential potentials (EXP) for the interactions among the functional endgroups and between functional endgroups and carbon surface were introduced as follows [8]:

$$U_{EXP}(r) = -\varepsilon_p \exp(-r/d) \quad (2)$$

where ε_p is endgroup functionality and d is the equilibrium distance. ε_p characterizes the interactions between PFPE and overcoat (see Table II) and among PFPEs (see Table III). The governing equations in this simulation are represented by a set of Langevin equations [12].

TABLE II
ENDGROUP FUNCTIONALITY (ε_p) OF ZDOL, ZTETRAOL, AND DDPA ON
DIAMOND, DLC, AND GRAPHENE (kcal/mol)

Overcoat PFPE	Diamond	DLC	Graphene
Zdol	−9.05	−24.9	−19.1
Ztetraol	−15.2	−30.1	−20.7
DDPA	−9.5	−18.1	−17.5

TABLE III
ENDGROUP FUNCTIONALITY (ε_p) BETWEEN PFPEs,
I.E., ZDOL, ZTETRAOL, AND DDPA (kcal/mol)

PFPE PFPE	Zdol	Ztetraol	DDPA
Zdol	−8.23	−8.51	1.25
Ztetraol	-	−14.1	−1.56
DDPA	-	-	−0.95

By varying molecular structures and ε_p, atomistically architectured PFPEs are represented in this simulation. Monolayer films fully covered by PFPE molecules were investigated with the dimensions of simulation box in the x and y directions were $40\sigma \times 40\sigma$, where σ is the diameter of the bead. After the system equilibration, the simulations were performed for 40 000 τ with the time step of 0.005 τ, where τ is $\sigma(m/\varepsilon)^{0.5}$, ε is the well depth of LJ potential energy, and m is the mass of the bead. Periodic boundary conditions were applied in the x and y directions.

III. RESULTS AND DISCUSSION

From the CGMD simulations, we analyzed the molecular conformation and mobility of PFPE lubricants (Zdol, Ztetraol, and Demnum di-propyl amine (DDPA) with 2000 g/mol molecular weight) on the carbon-overcoats (diamond, DLC, and graphene) by estimating anisotropic radii of gyration and self-diffusion coefficients.

A. Molecular Conformation

The thickness of monolayer films fully covered by PFPE molecules is mainly controlled by the molecular conformation on the surface. The conformations of monolayers were investigated by analyzing the anisotropy ratio for radius of gyration decomposing parallel $(R_\parallel^g)$ and perpendicular $(R_\perp^g)$ components

$$(R^g)^2 = \frac{1}{N_m} \sum_{i=1}^{N_m} \left[(x_i - x_g)^2 + (y_i - y_g)^2 + (z_i - z_g)^2 \right]$$
$$= (R_x^g)^2 + (R_y^g)^2 + (R_z^g)^2 = 2\left(R_\parallel^g\right)^2 + (R_\perp^g)^2 \quad (3)$$

where, x_i, y_i, and z_i are the position of the bead and x_g, y_g, and z_g are the center of the mass of PFPE molecule.

As shown in the Table IV, all PFPEs (Zdol, Ztetraol, and DDPA) show flat conformation $(R_\perp^g/R_\parallel^g < 1)$ on all carbon surfaces (diamond, DLC, and graphene). By comparing the endgroup functionalities listed on Tables II and III. Table V illustrates that the strength of interactions among endgroups

TABLE IV
THE RATIO OF PERPENDICULAR TO PARALLEL RADII OF GYRATION $(R_\perp^g/R_\parallel^g)$ FOR ZDOL, ZTETRAOL, AND DDPA ON DIAMOND, DLC, AND GRAPHENE OVERCOAT SURFACES, RESPECTIVELY

Overcoat PFPE	Diamond	DLC	Graphene
Zdol	0.4906	0.5012	0.5029
Ztetraol	0.4257	0.4594	0.4629
DDPA	0.5364	0.5421	0.5547

TABLE V
THE PERPENDICULAR COMPONENT OF RADII OF GYRATION $(R_\perp^g)$ FOR ZDOL, ZTETRAOL, AND DDPA ON DIAMOND, DLC, AND GRAPHENE SURFACES, RESPECTIVELY

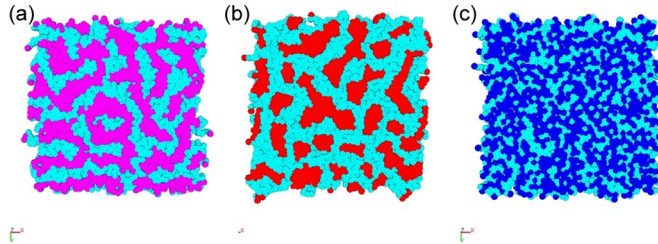| Overcoat PFPE	Diamond	DLC	Graphene
Zdol	0.7026	0.7182	0.7156
Ztetraol	0.6492	0.7024	0.6951
DDPA	0.7415	0.7522	0.7523

Fig. 3. Bottom view snapshots of (a) Zdol, (b) Ztetraol, and (c) DDPA on diamond overcoat surface. Light blue: backbone, pink: Zdol endgroup, red: Ztetraol endgroup, and blue: DDPA endgroup.

and surface barely affects the perpendicular molecular conformation as long as the total number of beads (i.e., molecular weight) remains constant. Especially, similar $R_\perp^g$ values of all cases, which mainly determines the film thickness in a monolayer lubricant system, indicates that intramolecular factors such as chain flexibility, molecular weight, or molecular structural complexity may affect film thickness and conformation more dominantly than intermolecular factors such as endgroup functionality or carbon-overcoat material.

Although our resulting statistical analysis of the molecular configurations away from the surface were the same for all PFPEs, we observed that the endgroup clusters on the surface varied. Fig. 3 shows the bottom view of Zdol, Ztetraol, and DDPA, where the endgroups are located on the surface. Both Zdol and Ztetraol [see Fig. 3(a) and (b)] exhibit clusters and network structures, and the endgroups of Zdol form less severe clusters, while DDPA lubricant film, which has the lowest endgroup functionality (-0.95 kcal/mol) between endgroups (Table II), does not display any cluster. In addition to the PFPEs on the diamond surface in Fig. 3, we also found that PFPEs on the other surfaces (i.e., DLC and graphene) form similar endgroup distributions as on the diamond surface.

From this result, we observed that the clusters formed in PFPE films depend on the interactions between endgroups (Ztetraol > Zdol ≫ DDPA) while the kind of carbon surfaces and their interactions to endgroup merely affect the forms

TABLE VI
PARALLEL COMPONENT OF SELF-DIFFUSION COEFFICIENTS $(D_\parallel \times 10^4)$ FOR ZDOL, ZTETRAOL, AND DDPA ON DIAMOND, DLC, AND GRAPHENE, RESPECTIVELY

Overcoat PFPE	Diamond	DLC	Graphene
Zdol	6.467	5.438	5.825
Ztetraol	6.706	3.636	1.984
DDPA	11.139	10.029	11.425

of clusters by observing the similarity of endgroup distributions for various carbon surfaces.

B. Mobility

As previously reported [13], the endgroup functionality dominantly controls the mobility of PFPE films, which is critical for the self-healing ability of lubricant on the depleted part of the disk [14]. Here, we quantified the mobility of PFPE lubricants by comparing the self-diffusion coefficient (D). The self-diffusion coefficient of a tagged molecule using Einstein's relationship is adopted to characterize the mobility of lubricant, and is decomposed to parallel and perpendicular components

$$D = \lim_{t \to \infty} \frac{1}{6t} \left\langle |\mathbf{r}(t) - \mathbf{r}(0)|^2 \right\rangle$$
$$= \frac{1}{3}(D_x + D_y + D_z) \equiv \frac{1}{3}(2D_\parallel + D_\perp). \qquad (4)$$

Here, $\mathbf{r}$ is the position of the molecular center of mass; $D_\parallel$ and $D_\perp$ are the components of the diffusion coefficient parallel and perpendicular to the surface, respectively.

Tables VI and VII compare self-diffusion coefficients of each component for Zdol, Ztetraol, and DDPA on the diamond, DLC, and graphene. The comparison between $D_\parallel$ and $D_\perp$ values indicates that $D_\parallel$ is the dominant diffusion process since perpendicular diffusion is confined by the monolayer thickness of PFPE films. The $D_\parallel$ of PFPEs is on the reverse order of the interaction strength between endgroups (Ztetraol < Zdol < DDPA) compared to the cluster formation ability. Also, the self-diffusion is affected by the kind of surfaces examined. Zdol exhibits the similar mobility for all carbon surfaces, while Ztetraol shows minimal mobility, which is sensitive to the carbon surface. DDPA, containing different type of endgroup from Zdol and Ztetraol (hydroxyl endgroups) shows significantly higher self-diffusion coefficients on all carbon-overcoats. By also considering the molecular conformations of PFPEs, this result indicates that Ztetraol may not be the best choice for the carbon-overcoat beyond the conventional materials, since a significant disadvantage on the self-healing ability exists. Zdol especially shows better mobility than Ztetraol on the graphene while the quantitative value is similar on the DLC and diamond overcoats. The mobility of DDPA is slightly increased on the graphene.

Here, we found that the changes in the monolayer film conformation affected by the perpendicular profile of PFPE molecular structures on the surface are insensitive to the kind of the endgroups or carbon surfaces. However, we observed the endgroup distributions on the surface changes depend on the endgroup-endgroup interactions. Also, different chemical types of endgroups on PFPEs vary the mobility of PFPEs with respect to the

TABLE VII
PERPENDICULAR COMPONENT OF SELF-DIFFUSION COEFFICIENTS ($D_\perp \times 10^4$)
FOR ZDOL, ZTETRAOL, AND DDPA ON DIAMOND, DLC, AND
GRAPHENE, RESPECTIVELY

Overcoat PFPE	Diamond	DLC	Graphene
Zdol	0.6195	0.5321	0.6066
Ztetraol	0.4686	0.2440	0.3922
DDPA	0.9399	0.7867	0.7516

surface characteristics. Due to the advantages of the graphene including the single atomic thickness of graphene and superior mechanical and thermal characteristics, HDI with graphene will provide the significant reduction of HMS along with high reliability if we optimize the lubricant structures beyond DDPA.

IV. CONCLUSION

Physiochemical properties of various PFPE lubricant films including Zdol, Ztetraol, and DDPA on diamond, DLC, and graphene were investigated via large scale CGMD based on the coarse-graining procedures from atomistic level theory. PFPE molecular conformations were characterized by analyzing anisotropic radius of gyration, where perpendicular component determines thickness of monolayer lubricant film, and the distribution of functional endgroups as a function of PFPEs and carbon-overcoat structures.

From this study, we observed that the PFPE endgroup cluster formation on the surface and the mobility depend on the interactions between endgroups while the film thickness barely changes for the PFPEs with the same backbone structure even though the type of surface varies. Also, different chemical structures of endgroups on PFPEs significantly vary the lubricant mobility as a function of the surface characteristics. This study exhibits the rigorous comparisons of the combinatorial possibilities among PFPEs and carbon-overcoats, by presenting the multiscale solutions from the first principle to mesoscale. In order to achieve the advantages of the graphene in future HDI, we will further investigate the critical properties beyond the static and dynamic responses (e.g., surface morphology and rheological responses) with the wide range of combinations for the future HDI candidates. Our study will naturally lead to various novel HDI designs, which hybridize solid/liquid lubricants with different types of carbon overcoats (e.g., graphene/carbon nanotube or fullerene/PFPE) and nano blend of PFPEs by utilizing dimer interaction energies as listed in Table III.

ACKNOWLEDGMENT

REFERENCES

[1] S. H. Vemuri, P. S. Chung, R. Smith, and M. S. Jhon, "Novel head-disk interface design in magnetic data storage," *J. Appl. Phys.*, vol. 111, April 2012, to be published.

[2] S. Izvekov and G. A. Voth, "A multiscale coarse-graining method for biomolecular systems," *J. Phys. Chem. B*, vol. 109, p. 2469, 2005.

[3] S. Izvekov and G. A. Voth, "Multiscale coarse-graining of liquid-state systems," *J. Phys. Chem. B*, vol. 123, p. 134105, 2005.

[4] R. Smith, P. S. Chung, J. A. Steckel, M. S. Jhon, and L. T. Biegler, "Force field parameter estimation of functional perfluoropolyether lubricants," *J. Appl. Phys.*, vol. 109, p. 7B728, 2011.

[5] R. Smith, P. S. Chung, S. H. Vemuri, and M. S. Jhon, "Atomistic simulation method in head-disk interface of magnetic data storage system," *J. Appl. Phys.*, vol. 111, April 2012, to be published.

[6] Q. Guo, S. Izumisawa, M. S. Jhon, and Y.-T. Hsia, "Transport properties of nanoscale lubricant films," *IEEE Trans. Magn.*, vol. 40, no. 4, p. 3177, Jul. 2004.

[7] Q. Guo, S. Izumisawa, D. M. Phillips, and M. S. Jhon, "Surface morphology and molecular conformation for ultrathin lubricant films with functional end groups," *J. Appl. Phys.*, vol. 93, p. 8707, 2003.

[8] M. S. Jhon, S. Izumisawa, Q. Guo, D. M. Phillips, and Y. T. Hsia, "Simulation of nanostructured lubricant films," *IEEE Trans. Magn.*, vol. 39, no. 2, p. 754, Mar. 2003.

[9] A. Agarwal, L. T. Biegler, and S. E. Zitney, "Simulation and optimization of pressure swing adsorption systems using reduced-order modeling," *Ind. Eng. Chem. Res.*, vol. 48, p. 2327, 2009.

[10] Y. Lang, S. E. Zitney, and L. T. Biegler, "Optimization of IGCC processes with reduced order CFD models," *Comput. Chem. Eng.*, vol. 35, p. 1705, 2011.

[11] K. Kremer and G. S. Grest, "Dynamics of entangled linear polymer melts—A molecular-dynamics simulation," *J. Chem. Phys.*, vol. 92, p. 5057, 1990.

[12] G. S. Grest, "Grafted polymer brushes in polymeric matrices," *J. Chem. Phys.*, vol. 105, p. 5532, 1996.

[13] Y.-T. Hsia, Q. Guo, S. Izumisawa, and M. S. Jhon, "The dynamic behavior of ultrathin lubricant films," *Microsyst. Technol.*, vol. 11, p. 881, 2005.

[14] T. M. O'Connor, Y. R. Back, M. S. Jhon, B. G. Min, D. Y. Yoon, and T. E. Karis, "Surface diffusion of thin perfluoropolyalkyletherfilms," *J. Appl. Phys.*, vol. 79, p. 5788, 1996.