

Force Field Parameter Estimation of Functional Perfluoropolyether Lubricants

Robert Smith,¹ Pil Seung Chung,¹ Janice A. Steckel,² Myung S. Jhon,^{1,3,a} and

Lorenz T. Biegler,¹

¹Department of Chemical Engineering and Data Storage Systems Center, Carnegie Mellon University, Pittsburgh, Pennsylvania 15213, USA

²U.S. Department of Energy, National Energy Technology Laboratory, 626 Cochran Mill Rd. Pittsburgh, Pennsylvania 15236-0940, USA

³School of Advanced Materials Science and Engineering, Sungkyunkwan University, Suwon, Korea

(Presented 17 November 2010; received 24 September 2010; accepted 20 November 2010;

published online 00 April 2011)

The head disk interface in hard disk drive can be considered one of the hierarchical multiscale systems, which require the hybridization of multiscale modeling methods with coarse-graining procedure. However, the fundamental force field parameters are required to enable the coarse-graining procedure from atomistic/molecular scale to mesoscale models. In this paper, we investigate beyond molecular level and perform *ab-initio* calculations to obtain the force field parameters. Intramolecular force field parameters for the Zdol and Ztetraol were evaluated with truncated PFPE molecules to allow for feasible quantum calculations while still maintaining the characteristic chemical structure of the end groups. Using the harmonic approximation to the bond and angle potentials, the parameters were derived from the Hessian matrix, and the dihedral force constants are fit to the torsional energy profiles generated by a series of constrained molecular geometry optimization.

Introduction

The head disk interface (HDI) in hard disk drive (HDD) system includes atomic/molecular scale thin lubricant film adjacent to the air-bearing and overcoat regions.¹⁻³ An integration of physical models ranging from the atomistic to the macroscopic is essential to accomplish a multiscale model of the perfluoropolyether (PFPE) that will lead to optimal selection of lubricant. This integration involves first establishing an accurate description at each level of the model to ensure physical insight is passed from one scale to the next. The foundation of the multiscale framework is the atomistic PFPE description based on *ab-initio* calculations. Atomistic PFPE models are suitable for studying dynamic and equilibrium properties of PFPE lubricants over small length/short time scales.

However, detailed models of PFPEs at the fully atomic scale must be mapped onto coarse-grained structures to allow for simulations over much longer time/length scales. In order to link the atomistic to the molecular/mesoscale, a coarse-graining procedure can be adopted that will pass essential physical information to the subsequent scales. This new coarse-grained system may then be naturally extended to investigate meso/macro scale physics.

In this paper, we start with an *ab-initio* treatment of the functional PFPE (Zdol and Ztetraol) intramolecular force field as the foundation for larger scale models so that the fundamental physics of the microscopic scale is linked with the macroscopic. To establish this linkage, we also demonstrate a systematic coarse-graining procedure to map the atomistic onto the molecular/mesoscale, thereby, facilitating a further linkage to the meso/macro scale description.

Atomistic Force Field Development

A fully atomistic treatment of PFPE is essential in investigating the physical-chemical characteristics of the molecular oligomer. In order to examine Zdol and Ztetraol oligomers with computationally intensive *ab-initio* methods, simplified models of the oligomers were designed such that the essential structural characteristics of the endgroups were preserved. The Zdol and Ztetraol were modeled as:

Zdol: HOCH2CF2OCF2CF3

Ztetraol: HOCH2HOCHCH2OCH2CF2OCF2CF3

The equilibrium geometries are first constructed, followed by the atomistic intramolecular force field parameters using the method of Seminario.⁴ An in-house code, which uses LAPACK⁵ routines for eigenvalue analysis, was developed to calculate stretching and bending parameters from the *ab-initio* Hessian matrix for harmonic potentials of the form:

$$U_r = (1/2)K_r(r - r_o)^2 \text{ and } U_\theta = (1/2)K_\theta(\theta - \theta_o)^2 \quad (1)$$

where U_r and U_θ are the stretching and bending potentials, respectively, K_r is the stretching force constant, K_θ is the bending force constant, r_o & θ_o are the equilibrium bond length and angle. The stretching interactions take place between two bonded atoms, while the bending accounts for the bending of the angle formed by two adjacent bonds. The torsional potential parameters, describing four bonded atoms, were calculated by generating the *ab-initio* torsional energy profiles via a series of constrained geometrical optimizations. The form of the torsional potential is: