

A Holistic Strategy in Multiscale Modeling of Perfluoropolyether Lubricants and Carbon Overcoat Materials

The physiochemical properties of oligomeric/polymeric materials are controlled by molecular level architecture, and the many polymer internal degrees of freedom span a range of time/length scales requiring an integrated multiscale description [1]. Many engineering applications involve polymeric fluids interacting with solid surfaces adding to the complexity of the theoretical description [2]. A natural modeling path towards linking disparate scales in two-phase material design is a bottom-to-top approach. The essence of this multiscale integration approach is in constructing models with varying degrees of resolution while passing only the most relevant physical information from high resolution, highly complex models to lower resolution descriptions at higher scales. This reduction in the degrees of freedom facilitates efficient computation of models approaching the macroscopic device scale for the purpose of technological advancement.

We primarily utilize atomistic/ molecular scale modeling and integration techniques in modeling polymers with varied molecular architecture including linear di-block and random copolymers as well as branched/starlike polymers on a variety of solid surfaces. Our benchmark case study involves perfluorinated polymer nano films coating various allotropes of carbon, illustrating our approach in the area of nano tribology. Bottom-level descriptions are established utilizing models of polymer-polymer and polymer-surface interactions based on first principle, electronic structure method calculations and are linked with lower resolution molecular descriptions via coarse-graining procedures to enable simulation over larger time/length scales. Our ab initio studies reveal the role of hydrogen bonding in promoting strong interactions among polymers with hydroxylated functional groups and the strong adhesion of these functional groups on carbon surfaces with high sp^2 bonding content. The atomistic scale interactions are incorporated into coarse-grained molecular dynamics simulations of the polymer/solid surface system to quantify static and dynamic physiochemical properties. Coarse-grained molecular dynamics simulations predict high mobility of polymers with weaker functional group interactions indicating highly desirable self-healing ability. In addition, strong polymer-surface adhesion creates small perpendicular radii of gyration and, consequently, thin film heights. Thus, we have established a correlation between atomistic/molecular architecture and mesoscale/macroscopic material performance.

Our approach for material design will open a new paradigm in areas such as energy, tribology, and catalysis which must meet the challenge of accurately and efficiently designing polymer melt/solid surface materials governed by multi-physical/multiscale phenomena.

1. P. S. Chung, M. S. Jhon, and L. T. Biegler, "Chapter 2- The Holistic Strategy in Multi-Scale Modeling", *Advances in Chemical Engineering*, Ed. G. B. Martin, New York: Academic Press 2011, 59-118.

2. P. S. Chung, R. Smith, S. H. Vemuri, Y. I. Jhon, K. Tak, I. Moon, L. T. Biegler, and M. S. Jhon, "Multi-scale/mult-physical modeling in head/disk interface of magnetic data storage," *J. Appl. Phys.* **111**, 07B712 (2012).