Figure 1. Recent image from the North Pole Web Cam. http://www.arctic.noaa.gov/gallery_np.html Used with explicit permission of NOAA/Pacific Marine Environmental Laboratory.

Molecular-Level Design of Fluid Lubricants for Arctic Service

Researchers are coordinating molecular-level simulation with experimental synthesis and characterization to understand the relationship between molecular architecture and friction

Nothing in life is easy in the Arctic. Everything must be designed to adapt to the bitter temperatures, where the Arctic average in January and February is -29°F (-34°C). Nature has responded to this challenge by insulating Arctic animals with a thick layer of blubber. When a person wants machinery to function in the Arctic, however, blubber won't cut it. Instead, they turn to synthetic lubricants, designed for extreme environments.

The problem with conventional hydrocarbon-based lubricants like those used in automobiles is that they stop behaving like liquids below a certain temperature. An alternative to conventional lubricants is a family of compounds called perfluoropolyethers (PFPE). If one replaces all of the small hydrogen atoms on a conventional oil with large fluorine atoms and makes sure that some oxygen reside along the carbon backbone for flexibility, then one has a PFPE. PFPEs are ideal lubricants for extreme environments (Arctic applications, space applications, and in nuclear reactors) due to the fact that they are very stable and they remain liquids at very low temperatures. Moreover, PFPEs exhibit the same low friction that makes Teflon® (a similar compound—a perfluoropolyalkene) a commercial success.

PFPEs have long been of interest to the lubricant industry. Recent work at the University of Tennessee in Knoxville is taking the research a step further by coupling molecular-level simulation with experimental synthesis and characterization. The experimental part of the team, led by fluorine chemist, Jamie Adcock, synthesizes the model PFPE compounds and measures their physical properties in the laboratory. The computational part of the team, led by chemical engineers, David Keffer and Brian Edwards, perform computer simulations using models of the PFPEs. These molecular-level simulations allow researchers to examine how each part of a molecule contributes to a particular property, such as the viscosity. For example in Figure 2, we show model compounds under study. The top compound is a base model. The second compound deviates from the base in that it has a shorter backbone. The third compound has different groups at the end of the chain. The fourth compound has a OCO group in the middle of the molecule. Using molecular simulation, we are able to determine the effect of these differences in molecular architecture on the viscosity. We can then put all this information

together to intelligently design the optimal lubricant that has whatever properties of interest to a specific application, including low viscosity, strong resistance to thermal and oxidative degradation, low freezing point, etc.

Results thus far indicate that the effect of the individual fluorine atoms is very different depending upon the local environment in which they sit. In other words, if a fluorine sits very close to an oxygen, it will behave differently than those on other parts of the chains. This type of information is necessary for a predictive understanding of the relationship between molecular architecture and lubricating properties.

We have developed a model that is able to reproduce the experimentally measured viscosity of these first four compounds. Using this model, we are now examining how the molecular architecture can be modified to make the lubricant resistant to a chemical attack by compounds sitting on the stainless steel surface that the PFPE is lubricating, that would otherwise tear the lubricant apart. The trick here is to enhance the chemical stability without comprising the viscous properties. Through the use of molecular level simulations, which provide a uniquely detailed insight into the system, coupled with rigorous comparison to experimental standards, we anticipate the development of new lubricants in the near future.

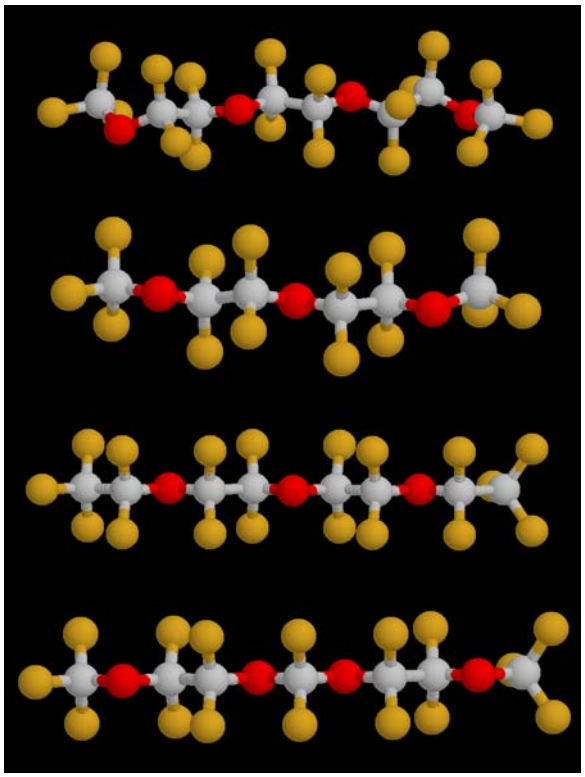

Figure 2. Schematic of PFPE lubricant structures. from top: (a) $C_8O_4F_{18}$, (b) $C_6O_3F_{14}$, (c) $C_8O_3F_{18}$, (d) $C_7O_4F_{16}$. Carbon are gray, oxygen red; and fluorine gold.

Dr. Ed Snyder and Dr. Lois Gschwender of the Air Force Research Laboratory have studied the tribological properties of PFPEs for over a decade. Recently a team at the University of Tennessee, led by Professors David Keffer (Chemical Engineering), Brian Edwards (Chemical Engineering) and Jamie Adcock (Chemistry) have taken up this work and added molecular-level simulation to complement the experimental effort. David Keffer wrote this article. For more information, contact dkeffer@utk.edu.