

Using Theory to Model Polymer Properties

There are two general themes to this research: (1) polymer degradation that occurs when polymers are exposed to low earth orbit conditions, and (2) polymer mechanical properties (stress/strain performance including fracture) and how the properties can be improved by combining the polymer with nanoinclusions of carbon nanotubes and graphene sheets and other structures.

Polymer degradation in the low earth orbit environment

This is an Air Force MURI project which involves a team of researchers, including Steve Sibener (Chicago), Yuping Lu (Chicago), John Tully (Yale), Bill Hase (Wayne St.), Barbara Garrison (Penn State), Tim Minton (Montana State) and Dennis Jacobs (Notre Dame).

The Schatz group is contributing to this project through electronic structure and molecular dynamics studies. A primary interest is in using direct dynamics and QM/MM methods to simulate collisions of 5 eV oxygen atoms with hydrocarbon polymers and polyimides.

Our initial work in this area has been concerned with O atom reactions with small hydrocarbons and other molecules. We wrote a front end and back end program to the GAMESS code which enables us to calculate reactive cross sections using direct dynamics (in which the trajectory integration is done on the fly with the electronic structure calculations). The front end defines the initial conditions for the trajectories, while the back end analyzes the results, determining energy and angular distribution information in addition to reactive cross sections.

Our initial applications of this code using B3LYP density functional theory¹ revealed that hyperthermal oxygen reacts quite differently from thermal oxygen. We discovered that in collisions of O with methane, ethane and propane at several eV collision energies, abstraction to give OH + alkyl is not the only important outcome. Instead, the oxygen can add to carbon to give oxy radical + hydrogen atoms as a significant product. Water plus triplet carbenes can also be produced. We have also seen direct C-C bond breaking, and direct production of aldehydes and alcohols.

In more recent work we have turned our attention to a semiempirical electronic structure method called MSINDO. We found that for O atom reactions with hydrocarbons, this approach gives reaction barriers that are comparable to what one gets from density functional theory, while the computational effort is orders of magnitude smaller. With this technology we have been able to perform detailed studies of O + hydrocarbon reactions, making extensive comparisons with crossed molecular beam experiments done at Montana State.²

The MSINDO method is sufficiently simple that we have been able to extend it to studies of O reacting with alkane thiol self assembled monolayers on Au(111) surfaces. We find the same reaction mechanisms as in the gas phase, but of course the surface collisions give additional dynamical processes such as trapping-desorption, and secondary reactions.³ The figure below shows a schematic of what we simulated.

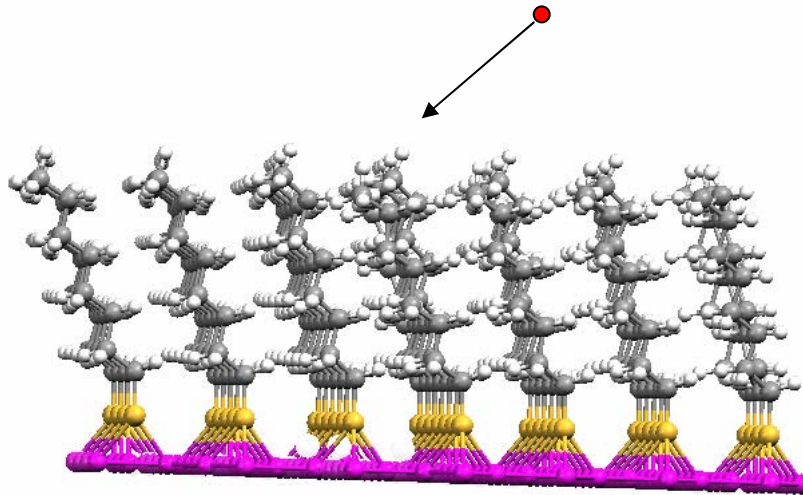


Figure 1. Schematic of hyperthermal oxygen/alkane thiol self-assembled monolayer/Au(111) system that we simulated using molecular dynamics calculations. In this system, the oxygen atom, the top-most four carbons of seven alkane chains and the associated hydrogens were described using quantum mechanics, while the remainder were described using molecular mechanics.

¹Hyperthermal reactions of O(³P) with alkanes: observations of novel reaction pathways in crossed-beams and theoretical studies, D. J. Garton, T. K. Minton, D. Troya, R. Pascual and G. C. Schatz, *J. Phys. Chem. A* 107, 4583-4587 (2003).

²Hyperthermal reactions of O(³P) with alkanes: observations of novel reaction pathways in crossed-beams and theoretical studies, D. J. Garton, T. K. Minton, D. Troya, R. Pascual and G. C. Schatz, *J. Phys. Chem., A* 107, 4583-4587 (2003).

³Theoretical Studies of Hyperthermal O(³P) Collisions with Hydrocarbon Self-Assembled Monolayers, Diego Troya and George C. Schatz, *J. Chem. Phys.*, 120, 7696-7707 (2004).

Polymer mechanical properties

The goal of this project is to learn how to use theoretical methods to describe the mechanical properties (stress/strain performance) of nanocomposites composed of polymers and nanomaterials. One project supporting this work is a NASA funded project that started in September, 2002. My collaborators on this project are mostly folks from the Mechanical Engineering Department at Northwestern (Ted Belytschko, Rod Ruoff), but the NASA center also has participation from Princeton, North Carolina, Santa Barbara and NASA Langley.

Our initial goal has been to understand what happens when you fracture carbon nanotubes and other materials using tensile stress. For any amount of applied force (stress) there is a displacement (strain) that can be used to define a force constant (Young's modulus) that is an important parameter in determining material performance (differentiating a brick from a piece of rubber, for instance). In addition, if you stretch a material far enough, it will fracture, so the stress and strain associated with fracture are important parameters.

The primary activity of this project has been to use density functional theory and semiempirical quantum mechanical methods to study the Young modulus and fracture behavior of defected carbon nanotubes. Here we found that the PM3 semiempirical method gives results that are reasonably close to what density functional theory predicts, so we have used this method to study the role of a variety of defects (Stone-Wales, vacancy defects, chemical functionalization) on fracture stress.¹ Figure 1 below shows typical tube structures for zero strain and after fracture.

A second project in this area is concerned with Ultrananocrystalline Diamond (UNCD). This NSF supported project is joint with Ted Belytschko, Horatio Espinosa and Mark Hersam at Northwestern, and there are some important collaborators from Argonne (where UNCD was discovered). The goal of this work is to use QM and continuum mechanics methods to model UNCD mechanical properties including their variation with doping. Here we have extensively used the MSINDO electronic structure method, and we find that nitrogen doping has a relatively small effect on modulus or fracture stress, so this may be a useful way to produce a conductive material as nitrogen doping enhances conductivity.

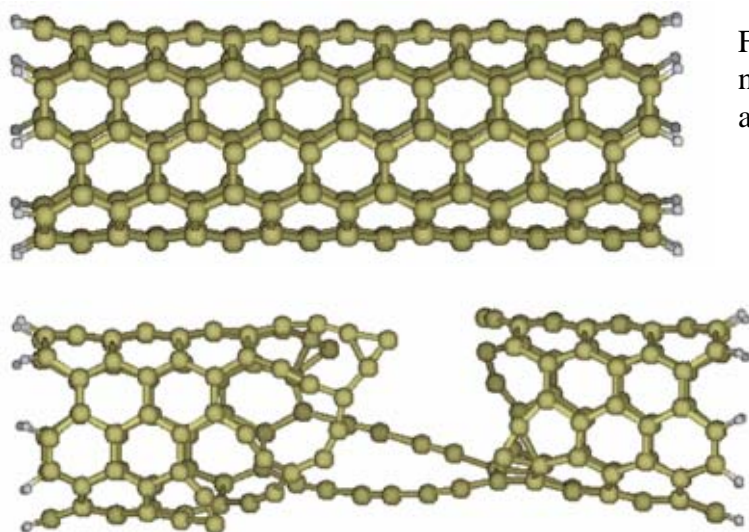


Figure 1. An undefected carbon nanotube and the structure that results after fracture.

¹Carbon nanotube fracture—differences between quantum mechanical mechanisms and those of empirical potentials, Diego Troya, Steven L. Mielke, and George C. Schatz, *Chem. Phys. Lett.*, 382, 133-41 (2003). The role of vacancy defects and holes in the fracture of carbon nanotubes, Steven L. Mielke, Diego Troya, Sulin Zhang, Je-Luen Li, Shaoping Xiao, Roberto Car, Rodney S. Ruoff, George C. Schatz, and Ted Belytschko, *Chem. Phys. Lett.*, 390, 413-20 (2004).