

Summary of Research

Title of Grant: Carbon Nanotubes: Building Blocks for Nanometer-Scale Engineering

Type of Report: Final Report - Summary of Research

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Period Covered: January 1, 1997 - December 31, 1999

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Grant Number: NAG 2-1121

The proposed work consisted of two projects: the investigation of fluid permeation and diffusion through ultrafiltration membranes composed of carbon nanotubes and the design and study of molecular transistors composed of nanotubes. Below I will outline the progress made on each project and also discuss additional projects, one of which is a continuation of work supported by an 1995-1996 NASA Ames Computer grant.

- 1) Liquid Interactions within a Nanotubule Membrane:
 - A) The first goal was to characterize the interactions of molecules and molecular mixtures with carbon nanotubes. This was done with a combination of classical, molecular dynamics simulations of the dynamic and diffusive flow of non-polar molecules through carbon nanotubes and with electronic structure calculations using density functional theory within the pseudopotential approximation. The latter approach is being used to study charge transfer that occurs between various molecules and tubule walls. This work has resulted in one published journal article and one publication in review. Two additional publications (not listed) are in preparation.
 - B) The second goal was to modify the many-body, empirical hydrocarbon potential developed by Brenner to include oxygen atoms. This work is complete and some of the results predicted by the potential are shown in the following table. As shown in the table, the potential shows excellent agreement with ab initio values. Extensive testing of the potential has been performed and have determined that the potential is bug-free. Work on this project did not proceed as quickly as originally intended since the potential developer, Mr. Lifeng Qi, left the University of Kentucky to begin

work at Ford Motor Company's research labs in Dearborn. He still plans to complete his PhD and as part of that effort he must complete writing up the results for development of the potential.

Molecule	Bond	Bond Length(Å)	Bond E(eV)	Total E (eV)	Literature Value (eV) (Ab Initio)
CH ₃ OH	H-O	2.96	4.43	20.195	21.292
	C-O	1.43	3.95		
	C-H	1.09	4.30		
CH ₂ CH ₃ OH	H-O	0.97	4.54	33.602	32.154
CH ₃ OOH	O-O	1.47	1.87	23.262	22.527
	C-O	1.45	3.96		
	O-H	0.97	4.54		
CH ₃ OCH ₃	C-O	1.43	3.48	32.756	32.210
CO ₂	C-O	1.16	5.54	11.072	11.470
O ₂	O-O	1.21	1.87	1.870	1.717
O ₃	O-O	1.27	1.13	3.000	5.184

2) Design of Nanometer-Scale Hydrocarbon Electronic Devices

This project was to examine the electronic structure of nanometer-scale transistors made of carbon nanotubes. We have stopped work on this project as results for similar systems appeared in the literature before we could get our results to press.

3) Mechanical Properties of Nanotubes and Nanotubule Bundles

We have made major progress in this area that has resulted in three journal papers published, one manuscript in review, and one manuscript in preparation. We have developed quantitative relationships between the buckling force of carbon nanotubes and the number of buckles that develop in the body of the tubule during compression:

$$F = YI (n\pi/L)^2$$

where F is the buckling force, I is the stress moment over the cross section of the nanotubule (CNT) radius ($I \gg \pi r^4/4$), n is the number of buckles that develop within the body of the tubule, and L is the length of the tubule. This equation corresponds to the Euler buckling force when there is only one buckle (n=1):

$$F_{\text{EULER}} = (\pi^2 YI)/L^2$$

This work showed that the magnitude of the buckling force is strongly dependent on the degrees of freedom available to the end of the CNT tip. When the CNT tip indented hydrogen-terminated diamond (111), the interactions between the tip and surface were highly repulsive and the tip was able to deform several different ways in addition to buckling, such as through cap inversion and slip on the surface (analogous to a person slipping on a banana peel). This resulted in lower overall buckling forces than compressions done in free space where the ends of the CNT are fixed, thus removing the strain-reduction mechanisms of cap inversion and slip. These simulations also indicate that in the case of highly reactive surfaces strong adhesion can occur between the CNT and the surface that destroys the CNT.

As part of this work we have also investigated how bundles of nanotubes and multi-walled nanotubes respond to indentation against hydrogen-terminated diamond (111) and graphene. The results showed that there are significant differences in the force curves that are non-intuitive but that the overall mechanisms of cap inversion, buckling and slip are unchanged.

Studies of the effect of chemical functionalization on the mechanical properties of carbon nanotubes show that chemical attachments degrade the mechanical properties by an average of 15% regardless of the diameter of the nanotubes or the helical symmetry of the tube. A new study uses classical atomistic simulations to predict a new mechanism for the chemical functionalization of nanotubes through ion bombardment. The paper describing these results is currently in review. Finally, studies to investigate the tribological properties of nanotube bundles between two sliding diamond surfaces as a function of the orientation of the bundles has been completed, with the manuscript in preparation at this date.

4) Growth Mechanisms of Carbon Nanotubes

Simulations combined with experimental efforts at the University of Kentucky have studied the growth of carbon nanotubes through chemical vapor deposition. The results strongly indicate that the size and type of nanotubes (single-walled versus multi-walled) grown depends heavily on the size of the metal catalyst particles. Larger particles lead to the formation of multi-walled nanotubes while small particles lead to the growth of single-walled nanotubes. Reaction temperature, substrate type, method of catalyst formation/deposition, and other reaction conditions are all shown to have an effect on the nanotubes formed. This information is important to tailor the mass-production of nanotubes for a variety of applications, in composites, electronic devices, and membranes.

Publications:

- 1) “Interactions of Carbon-Nanotubule Proximal Probe Tips with Diamond and Graphene”, A. Garg, J. Han and S. B. Sinnott, *Phys. Rev. Lett.* **81**, 2260-2264 (1998).

Abstract: Interactions between proximal probe tips composed of carbon nanotubes (CNTs) and diamond and graphene surfaces are investigated using molecular dynamics simulations. The simulations reveal the mechanisms of buckling, bending, slipping, and elastic recovery of the CNT tips on these surfaces and suggest that they will not wear out when "crashed" as conventional tips often do unless the surface is highly reactive. The simulations also show how the deformation mechanism changes as a function of tubule length and the effect of these changes on the buckling force is discussed quantitatively.

- 2) “Effect of chemical functionalization on the mechanical properties of carbon nanotubes”, A. Garg and S. B. Sinnott, *Chem. Phys. Lett.* **295**, 273-278 (1998).

Abstract: Carbon nanotubes (CNTs) have been proposed as ideal fibers for the manufacture of the next generation of composite materials. To ultimately increase the interaction of the CNTs with polymer matrices, researchers have attached chemical functional groups to the nanotube walls. The effects of covalent chemical attachments on the mechanical properties of single-wall CNTs are examined with classical molecular dynamics simulations. The maximum compressive (buckling) force for various functionalized and non-functionalized CNTs is calculated. It is found that covalent chemical attachments decrease the maximum buckling force by about 15% regardless of tubule helical structure or radius.

- 3) “Molecular Dynamics Simulations of the Filling and Decorating of Carbon Nanotubes”, Z. Mao, A. Garg and S. B. Sinnott, *Nanotechnology* **10**, 273-277 (1999).

Abstract: Carbon nanotubes (CNTs) have been proposed as ideal fibers for the manufacture of the next generation of composite materials and as excellent materials for the construction of ultrafiltration membranes. In this paper classical molecular dynamics simulations are used to investigate the potential use of CNTs in these applications. To ultimately increase the interaction of the CNTs with polymer matrices, chemical functional groups have been attached to the walls of CNTs. We examine the effects of covalent chemical attachments on the mechanical properties of single-wall CNTs. The diffusive flow of methane and ethane through the tubules at room temperature are also studied. The simulations predict normal-mode molecular diffusion for methane. However, a transition from normal to single-file diffusion is predicted for ethane.

- 4) “Effects of van der Waals Forces on Compression of Carbon Nanotubes: Molecular Dynamics Simulations”, A. Garg and S. B. Sinnott, *Phys. Rev. B* **60**, 13786-13791 (1999).

Abstract: The mechanisms by which carbon nanotubule (CNT) proximal probe tips deform during the indentation of surfaces are explored using classical molecular dynamics simulations. The

forces acting on the atoms in the simulations are calculated using the Brenner empirical bond-order potential for hydrocarbons. The results show that open and capped single-walled CNT tips indented against hydrogen-terminated diamond and graphene surfaces buckle and slip to relieve the applied stress. The study also examines the indentation of capped multi-walled tubules against these surfaces to investigate the effect of multiple shells on the deformation process. It is found that while shell-shell interactions have little effect on the deformation mechanisms, the multi-walled tubule is significantly stiffer than comparably sized single-walled tubules. No bond-formation between the shells is predicted as a result of deformation. Finally, a small CNT rope is indented against diamond and graphene to assess the effect of intertubule interactions on deformation. The simulations reveal how the deformation of the rope leads to the distortion of its end and allow for the determination of the effect of shear stress within the bundle on the buckling force of the rope.

- 5) “A Computational Study of Diffusion and Dynamic Molecular Flow Through Carbon Nanotubes”, Z. Mao and S. B. Sinnott, *J. Chem. Phys.* (in review).

Abstract: Molecular dynamics simulations are used to study the flow of methane, ethane and ethylene through carbon nanotubes at room temperature. The interatomic forces in the simulations are calculated using a classical reactive empirical bond-order hydrocarbon potential coupled to Lennard-Jones potentials. The simulations show that relatively weak intermolecular and molecule-nanotube interactions strongly affect both dynamic molecular flow and molecular diffusion. Specifically, molecules with initial hyperthermal velocities slowed to thermal velocities in nanotubes with diameters below 36 Å. In addition, molecules moving at thermal velocities at room temperature are predicted to diffuse from areas of high density to areas of low density through the nanotubes. Normal-mode molecular thermal diffusion is predicted for methane while ethane and ethylene are predicted to diffuse at a rate that is transitional between normal-mode and single-file diffusion. A new model is presented to characterize this transitional diffusive flow. The simulations also examine the effects of atomic termination at the nanotube opening and pore-pore interactions within a nanotube bundle on the diffusion results.

- 6) “Theory of Atomic-Scale Friction”, **S.B. Sinnott***, Chapter 12 in Volume 2 of *Handbook of Nanostructure Materials and Nanotechnology*, Ed. H. Nalwa, (Academic Press, San Diego, CA, 2000), pp. 571-618.

Review article - no abstract available.

- 7) “Model of Carbon Nanotube Growth Through Chemical Vapor Deposition”, S.B. Sinnott, R. Andrews, D. Quan, A.M. Rao, Z. Mao, E.C. Dickey and F. Derbyshire, *Chemical Physics Letters* **315**, 25-39 (1999).

Abstract: This letter outlines a model to account for the catalyzed growth of nanotubes by chemical vapor deposition. It proposes that their formation and growth is an extension of other known processes in which graphitic structures form over metal surfaces at moderate temperatures through the decomposition of organic precursors. Importantly, the model also states that the form

of carbon produced depends on the physical dimensions of the catalyzed reactions. Experimental data is presented that correlates nanotube diameters to the size of the catalyst particles. Nanotube stability as a function of nanotube type, length and diameter are also investigated through theoretical calculations.

- 8) "Chemical Functionalization of Carbon Nanotubes Through Energetic Radical Collisions", B. Ni and S.B. Sinnott, *Physical Review B* (in review)

Abstract: Classical molecular dynamics simulations are used to model the bombardment of a bundle of single walled carbon nanotubes by CH₃ radicals impacting with incident energies of 10, 45 and 80 eV. The simulations show that there is a high probability of adhesion of either the radicals or their fragments to the nanotube walls at all the incident energies considered. They therefore predict a new pathway to the chemical functionalization of the walls of carbon nanotubes. The simulations also show how at 80 eV the incident radicals can induce cross-linking between the nanotubes.

Presentations of NASA-Supported Research Results:

1. "Theoretical Investigation of the Mechanical Properties of Carbon Nanotubes, Fibers and Composites", S. B. Sinnott, Workshop of the Science of Carbon Nanotubes in Lexington, KY, July 9-11, 1997. (*Invited Oral*)
2. "Engineering of Nanostructures from Carbon Nanotubes", S. B. Sinnott, 6th Annual Consortium on Nanostructured Materials, Lexington, Kentucky, October 24-25, 1997. (*Invited Oral*)
3. "Computational Investigations of Material Surfaces and Interfaces", S. B. Sinnott, The Department of Materials Science and Engineering Colloquium, The University of Illinois at Urbana-Champaign in Urbana, IL, February 23, 1998. (*Invited Oral*)
4. "Computational Studies of the Properties and Processing of Surfaces", S. B. Sinnott, Department of Physics Colloquium, The University of Kentucky in Lexington, KY, April 24, 1998. (*Invited Oral*)
5. "Engineering of Nanostructures from Carbon Nanotubes", S. B. Sinnott and A. Garg, 5th Foresight Conference on Molecular Technology in Palo Alto, California, November 5-7, 1997. (*Contributed Oral*)
6. "Properties of Carbon Nanotubule Proximal Probe Tips", A. Garg and S. B. Sinnott, March Meeting of the American Physical Society in Los Angeles, California, March 16-20, 1998. (*Contributed Oral*)

7. "Investigation of the Mechanical Properties of Carbon Nanotubule Proximal Probe Tips", A. Garg, J. Han and S. B. Sinnott, 72nd Colloid and Surface Science Symposium in State College, Pennsylvania, June 21-24, 1998. [Chem. & Eng. News, May 11, 1998, p. 38]. **(Contributed Oral)**
8. "Molecular Dynamics Simulations of the Filling and Decorating of Carbon Nanotubes", Z. Mao, A. Garg and S. B. Sinnott, 6th Foresight Conference on Molecular Nanotechnology in Palo Alto, California, November 13-15, 1998. **(Contributed Poster)**
9. "Computational Studies of Carbon Nanotubule-Based Probes, Membranes and New Materials", S. B. Sinnott, The Department of Physics Colloquium, University of Louisville in Louisville, KY, January 29, 1999. **(Invited Oral)**
10. "Studies of Carbon Nanotubule-Based Probes and New Materials: Theory and Experiment", S.B. Sinnott, Solid State Division, Oak Ridge National Laboratory in Oak Ridge, TN, February 22, 1999. **(Invited Oral)**
11. "Computational Studies of Carbon Nanotubule-Based Probes, Membranes and New Materials", S. B. Sinnott, Workshop on *Emerging Methods in Computational Chemistry and Materials Science* in Aberdeen, MD, April 29-30, 1999. **(Invited Oral)**
12. "Proximal Probes, Membranes, and New Materials from Carbon Nanotubes: Computational Studies", S.B. Sinnott, 9th Conference on Computational Research on Materials in Morgantown, WV, May 19-21, 1999. **(Invited Oral)**
13. "Atomistic Simulations of Intercalation and Fluid Flow in Carbon Nanotubes", Z. Mao and S. B. Sinnott, Fall Meeting of the Materials Research Society in Boston, Massachusetts, November 30 - December 4, 1998. **(Contributed Oral)**
14. "Computational Design of New Nano-Composite Materials", B. Ni and S.B. Sinnott, 7th Foresight Conference on Molecular Nanotechnology in Santa Clara, California, October 15-17, 1999. **(Contributed Oral)**
15. "Selectivity and Diffusion of Binary Fluids in Carbon Nanotubes", Z. Mao and S.B. Sinnott, 46th International Symposium of the American Vacuum Society in Seattle, Washington, October 25-29, 1999. **(Contributed Oral)**
16. "Nanoindentation and Nanotribology with Carbon Nanotubes", B. Ni, A. Garg, and S.B. Sinnott, 46th International Symposium of the American Vacuum Society in Seattle, Washington, October 25-29, 1999. **(Contributed Oral)**