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NANOMATERIALS PHYSICAL PROPERTIES SIMULATION AND MODELING APPLICATIONS

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Abstract: *Modeling of nanomaterials requires realistic description of the system across various length and time scales. In order to illustrate how atomistic modeling is being used to determine the structure, physical, and chemical properties of materials at the nanoscale, molecular dynamics (MD) simulations will be presented for nanoscale assemblies based on carbon nanotubes, diamond surfaces, metal alloy nanowires, and ceramics. Some possible applications of atomistic modeling to carbon nanotubes, diamond surfaces, metallic nanowires, and organic liquids confined to nanoscale slits and structural transitions in ceramics will be also presented. These simulations use recent developments in force fields for metals, alloys, ceramics, and various phases of carbon which are also summarized here. This gives some glimpse of the enormous role that theory and modeling is likely to play as nanoscale science becomes a central theme in the 21st century technology.*

Keywords: nanomaterial, Quantum Mechanics, Molecular Dynamics simulation

1. Introduction

Nanotechnology, as defined in literature, is concerned with the structures, properties, and processes involving materials having organizational features on the spatial scale of 1–300 nm. At this scale devices may lead to dramatically enhanced performance, sensitivity, and reliability with dramatically decreased size, weight, and cost. Indeed these scales can lead to new phenomena providing opportunities for new levels of sensing, manipulation, and control. However, being much smaller than the wavelength of visible light but much larger than simple molecules, it is difficult to characterize the structure and to control the processes involving nanomaterials. From the experimental point of view, the fundamental problem in the nanoscale region is that the units are too small to see and manipulate and too large for single pot synthesis from chemical precursors. Because it is difficult to see what we are doing at the nanoscale, it is essential to develop theoretical and computational approaches sufficiently fast and accurate that the structure and properties of materials can be predicted for various conditions (temperature, pressure, concentrations) as a function of time. In this regard, a multiscale modeling approach of the system starting from quantum mechanical modeling to describe the electronic structure and optical properties, atomistic molecular dynamics (MD) calculations to describe diffusion processes, and meso scale simulation to describe the morphology of soft materials takes prominence.

1.2. Multiscale, hierarchical approach

Using preemptive theoretical predictions over the properties of new materials represents a particular advantage before experimental approaches. This allows the system to be designed (adjusted and refined) so as to obtain the optimal properties before the arduous experimental task of synthesis and characterization. However, there are significant challenges in using theory to predict accurate properties for nanoscale materials. Thus, a cube of polyethylene (PE) 100nm on side would have -64 million atoms, much too large for standard classical molecular dynamics (MD) and enormously too large for quantum mechanics (QM). Thus, the usage of multiscale (MSC) hierarchical strategy is better suited (Figure 1). The idea is to start with accurate first principles QM on small system (10s or 100s of atoms) at a level sufficient to describe bond breaking and formation processes (reactions). Based on the QM results, we then find force fields (FF) to replace the electrons in terms of springs. Using the

FF allows classical MD simulations with 1000s of atoms. With current methods and hardware, MD is practical up to -1 million atoms, but a million atoms of PE is a cube of only -25 nm on a side. To treat much larger systems, it is essential to average the atoms into collective units (segments, grains, pseudoatoms). This is the mesoscale region at the heart of nanoscale technology. Progress is being made in mesoscale simulations, but the demands of nanoscale technology require many additional advances. The simulations at the mesoscale can then be used to determine the parameters for finite element grids used in continuum calculations.

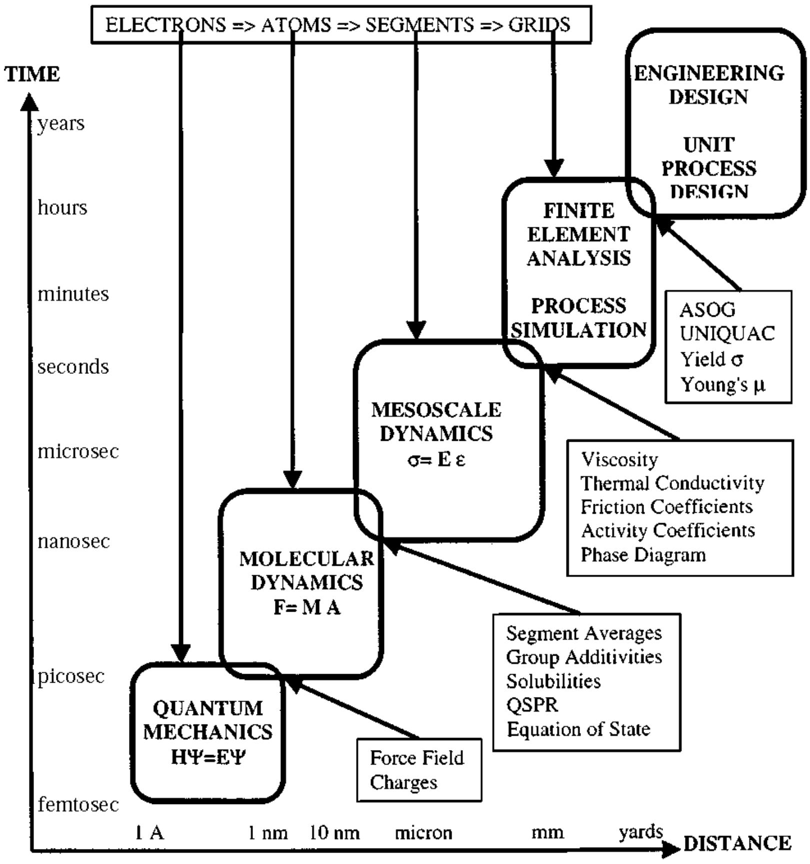

Figure 1. Multiscale computational hierarchy of materials simulations

1.3. Nanoscale approach

Nanomaterials may include carbon nanotubes, fullerenes, dendrimers, ceramics, zeolites, semiconductors, metals, polymers, and liquid crystals. These might be in the vapor/gas, liquid or solid phase (or all three phases may be present and interacting through vapor–liquid, solid–liquid, vapor–solid interfaces). The properties needed to predict include:

- *Structural properties*: Internal structure (bond topology, distances and angles), morphology, microstructure
- *Mechanical properties*: Vibrational modes, elastic moduli, yield limits, strength, toughness, temperature and pressure effects on mechanical properties (plasticity, yield, fracture, creep)
- *Surface properties*: Reconstruction, oxidation, adhesion, friction, and wear
- *Transport properties*: Diffusion and thermal conductivity
- *Rheological properties*: Viscosity and flow of fluids in the nanoscale regime, non-Newtonian behavior, flow and transport properties of nanoparticles to make electro-rheological or magneto-rheological fluids, structure–fluid interactions and their effect on transport properties, time, and frequency dependence of the flow properties.

Forecasting the structure, dynamics, and properties at the nanoscale require substantial improvements in theory (FF and simulation methodologies) and the software (the algorithms implementation to do the calculations).

2. Methods for simulating nanoscale materials

2.1. Quantum mechanics

QM is the foundation for the theoretical description of materials. QM is particularly important for describing processes in which bonds are broken and formed. Only with QM accurate barrier heights and bond energies can be obtained. In most recent studies there has been remarkable progress in such first principles electronic structure methods; however, the calculations are often far too slow for studying the applications of interest to nano-technology. Quantum mechanical methods capable of giving accurate barriers for the reactions of nanoscale materials:

- Generalized valence bond GVB,
- Psuedospectral generalized valence bond PS-GVB,
- Multireference configuration interaction MR-CI,
- Gaussian dual space density functional theory GDS-DFT

2.2. Force fields

For convenient calculations on large systems, its need to average over electrons from QM to obtain a FF that can describe the energy and forces in terms of atomic positions. Using results from QM we can develop FF adequate for predicting the energetics needed to simulate the structure and properties of nanomaterials. The FF must be accurate enough to obtain the correct energy differences for different phases of materials but must also describe the intermediate structures involved in phase transformations and interfacial phenomena. Standard FF generally use simple springs to represent bonds and angles in describing structures and vibrations of molecules. Such simple FF generally does not accurately describe the vibrational properties of molecules, which require cross terms and more complicated springs. The best FF are fit to the QM using the Hessian-Biased FF (HBFF) approach, which allows experimental information (about frequencies, polarizabilities, etc.) to be combined with normal mode information from QM. This HBFF approach has been used to develop accurate FF for polymers, ceramics, semiconductors, and metals.

For fast qualitative considerations of new systems, generic FF is suitable for general classes of systems. This includes the DREIDING FF (for the main group elements) and the Universal FF (UFF) (all elements: any inorganic, organo-metallic, or organic molecules).
In recent years, critical advances have been made in developing FF for describing:

- metals, where many body interactions play critical role on their physical properties;
- oxides, ceramics, and zeolites, where competition between ionic and covalent bonding is very important, especially in describing polymorphic phase transitions, reactions, defects, surface, and interface properties;
- covalent bonded system such as carbon, hydrocarbons, silicon, germanium and their behavior far from equilibrium where the description of bond breaking and formation must be included to obtain an accurate description.

2.3. Molecular dynamics

Using FF to predict the forces, the coupled sets of Newton's equations can be solved to describe the motion of the N interacting atoms this being referred as MD. The trajectories (R_i, V_i; i = 1, N) can be connected (generated by MD) to obtain macroscopic properties through the use of statistical mechanics and thermodynamics. MD simulations of heterogeneous nanomaterials may require thousands to millions of atoms to be considered explicitly. Accurate evaluation of the long-range interactions (electrostatic and dispersion), which decrease slowly with distance, is the most time-consuming aspect for MD simulations of such large systems. This cost is order (N^2) for N particles. Thus, a system of 10 million atoms requires the evaluation of 10^{14} terms each time step. The standard approach to simplifying such calculations, for finite systems, has been to ignore the interaction beyond some nonbond cutoff. However, for one million particles this requires maintaining an enormous nonbond list and also leads to errors orders of magnitude too large. For periodic systems such cutoffs lead to unacceptable errors, requiring Ewald approaches which require Fourier transforms. This leads to a scaling of $N^{1.5}$, totally impractical for systems with million atoms. Because nanoscale simulations require simulations of millions of atoms, methods and optimized parallel computer programs (MPSim) were developed for efficient high capacity MD. Special features include:

- Cell Multipole Method (CMM) which dramatically reduces the cost of long-range Coulomb and van der Waals interactions while retaining high accuracy. The cost scales linearly with size, allowing atomic-level simulations for million atom systems.
- Reduced Cell Multi-pole Method (RCCM) which handles the special difficulties with long-range Coulomb interactions for crystals by combining a reduced unit cell plus CMM for interaction of the unit cell with its adjacent cells. The cost scales linearly with size while retaining high accuracy, allowing simulation of crystals having a million atoms per unit cell (the major use is for models of amorphous and semi-crystalline materials).
- Newton Euler Inverse Mass Operator method (NEIMO) for internal coordinate dynamics (e.g., treats torsions only). This allows the solution of the dynamical equations for internal coordinates without inverting the mass tensor (moment of inertia tensor). The cost of NEIMO is linear in the number of degrees of freedom and small compared to other costs for million atom systems. More recently we also developed a new constrained force algorithm (CFA) for massively parallel MD simulation of polymers and dendrimers.
- Steady state MD methods are used to simulate nonequilibrium processes such as friction and wear in diamond, metals, and metal oxides. Here, the external work is dissipated through material and coupled to a thermal bath using Langevin equation.

3. Applications of modeling and simulation for nanomaterials

To summarize some recent applications in nanoscale systems illustrating the role of new developments in simulation technology:

1. Characterization of SWNTs with accurate (QM derived) FF using MD.
2. MD studies of alkali doped single-walled nanotubes.
3. Plastic deformations and mechanical behavior of multi-walled nanotubes.
4. MD Simulation of Friction and Wear Processes on Diamond.
5. MD Simulation of Friction and Flow Process for iron oxide slabs separated by 8 nm covered by a SAM and lubricated with n–$C_{16}H_{34}$.
6. Plastic deformation behavior of metallic nanowires.
7. Phase behavior of ceramics under compressive loads.

Single-Walled Carbon Nanotubes – energetics and structure properties

Carbon nanotubes were discovered in 1991 by Iijima. Since then, there have been many advances in synthesis, in characterization, and in the theoretical understanding of such nanotubes. The novel mechanical and electronic properties of these nanotubes suggest many applications to nanotechnology.

The single-walled carbon nanotubes (SWNT) are the simplest carbon nanotubes which and they were discovered simultaneously by the Iijima group and an IBM-Caltech team. These SWNT, which can be regarded as a graphite sheet rolled-up into a cylinder, show remarkable mechanical and electrical properties. They present tremendous potential as components for use in nanoelectronic and nanomechanical device applications or as structural elements in various composite materials. Tightly bundled linear ‘ropes’ of SWNT are expected to have remarkable mechanical properties, as well as superior electronic and magnetic properties. Various levels of theory have been used to characterize properties of the SWNT. This includes classical molecular mechanics (MM), lattice dynamics, MD, – tight binding QM, and *ab initio* QM methods.

Assessing the mechanical stability of SWNT, tubes with three different chiral forms (n, n) armchair, (n, 0) zigzag, and (2n, n), must be taken into consideration. Thus for diameters less than 60 Å it was demonstrated that circular SWNT are most stable, but that larger SWNT collapse into a shape in which the opposite walls in the middle section are 3.4 Å apart (the van der Waals distance) while each end has a nearly circular diameter of ~10.7 Å. To mimic long isolated nanotubes, periodic boundary conditions in the c-direction (tube direction) have to be imposed. To eliminate the inter tube interactions, the cell parameter a and b must be set as 50 times of the circular tube diameter.

Energy and structural optimizations can be resolved using MPSim. To extract mesoscale parameters characterizing the basic energetics of tubes, the tube can be approximated as a membrane with a radius of curvature R and a bending modulus of κ. Using continuum theory, a tube with wall thickness *a* and length *L* has an elastic energy stored of:

$$E_{\text{strain}} = \frac{\pi \kappa L a^2}{12R} \tag{1}$$

thus, the energy per atom becomes:

$$E_{\text{C}} = \frac{\pi \kappa L a^2}{12RN} + E_o \tag{2}$$

where N is the number of carbon atoms per slab and E_0 is energy per carbon atom for tubes with R = ∞ (i.e. flat sheets). Letting $N = 2\pi \rho L R$, where ρ is the number of carbon atoms per unit area of tube wall, we obtain:

$$E_{\text{C}} = \kappa \frac{a^2}{24\rho} \frac{1}{R^2} + E_o \tag{3}$$

The armchair SWNT is expected to have the lowest energy for a growing exposed edge. Good crystals of bucky tubes have not been reported experimentally. However, the mechanical properties can be predicted for crystalline (n,n) armchair, (n,0) zigzag, and (2n,n) chiral tubes. These all have similar cross section radii. The MD and MM studies lead to a hexagonal closest packing as the most stable form for all three forms.

K-doped SWNT crystals – the structure

Development of methods to control the catalytic synthesis of SWNT to form ordered ropes containing 100s–1000s of tubes gives hope for developing structures useful for new generations of nanoscale devices. Recent reports that these SWNT ropes can be doped to form metallic conductors give further hope for interesting devices.

There is no data on the structure for such doped systems. To provide this data the predicted minimized crystal structure for armchair (10, 10) SWNT is used. Supposing up to 6 independent SWNT per unit cell and appropriate numbers of K atoms distributed in various ways to which 20 ps of MD is applied to equilibrate the system and quench the structures by minimizing the energy. Then analyzing each case to see if the pattern of K binding sites would suggest new structures to build and minimize. For triangular crystals with n up to 2, the K intercalates between three tubes, leading to essentially the same spacing as in pristine SWNT.

Figure 3 shows the energy per carbon atom as a function of number of intercalated K ions for two different packing schemes (square and triangular) and different doping types: exo (K atoms allowed only outside the tubes) and endo (K atoms allowed only inside the tubes). Assuming exo K, the global minimum is the triangular structure for K_5C_{80} = KC_{16}. The optimum structure has the K packed in the same (2 x 2) pattern observed for intercalated graphite, KC_8. The difference for the KC_{16} SWNT is that the K are only on the outside of the tube (vide infra), leading to half the amount of K. For n > 7, the K causes significant distortions in the tube shells.

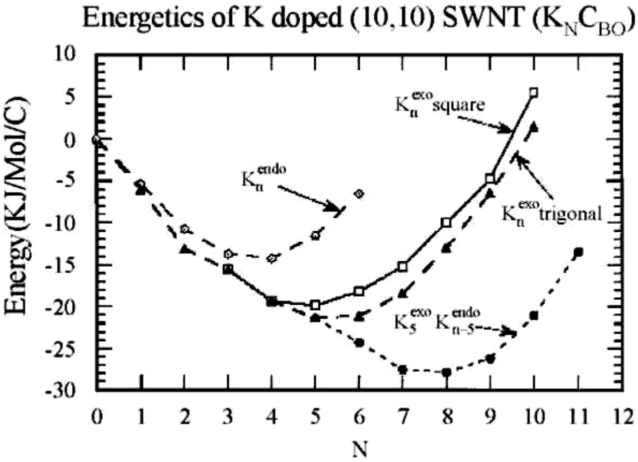

Figure 2. Energy per carbon atom for triangular and square packing of K doped SWNT

Diamond surfaces – MD simulation of friction

Theoretical investigation of wear and friction is especially important in the design of micro-electromechanical systems (MEMS) and nano-electromechanical systems (NEMS). In order to describe wear, it is essential that the calculations properly describe bond formation and breaking. Thus, we use the GEE-BOD FF. Low friction is a crucial factor in determining the performance, efficiency, and durability of MEMS.

Since silicon is available in large single crystals which can be etched easily to form micron scale devices, most MEMS are made of silicon. However, studies have shown that the friction between such Si systems is very high, leading to very rapid wear. As a result, the use of diamond is proposed for MEMS involving moving parts. In addition to diamond being the hardest material, polycrystalline diamond (PCD) has a friction coefficient several times smaller than silicon.

Considering two diamond crystals with hydrogenated surfaces put in contact, the ratio between the external force applied for maintaining the moving block at a constant velocity and the average calculated normal force of the static block gives the friction coefficient.

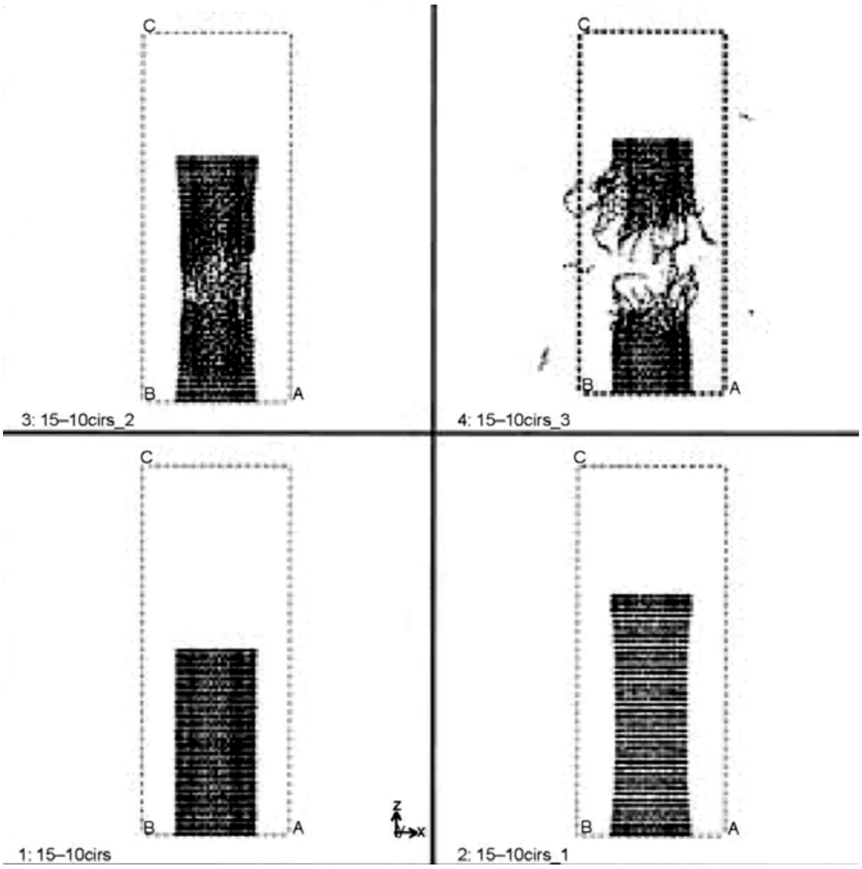

Figure 3. Time evolution of structure under tensile load

Figure 4 shows the running average of the force in the normal direction with respect to sliding direction with the sliding velocity maintained at a constant value. The initial oscillations represent the approach a steady state. The average normal force is very similar for different sliding directions. This indicates that differences in the differential friction coefficients arise from differences between the surfaces. Figure 5 presents the running averages of calculated friction coefficients. As expected, the xy direction has the lowest friction coefficient while the x and y directions are nearly identical. If the two surfaces were perfectly aligned, sliding in the x and y directions would have yielded identical friction coefficients.

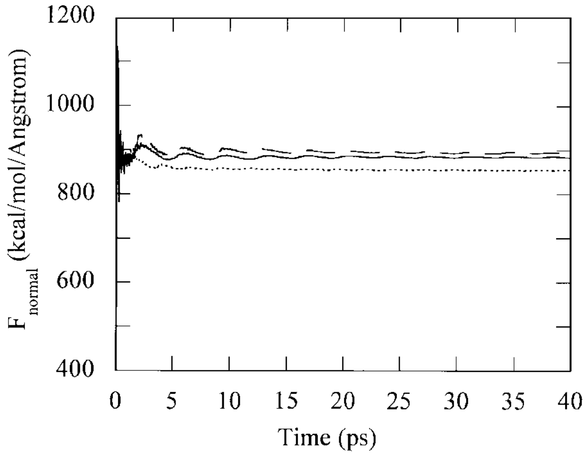

Figure 4. Average of the normal force for constant sliding speed

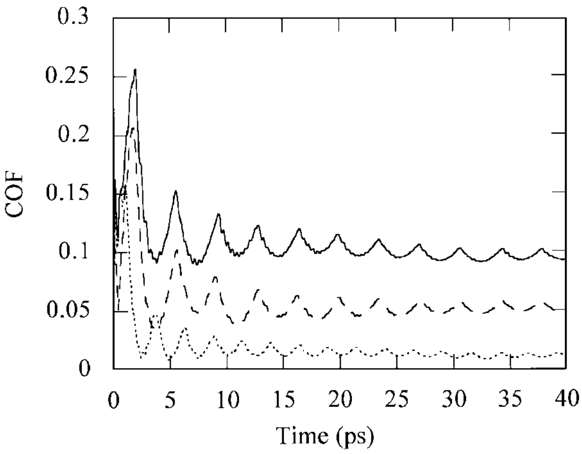

Figure 5. Average of friction coefficients calculated for different sliding

4. Synopsis

Properties of interest: surface reactivity, dispersion forces, interfacial structure / bonding / adhesion, tensile / shear strength, ductility, fracture, band gap, optical spectra, transport (diffusion, electrical conductivity and conductance).
Materials of interest to industry: metal oxides/nitrides/carbides, polymers, ceramic coatings, metal alloys, composites, amorphous structures.
Predictive models are intended to tell us something about the future. The future is uncertain. Predictive models characterize uncertainty about the future. Probability offers the main theory suitable for predictive modeling. Constructing predictive models i.e., probability spaces, their associated random variables and stochastic processes is very tedious.
Predictive modeling takes a number of forms and requires a number of components
– Modeling is needed to make accurate measurements of the dimensions of nanomaterials, "size matters" and accurate dimensional measurements are extremely important;
– Modeling is needed to accurately determine what materials are present;
– Modeling is needed to understand the materials properties;
– Modeling is needed to predict the properties;
– Experimental input data is needed;
– Agreement between theory and experiment.
Stochastic differential equations having solutions that give probability law on important performance variables & stochastic processes are very rare. The computational burden associated with most practical predictive engineering models is very high.
Premises for accurate simulation and modeling applications:
– Selecting the appropriate theory for given phenomenon and material
– Must know approximations made and how they affect outcome (error estimates)
– Method should give right answer for right reason (correct physics, correct phenomenon)
Validation of predictions: critical – difficult to design appropriate experiment
Emerging areas are: Hybrid simulations with nanoparticles and colloids; Polyelectrolyte complexation; Supramolecular polymers; Nonequilibrium extensions to coupled flow and structure.
This is an exciting frontier research area that brings together topics from: Theoretical physics and applied math; Numerical and computational sciences; Materials science and Real world applications.

References

[1] Greeley, B.H., Russo, T.V., Mainz, D.T., Friesner, R.A., Langlois, J.-M., Goddard III, W.A., Donnelly, R.E., Ringnalda M.N., *J. Chem. Phys.* 101, 4028, 1994.
[2] Chen. X.J., Langlois, J.-M., Goddard, W.A., *Phys. Rev. B* 52, 2348, 1995.
[3] Dasgupta, S., Yamasaki, T., Goddard III W.A., *J. Chem. Phys.* 104, 2898, 1996.
[4] Karasawa, N., Goddard III, W.A., *Macromolecules*, 28, 6765, 1995.
[5] Dasgupta, S., Smith, K.A., Goddard III, W.A. *J. Phys. Chem.* 97, 10891, 1993.
[6] Musgrave, C.B., Harris, S.J., Goddard III, W.A., *Chem. Phys. Lett.* 247, 359, 1995.
[7] Rappe, A.K., Casewit, C.J., Colwell, K.S., Goddard III, W.A., Skiff, WM., *J. Am. Chem. Soc.*, 114, 10024, 1992.
[8] *International Congress on Glass*, Eds. M.K. Choudhary, N.T. Huff, C.H. Drummond III, pp. 11-15, July 5-10, 1998, San Fransisco, USA.
[9] Cagın T., *Computer aided innovation of new materials II*, Eds. M. Doyama, J. Kihara, M. Tanaka, and R. Yamamoto, pp. 255-259, 1993.
[10] Chen, Z.M., Cagın, T., Goddard, III, W.A., *J. Comp. Chem.* 18, 1365-70, 1997.
[11] Lim, K.T., Brunett, S., Iotov, M., McClurg, R.B., Vaidehi, N., Dasgupta, S., Taylor, S. Goddard III, W.A., *J. Comp. Chem.* 18, 501-521, 1997.

[12] Miklis, P., Cagın, T., Goddard III, W.A., *J. Am. Chem. Soc*., 119, 7458, 1997.
[13] Ding, H., Karasawa, N., Goddard III, W.A., *Chem. Phys. Lett*., 196, 6, 1992.
[14] Vaidehi, N., Jain, A., Goddard III, W.A., *J. Phys. Chem.* 100, 10508, 1996.
[15] Fijany, A. J-Botero, A., Cagın, T., *Parallel Computing: Fundamentals Applications and New Directions*, Eds. D'Hollander, G. Joubert, F. Peters, and U. Trottenberg, pp. 505-511 1998.
[16] Cagın, T., Goddard III, W.A., Ary, M.L., *Comp. Polymer Sci.* 1, 241, 1991.
[17] Dereli, G., Cagın, T., Uludogan, M., Tomak, M., *Phil. Mag. Lett.* 75, 83-102, 1997.
[18] Daw, M.S., Baskes, M.I., *Phys. Rev. B,* 29, 6443, 1984.
[19] Sutton, A.P, *J. Chen: Phil. Mag. Lett*., 61, 139, 1990.
[20] Cohen, R.E., Mazin, I.I., Isaac, D.G., *Science*, 275, 654, 1997.
[21] Liu, F., Garofalini, S.H., Kingsmith, D., Vanderbilt, D., *Phys. Rev.*, 49, 12528, 1994.
[22] Woodcock, L.V., Angell, C.A., Cheeseman, P., *J. Chem. Phys*. 65, 1565, 1976.
[23] Tsuneyuki, S., Aoki, H., Tsukada, M., Matsui, Y., *Phys. Rev. Lett.* 61, 869, 1988.
[24] Ogawaand, H., Waseda, Y., *Science Reports of The Research Institutes Tohoku University Series A Physics Chemistry and Metallurgy*, 36, 20, 1991.
[25] Rappe´, A.K., Goddard III, W.A., *J. Phys. Chem.* 95, 3358, 1991.
[26] Iijima, S., Brabec, C., Maiti, A., Bernholc, J., *J. Chem. Phys.* 104, 2089–2092, 1996.
[27] Bethune, D.S., Kiang, C.H., Devries, M.S., Gorman, G., Savoy, R., Vazquez, J., Beyers, R., *Nature,* 363, 605–607, 1996.
[28] Thess, A., Lee, R., Nikolaev, P., Dai, H., Petit, P., Robert, J., Xu, C., Lee, Y.H., Kim, S.G., Rinzler, A.G., Colbert, D.T., Scuseria, G.E., Tomanek, D., Fisher, J.E., Smalley, R.E. *Science* 273, 483–487, 1996.
[29] Krotov, Y.A., Lee, D.H., Louie, S.G., *Phys. Rev. Lett.* 78, 4245–4248, 1997.
[30] Hamada, N., Sawada, S., Oshiyama, A., *Phys. Rev. Lett.,* 78, 1579–1581, 1992.
[31] Saito, R., Fujita, M., Dresselhaus, G., Dresselhaus, M.S., *Appl. Phys. Lett.* 60, 2204–2206, 1992.
[32] Yakobson, B.I., Campbell, M.P., Brabec, C.J., Bernholc, J., *Comp. Mater. Sci.* 8(5) 341–348, 1997.
[33] Richter, E., Subbaswamy, K.R., *Phys. Rev. Lett.,* 79, 2738–41, 1997.
[34] Iijima, S., Brabec, C., Maiti, A., Bernholc, J., *J. Chem. Phys.* 104, 2089–2092, 1996.
[35] Rao, A.M., Richter, E., Bandow, S., Chase, B., Eklund, P.C., Williams, K.A., Fang, S. Subbaswamy, K.R., Menon, M., Thess, A., Smalley, R.E., Dresselhaus, G., Dresselhaus, M.S., *Science*, 275, 187–191, 1997.
[36] Presentations of: *Predictive Modeling of Nanomaterial Properties*, October 2007 organized by the *Network of computational nanotechnology* from Purdue University

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