

SYMPOSIUM II

Modeling of One- and Two-Dimensional Nanomaterials

November 29 - December 2, 2004

Chairs

Che Ting Chan

Dept. of Physics
Univ of Science and Technology
Clear Water Bay
Hong Kong, China
852-2358-7087

Gerhard Goldbeck-Wood

Accelrys
334 Cambridge Science Park
Cambridge, CB4 0WN United Kingdom
44-1223-228500

Ruth Pachter

AFRL/MLPJ
Air Force Research Laboratory
3005 Hobson Way
WPAFB, OH 45433-7702
937-255-3808 x-3177

Boris I. Yakobson

Dept Mechanical Engr & Materials Science
Rice University
MS 321
P.O. Box 1892
Houston, TX 77005-1892
713-348-3572

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SESSION III:
Chair: W. Goddard
Monday Morning, November 29, 2004
Room 204 (Hynes)

8:30 AM *III.1

Transport in Molecular Junctions: Kinetics, Molecular Substituents, in Inelastic Behavior and Control. Mark Ratner, Department of Chemistry, Northwestern University, Evanston, Illinois.

Molecular transport junctions comprise effectively linear structures, coupled to electrodes at either end. Utilizing what has become a standard nonequilibrium Green's function approach, we analyze both molecular substituent effects and inelastic effects on junction transport. We also compare to related work on long-range intramolecular electron transfer. We find that substituent effects are relatively minor - in striking contrast to molecular thin film transistor structures, in molecular transport junctions other electrostatic phenomena seem to dominate, so that only small effects on the conductance are seen with putting either electron donating or electron withdrawing groups on small ring compounds. For short junctions, inelastic effects are also relatively weak. Nevertheless, their observation tells a great deal about vibronic coupling, lifetimes and spectral densities in transport junctions. Finally, the relationship of spin behavior and transfer rate in linear triads is extended beyond the simple Anderson relationship, and the new theoretical formulation is compared to experiments on donor/bridge/acceptor systems. The talk will focus on analysis of the inelastic and electrostatic effects, and on some generalities concerning how they depend on molecular structure.

9:00 AM III.2

Electron Transport through Molecular Junctions: A TDDFT Approach. Xiaofeng Qian¹, Lin Xi¹, Ju Li² and Sidney Yip¹;

¹Department of Nuclear Engineering and Department of Materials Science and Engineering, MIT, Cambridge, Massachusetts;

²Department of Materials Science and Engineering, Ohio State University, Columbus, Ohio.

Electron transmission through molecular junctions is modeled in real time using time-dependent density functional theory with ultrasoft pseudopotentials. Special boundary conditions are developed to lift from equilibrium ground state to non-equilibrium steady state. Conductivity is estimated by the time-averaged flux. Analysis of charge transport based on Wannier type local orbitals are performed.

9:15 AM III.3

Electronic Properties of Complex Nanostructures from Maximally-Localized Wannier Functions. Young-Su Lee¹, Marco

Buongiorno Nardelli^{2,3} and Nicola Marzari¹; ¹Department of Materials Science and Engineering and Institute for Soldier Nanotechnologies, Massachusetts Institute of Technology, Cambridge, Massachusetts; ²Department of Physics, North Carolina State University, Raleigh, North Carolina; ³CCS-CSM, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

We have combined large-scale Gamma-point Car-Parrinello electronic-structure simulations and the maximally-localized representation of the Kohn-Sham orbitals in a novel approach that allows to calculate the band structure and the Landauer conductance of complex nanostructures. This approach relies on our ability to map Bloch orbitals into maximally-localized Wannier functions, and to derive in this representation exact "tight-binding" Hamiltonians at any ionic configuration. Application to carbon nanotubes highlights the importance of disentangling the appropriate pi bands from the conduction bands manifold, and the power of this approach in predicting with full first-principles accuracy the effects of chemical disorder in large-scale systems.

9:30 AM *II.1.4

Theory and Computation of the Optical, Transport, and Mechanical Properties of Nanostructures. Steven G. Louie,

¹Physics, University of California at Berkeley, Berkeley, California;

²Materials Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California.

The restricted geometry and symmetry of nanostructures often give rise to interesting quantum confinement, enhanced many-electron interaction, and other effects related to reduced dimensionality. These effects can lead to novel physical properties and phenomena, which also are potentially useful in applications. In this talk, I will discuss some of our recent theoretical studies on the unusual electron transport, optical, and mechanical properties of nanotubes and molecular junctions. For examples, molecular electronic devices, i.e., electrical transport through a single molecule, can produce highly nonlinear I-V characteristics. The optical spectra of small diameter carbon nanotubes exhibit dramatic excitonic effects, in both metal and semiconductor tubes. Also mechanical energy dissipation (or

friction) on the nanoscale may be very different from that on the human scale. We will present some results on the nonlinear transport behavior of molecular junctions calculated using an ab initio scattering-state method, the optical response of nanotubes employing a first-principles many-particle Green's function approach, and the behaviors of mechanical energy dissipation in double-walled carbon nanotube oscillators from molecular dynamics simulations. The physical origins of the calculated behaviors will be examined.

10:15 AM III.5

Non-equilibrium electronic transport in atomic wires and molecular junctions. Arrigo Calzolari¹, Vincent Meunier² and

Marco Buongiorno Nardelli^{3,2}; ¹Physics, U. of Modena and INFN-S3, Modena, Italy; ²CCS-CSM, ORNL, Oak Ridge, Tennessee; ³Physics, NCSU, Raleigh, North Carolina.

Understanding the electronic and conduction properties of nanostructures is a fundamental step towards further miniaturization of electronic devices. Notably, atomic-sized gold systems have attracted special attention because of their unique characteristics. Interestingly, the reduction of the dimensionality to quasi one-dimensional nanowire leads to the appearance of significantly different electric behavior when compared to the bulk material. It follows that they can be effectively used to design molecular devices of controllable geometry and property. Using a novel approach to calculate the electronic and the coherent transport properties of extended nanostructures from first principles (<http://www.wannier-transport.org>), we have investigated the electronic conductance of various atomic wires and molecular junctions, both in equilibrium and non-equilibrium electrostatic conditions. Special focus is brought to the effect of small molecule adsorption on ideal Au wires and the conductance properties of a benzene di-thiol molecule attached to various lead geometries.

10:30 AM III.6

Nonequilibrium Transport in Silicon Nanowires.

Fabiano A. Oyafo, Paul von Allmen, Seungwon Lee and Gerhard Klimeck; Jet Propulsion Laboratory, Pasadena, California.

In the past decade, Si-based nanowires have received increasing attention as potential candidates for use in a number of electronic devices, including single-electron transistors, chemical sensors, and single-photon detectors. Yet, modeling of electronic transport through such structures is still in its infancy. In this work, we present a non-equilibrium Green function-based approach that extends the 1D nanoelectronic modeling software (NEMO) to 3D. Electronic states are computed using a 20-orbital nearest-neighbor tight-binding basis. The coupling between orbitals is determined semi-empirically through a genetic algorithm package that optimizes the fit of various observables to experimentally measured values. The fitting also includes lattice deformations, so that strained or alloyed materials can be easily modeled. In this work, we examine the effect of the surface perturbations on the conductance of a finite Si nanowire. Two effects are examined. First, the dependence of transmission coefficient on surface boundary condition is studied. A comparison is made between conductance through a hydrogen-passivated nanowire and one in which dangling bonds are introduced. Second, a study of transport in Si nanowires embedded in Si/Ge is presented. In particular, the effects of interface interdiffusion of Ge atoms within the Si nanotube is discussed.

10:45 AM III.7

A Green's Function Formalism with Gaussian Broadening for Electrical Transmission in Atomic and Molecular Wires.

Tomofumi Tada^{1,2}, Masakazu Kondo³, Kazunari Yoshizawa³ and Satoshi Watanabe^{1,2}; ¹Department of Materials Engineering, The University of Tokyo, Tokyo, Japan; ²CREST, Japan Science and Technology Agency, Kawaguchi, Japan; ³Institute for Materials Chemistry and Engineering, Kyushu University, Fukuoka, Japan.

The understanding of the electrical transport in single molecules is an important issue for the development of molecular electronics. However, quantitative agreement on the conductance of single molecules has not been reached yet among experiments. For example, the measured conductance of benzene-1,4-dithiolate (BDT) between Au electrodes in the limit of the zero voltage is 0.0002 G_0 by Reed and co-workers [1] and 0.011 G_0 by Tao and co-workers [2], where G_0 is the quantum unit of conductance ($2e^2/h$). Similar conflict is also seen in theoretical estimation of conductance. Even among recent density functional calculations, computed conductance of the BDT wire varies from 0.06 to 0.45 G_0 . Therefore further studies are definitely needed. On theoretical side, methods that enables us to obtain reliable conductance values with relatively small computational costs are strongly desired to examine transport properties of various single molecules and the effects of several environmental factors, e.g., the binding site on electrodes and the orientation with respect to electrodes. In this study, we propose a novel theoretical approach for

electrical transmission for this purpose [3]. Our approach incorporates Green's function formalism with Gaussian broadening of discrete states. The broadening allows us to represent electronic states of an extended electrode by broadened density of states of a small cluster. Using this approach, we calculated the electrical conductances of molecular wires of BDT, benzene-1,4-dimethanethiolate (BDMT), 4,4'-bipyridine (BP), hexane dithiolate (HDT), and octane dithiolate (ODT) between Au electrodes. The binding site is assumed to be the on-top one, considering that molecules are likely to be bonded to this site in the recent experiments by Tao and co-workers [2,4]. The Au electrode was represented by an Au₇ cluster with broadening width of 1.4 eV, and B3LYP functional and the CEP-31G basis set were adopted. The computed/measured conductances of BDT, BDMT, BP, HDT, and ODT are 0.01512/0.011, 0.00085/0.0006, 0.00996/0.01, 0.00292/0.0012, and 0.00006/0.00025 G₀, respectively [2,3,4], and thus the agreement between our computations and their measurements is excellent. In the presentation, we will show the details of the computational scheme of our approach and computed results, together with technical issues to be overcome, such as how we should determine the Fermi level and where we should locate the boundaries between electrodes and a molecule. [1] M. A. Reed, C. Zhou, C. J. Muller, T. P. Burgin, and J. M. Tour, *Science* 278, 252 (1997). [2] X. Xiao, B. Xu, and N. J. Tao, *Nano Lett.* 4, 267 (2004). [3] T. Tada, M. Kondo, and K. Yoshizawa, *J. Chem. Phys.*, in revision (2004). [4] B. Xu and N. J. Tao, *Science* 301, 1221 (2003).

11:00 AM II.1.8

Mixed finite element-tight binding technique for studying the electromechanical behavior of single and multiwall carbon nanotubes. Antonio Pantano^{1,2}, Mary C. Boyce¹, David M. Parks¹ and Marco Buongiorno Nardelli³, ¹Mechanical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts; ²Mechanical Engineering, University of Palermo, Palermo, Italy; ³Physics, North Carolina State University, Chapel Hill, North Carolina.

Electrical transport properties of carbon nanotubes can be dramatically changed by mechanical deformations that alter the positions of the atoms comprising the tube wall. In principle, detailed atomic/electronic calculations can provide both the deformed configuration and the resulting electrical transport behavior of the tube. However, the computational expense of these simulations limits the size of the CNTs that can be studied with this technique, and a direct analysis of MWNTs or of SWNT of the dimensions used in nano-electronic devices seems prohibitive at the present. Here we simplify the process by refining a previously-developed nonlinear structural mechanics finite-element-based procedure for modeling mechanical behavior of carbon nanotubes to account explicitly for tube chirality. A novel quadrilateral element overlay procedure provides an isotropic finite element model of hexagonal cells within a graphene sheet, with the only nodal positions coincident with those of the atoms. The approach significantly reduces the computational cost with respect to atomistic simulations, allowing the investigation of multiwall nanotubes. After the mechanical deformation of the nanotube structure is simulated with finite elements, the evolving atomic [nodal] coordinates are processed within the FE program by using a tight-binding (TB) code to calculate deformation-induced changes in electrical transport properties of the nanotube. If our main objective is to predict the effect of deformation on the electrical properties of MWNTs, adopting a conventional TB code would negate the computational saving obtained by using the structural mechanics approach. That's why an innovative TB that is able to significantly reduce the computer power requirements was employed. Each CNT is divided along its length into a given number of smaller CNTs connected at their interfaces. Then the coherent transport properties of the system, which is equivalent to the original CNT, are calculated by a TB approach based on a surface Green's function matching technique and the Landauer formula. The proposed mixed finite element-tight binding technique could provide scientists with a valuable tool for studying the electromechanical behavior of large SWNTs and MWNTs.

11:15 AM II.1.9

Atomistic Electron Transport Modeling of π -Stacked Molecular Interconnects. X.-Y. Liu¹, J.E. Reynolds², C. Wells³, J. Welch³ and T.S. Cale¹, ¹Focus Center - New York, Rensselaer, Rensselaer Polytechnic Institute, Troy, New York; ²School of NanoScience and NanoEngineering, State University of New York at Albany, Albany, New York; ³Department of Chemistry, State University of New York at Albany, Albany, New York.

A fundamental theoretical understanding of transport in molecular systems and contacts will play an important role in interpreting and guiding the realization of molecular interconnects. We have performed local orbital basis DFT (density functional theory) and Green's functions based simulations to determine electronic structure and transport properties of π -stacked molecular interconnects, which

closely complement ongoing experimental studies. Surface slabs are used to model electrode contact with molecules. We have used simulations to study I-V characteristics, applied voltage effects, and band alignments. In addition, the electrode metal choice and the effect of the contact distance on the transport properties and Fermi level alignment are discussed. We also found the selection of the local orbital basis in the calculations has a dramatic effect on results. Finally, the thermal effect and the polaronic conduction mechanism in the system studied will be discussed.

11:30 AM *II.1.10

Electrical Conductance in Metal-Molecule-Metal Structures. Shashi P. Karna, Weapons & Materials Directorate, Army Research Laboratory, Aberdeen Proving Ground, Maryland.

Electrical conductance in quantized systems, such as molecules and atomic nanoclusters, has attracted a great deal of attention due to its potential applications in nanoelectronics. Organic systems, in general, offer a clear advantage over other nano-scale structures due to such attractive features as the ease in structure modification, self-assembling characteristics, and relatively low-cost of synthesis and device fabrication. However, unlike in the extended systems, the physics of electron transport in quantum confined systems, especially organic molecules, is not well established. In this talk I shall discuss our current understanding of the theory underlying electron transport in organic molecules and in metal-molecule-metal structures and identify key structural and electronic parameters that affect molecular electrical conductance.

SESSION II2:

Chair: S. Sinnott

Monday Afternoon, November 29, 2004
Room 204 (Hynes)

1:30 PM *II.2.1

Small is different: Non-scaleable behavior at the nano-scale, lower dimensions, and under extreme confinement.

Uzi Landman, School of Physics, Georgia Institute of Technology, Atlanta, Georgia.

At sufficiently small sizes the properties of materials are commonly observed to depend on size. Such dependencies may go beyond mere scaling with size, manifesting themselves in physical and chemical behavior that is new and different from that found at larger sizes. Such circumstances, when small is different in an essential way, may occur when one (or more) of the physical dimensions of the material aggregate approaches a length-scale characteristic to a physical phenomenon (with different phenomena being characterized by different length-scales). Basic research of these and related issues underlies future technologies, and it requires the development of new theoretical and experimental approaches. These physical and methodological issues will be discussed and illustrated using results obtained through "computational microscopy" - that is, large-scale classical and quantum simulations. Topics will include: Generation, stability and breakup of nanostructures - atomistic and stochastic hydrodynamical simulations of nanojets exploring the limit of validity of continuum approaches; morphological instability of cluster-deposited fractal islands; emergence of magnetism in free and surface-supported small palladium clusters; gold nanocatalysis; rheological and nanotribological properties of lubricating fluids in highly confined environments.

2:00 PM II.2.2

Structural, Elastic and Tribological Properties of Nanostructured Carbon Films Grown by Cluster Beam Deposition. Luciano Colombo¹, Davide Donadio² and Giorgio Benedek³, ¹Department of Physics, University of Cagliari, Monserrato (Ca), Italy; ²Computational Science, Department of Chemistry and Applied Biosciences, ETH Zurich, Zurich, Switzerland; ³Department of Materials Science, University of Milano-Bicocca, Milano, Italy.

By means of large-scale molecular dynamics (MD) simulations based on Tersoff empirical force field [1], we investigate the structural, elastic and tribological properties of nanostructured carbon (ns-C) films grown by cluster deposition [2]. Several deposition protocols are considered, so that a thorough structural characterization of the grown film is ruled out, consistently with experimental results [3,4]. We compute the frictional properties of the ns-C films by a direct MD simulation of a force-friction microscope experiment [3]. Present theoretical data support the interpretation of experimental AFM measurements based on a modified Amontons law of friction. The role of the local nanostructure to determine the actual value of the friction coefficient is discussed as well. Finally, we compute the elastic constants of the simulated ns-C films and we relate them to the average size of the deposited clusters by a constitutive power law [4].

Given the fractal self-affine nature of ns-C films, this result allows to extrapolate the present theoretical data to the scale of actual Brillouin scattering experiments, obtaining good agreement. [1] J. Tersoff, Phys. Rev. Lett. 61, 2879 (1988) [2] E. Barborini, P. Piseri, and P. Milani, J. Phys. D: Appl. Phys. 32, L105 (1999) [3] A. Podesta, G. Fantoni, P. Milani, M. Ragazzi, D. Donadio, L. Colombo, J. Nanosci. Nanotech. 2, 637 (2002) [4] D. Donadio, L. Colombo, and G. Benedek, submitted for publication (2004)

2:15 PM II2.3

Carbon Nanoscrolls: An Atomistic Molecular Dynamics

Investigation. Vitor R. Coluci¹, Scheila F. Braga¹, Sergio B. Legoas³, Ronaldo Giro², Douglas S. Galvao¹ and Ray H. Baughman⁴;

¹Applied Physics, UNICAMP, Campinas, Brazil; ²Instituto de Física, USP, Sao Paulo, SP, Brazil; ³Departamento de Física, UFAM, Manaus, AM, Brazil; ⁴Chemistry Department, University of Texas, Dallas, Texas.

Recent developments in synthesis using graphite intercalation/exfoliation structures have provide a simple, low-temperature, and efficient chemical route to a new carbon-based structure. This structure, named carbon nanoscroll (CNS) [1], is formed by curling up an isolated exfoliated graphite sheet (graphene). As CNSs do not have end caps they present a larger accessible surface area in comparison to equivalent CNTs. Such aspect can be useful for technological applications such as hydrogen storage and energy harvesting in super-capacitors. In this work we report atomistic molecular dynamics results of the structural and dynamical properties of different families of CNSs. We have used classical molecular dynamics methodologies with standard molecular force fields. We have analyzed both neutral and charge CNSs in order to investigate the effects of charge injection on scroll conformations. Electroactuation has been observed for CNTs and CNSs can exhibit a new type of actuation (scroll unwinding). Our results show that CNS formation is dominated by two major energetic contributions: the elastic energy increase caused by bending the graphite sheet (decreasing structural stability) versus the free energy decrease generated by the van der Waals interactions of overlapping regions. CNS structures can be more stable (in terms of energy per carbon atom) than its related graphite sheet. CNS formation is a self-sustained curling process after a critical overlap area is reached [2]. Consistent with experimental observations our results show that CNSs having inner diameters smaller than 20 Angs. are unstable with respect to an increase in their diameters and conical scrolls can be trapped as meta-stable states. For larger structures both tubular and conical shape scrolls can be formed. The obtained structural features are in very good agreement with the available experimental data. We also observed that charge injection causes unwinding of the CNSs, which might be an important feature to use CNSs as nano-mechanical actuators. [1] L. M. Viculis, J. J. Mack, R. B. Kaner, Science v.299 (2003) 1361. [2] S. F. Braga, V. R. Coluci, S. B. Legoas, R. Giro, D. S. Galvao, R. H. Baughman, Nano Lett. v.4 (2004) 881.

2:30 PM II2.4

One-dimensional nano-confinement allows effective modification of energetics in hydrogen storage processes.

Jian-jie Liang and Paul Kung; Accelrys Inc., San Diego, California.

Reducing hydrogen storage materials into nanoscale benefits the kinetics in hydrogen absorption/desorption processes. However, it is a challenge both in preventing the nanoparticles from aggregation, and to achieve favorable energetics of the absorption/desorption processes that directly translate into net energy changes in the storage processes. Magnesium was chosen here as the materials to be confined into carbon nanotubes. While the resulted nanorods are desirably shielded away from each other, density-functional-theory (DFT) calculations of a series of samples with incremental Mg-loading showed that the sorption energetics can be modified to meet US DOE requirement for hydrogen storage materials onboard vehicles.

2:45 PM II2.5

The Study of Alkali Doping Effect on Hydrogen Adsorption in Single-walled Carbon Nanotubes Using Monte Carlo

Simulation. Naiping Hu, Xiaoyang Sun and Andrew Hsu; Indiana University -Purdue University Indianapolis, Indianapolis, Indiana.

The primary objective of this study is to study the effect of dopants on hydrogen adsorption in carbon nanotubes. Monte Carlo simulations and Widom's test particle insertion method have been used to calculate the solubility coefficients (S) and the adsorption equilibrium constants (K) in single-walled (5, 5) armchair carbon nanotubes including single nanotubes, and nanotube bundles with different configurations and different alkali dopants. The hydrogen adsorption isotherms at room temperature were predicted by following the Langmuir adsorption model using the calculated constants S and K. The simulation results were in good agreement with experimental data as well as the Grand Canonical Monte Carlo (GCMC) simulation

results reported in literature. The simulations of nanotube bundle configurations suggest that the hydrogen adsorption increases with inter-nanotube gap size. It may be attributed to favorable hydrogen-nanotube interactions outside the nanotubes. The effect of alkali doping on hydrogen adsorption was studied by inserting 80 Na or 50 Li ions into nanotube arrays, respectively. The results on hydrogen adsorption isotherms indicate a increase on hydrogen sorption for Na-doping and Li-doping, in agreement with the experimental results obtained at 100 MPa and room temperature. The MC method used in this study provides a simpler route for the generation of isotherms than the more commonly used GCMC method.

3:30 PM *II2.6

Quantum mechanical computations to be able to predict new materials in nanotechnology. Y. Kawazoe and H. Mizuseki; Institute for Mat. Res., Tohoku University, Sendai, Japan.

Based on the recent progress in computer power and theoretical treatments, prediction of the structures and properties of new nanoscale materials is becoming possible. On the other hand, industrial requirement for higher-speed and higher-density computer could not be realized by the present day silicon technology, and a fundamentally new paradigm of nanotechnology based on the atomic and molecular assemblies is strongly expected. Present status of the nanotechnology is still in the research level and quantum mechanical computation plays an important role there for the future realization of the nanoscale devices. We have been developing a new materials design system TOMBO (TOhoku university Mixed-Basis Orbitals ab initio computation method) based on the density functional theory (DFT) with all electron formalism and higher Feynman diagrams to include the effects of electron correlations. The ordinary DFT with pseudopotentials provides real electronic states for most of the materials in the ground states. Therefore, structures of materials and properties such as magnetic moments at 0K are nicely reproduced, and it is possible to predict new materials without experimental observations. It, however, is not possible to deal with excited states, for which most of the experimental works have been performed. To solve the excited state problems, we have implemented GW approximation into TOMBO, and computed absolute values of ionization potential, electron affinity, and HOMO-LUMO gap values in various nanoscale materials. The program TOMBO also includes a feature of time dependent Shrodinger equation solver, which can predict chemical reactions including catalytic reaction process in general. Our another trial to include the electron correlation effects is to solve the quantum mechanical equations for the many body electron system by quantum Monte Carlo method. Recent progress in diffusion Monte Carlo method makes it possible to serve a fundamentally good electronic states for many body correlated electron system, and we have already obtained satisfactorily convergence for several nanoscale materials to be able to show the origin of Hunt's rule and more. Several new nanoscale materials have also been predicted by our quantum mechanical computations, such as silicon fullerenes, silicon nanotubes, metallic clusters having special magnetic properties, surfaces modified with various atoms, hydrate clathrates for hydrogen storage, and so on, which are expected to be used in the nanotechnology as building blocks. In the talk, I will introduce the present status of the nano-science and technology focusing on quantum mechanical computations and try to distinguish genuine and false nanotechnologies in general.

4:00 PM II2.7

A First Principles Study of Interaction of Lithium with Graphene, a Single Wall Carbon Nanotube and with Other Lithium inside a Nanotube. Mahadevan Khantha and Lou Girifalco; Department of Materials Science and Engineering, University of Pennsylvania, Philadelphia, Pennsylvania.

A study of Li interactions with graphene and SWNT will be presented using the local density approximation to the density functional theory. The charge redistribution between lithium and carbon atoms for different densities and positions of the Li atoms will be discussed. Its implications for the screening of Li-Li interactions will be assessed and compared with the calculated Li-graphene, Li-nanotube and Li-Li interaction potentials. The applications of the results to study single file diffusion of Li inside SWNT will be outlined.

4:15 PM II2.8

Effects of Alkali Metals on the Properties of Single-Wall Carbon Nanotubes: A Theoretical Study. Brahim Akdim¹, Xiaofeng Duan² and Ruth Pachter¹; ¹AFRL/Materials & Manufacturing Directorate, WPAFB, Ohio; ²AFRL/ASC MSRC, WPAFB, Ohio.

In our ongoing interest to gain insight into the enhancement of field emission properties of single-wall carbon nanotubes (SWCNTs), particularly with respect to Cs incorporation, we carried out a

comprehensive investigation of the effects of alkali-metal adsorption, applying density functional theory calculations. In our comparative study, between capped and uncapped tubes with varying Cs uptake, the importance of the tip structure on the emission enhancement is emphasized. The results show that the physisorption of Cs leads to a significant increase of the ionization potential, consistent with experiment. The effects of the applied local field will also be discussed. Furthermore, for a detailed understanding of Cs intercalation and encapsulation in SWCNTs, we examined the radial breathing modes (RBM) and tangential modes (TM) for different adsorption sites. Among the adopted models, intercalation was shown to cause the significant downshift reported experimentally, upon Cs, Rb, and K adsorption. Finally, a detailed examination of structural parameters and electronic structure will be outlined.

4:30 PM II2.9

First Principles Calculation of the Field Emission of Boron/Nitrogen Doped Carbon Nanotube. Hyo-Shin Ahn^{1,2}, Seungwu Han³, Kwang-Ryeol Lee¹ and Doh-Yeon Kim²; ¹Future Technology Research Division, Korea Institute of Science and Technology, Seoul, South Korea; ²Department of Materials Science and Technology, Seoul National University, Seoul, South Korea; ³Department of physics, Ehwa Womans University, Seoul, South Korea.

Field emission properties of nitrogen and boron doped carbon nanotubes (CNTs) were studied with a first-principles approach. Emission currents were calculated by integrations of the time-dependent Schrödinger equation. In the case of undoped CNT, the field emission from localized states at the tip end is more relevant than that from extended metallic (π and π^*) states. Nitrogen incorporation substantially changes the electronic structure of the nanotube; the localized and the extended states couple and the energy levels of the localized states shift to the Fermi level. The field emission is much enhanced by the structural change, which is more significant when the nitrogen is located near the tip of the nanotube. On the other hand, doped boron appears to suppress the electron emission by raising the energy level of the localized states from the Fermi level. The present results show that the electron emission from CNT is dominated by the localized states in the carbon network that can be engineered by the third element doping.

4:45 PM II2.10

Diffusion of Gases Adsorbed on Nanotube Bundles: Dimensionality Effects. M. Mercedes Calbi, Physics, Southern Illinois University, Carbondale, Illinois.

A study of the diffusion properties of gases adsorbed on carbon nanotube bundles is presented. In particular, the diffusion behavior of gases on the external surface is investigated and compared with the case of diffusion within the bundle. Diffusion coefficients are obtained by means of a computational scheme based on an n-fold way kinetic Monte Carlo algorithm used to describe the evolution of the system through different accessible states according to specific transition probabilities. The results are compared with mobility measurements of methane and hydrogen in nanotube bundles obtained from quasi-elastic neutron scattering experiments [1,2]. [1] M. Bienfait, B. Asmussen, M. Johnson, P. Zeppenfeld, Surface Science 460, 243 (2000). [2] D.G. Narehood, J.V. Pearce, P.C. Eklund, P.E. Sokol, R.E. Lechner, J. Pieper, J.R.D. Copley and J.C. Cook, Phys. Rev. B 67, 205409 (2003).

SESSION II3:

Chair: S. Louie

Tuesday Morning, November 30, 2004

Room 204 (Hynes)

8:30 AM *II3.1

Excitonic Effects in the Optical and Energy-Loss Response of Nanotubes. Angel Rubio, ¹Dpto. Fisica de Materiales, UPV/EHU, San Sebastian, Spain; ²Donostia International Physics Center (DIPC), San Sebastian.

Optical absorption spectroscopy is an important tool for the characterization of nanotubes. The first order explanation in terms of single-particle excitations from occupied to unoccupied states is straight-forward. For quantitative predictions, however, a simple calculation based on the assumption of non-interacting particles and on the electronic band-structure on the DFT level is not accurate enough. In particular, electron-hole interaction has a large impact on the absorption spectra and leads to excitonic peaks with large binding energies. We have calculated these excitonic effects through the solution of the Bethe-Salpeter equation. We discuss the resulting spectra of bound excitonic peaks in the quasi-one dimensional tubes and compare with the spectra of the quasi-two dimensional single

sheet of hexagonal BN and of bulk hexagonal BN. We will also present results from the optical response of carbon nanotubes. Work done in collaboration with Ludger Wirtz, Andrea Marini and Lucia Reining. This work was supported by the European Community Research Training Network NANOPHASE (HPRN-CT-2000-00167), Network of Excellence NANOQUANTA (NOE 500198-2), Spanish MCyT (MAT2001-0946) and the University of the Basque Country (9/UPV 00206.215-13639/2001).

9:00 AM II3.2

Scaling of excitons and exciton-phonon effects in carbon nanotubes. Vasili Perebeinos, Jerry Tersoff and Phaedon Avouris; IBM, Yorktown Heights, New York.

Light emission from carbon nanotubes has generated great interest because of the potential for nanoscale electro-optical devices. Light emission and absorption are expected to be dominated by excitons. We calculate the properties of excitons in nanotubes embedded in a dielectric, for a wide range of tube radii and dielectric environments, by solving the Bethe-Salpeter Equation in a tight binding basis. We find that simple scaling relationships give a good description of the binding energy, exciton size, and oscillator strength as a function of the tube radius, the dielectric constant of the embedding material, and the chirality [1]. In addition we calculate optical absorption including the exciton-phonon interaction. We find a phonon sideband at 200 meV above the zero phonon line, due to the creation of exciton plus one optical phonon. Inspection of published data confirms the presence of the phonon sideband. We calculate the spectral line shape and relative sideband intensity as a function of tube diameter and dielectric environment. [1] V. Perebeinos, J. Tersoff, and Ph. Avouris, Phys. Rev. Lett. (in press).

9:15 AM *II3.3

Applications of First Principles Multiscale Modeling to Molecular Based Switches and to Nanotube Synthesis.

W. Goddard, California Institute of Technology, Pasadena, California.

We will discuss recent advances in first principles multiscale methods in the context of two applications of these methods to real materials. The topics to be covered are: The mechanism for molecular switches based on self assembled monolayers of rotaxanes and catenanes on electrode surfaces Application of the ReaxFF reactive force field and QM methods to determine the role of various metals in the nucleation and growth processes involved in gas phase synthesis of single wall nanotubes

9:45 AM II3.4

The first principles calculation of nitrogen effect on the growth of carbon nanotube. Hyo-Shin Ahn^{1,2}, Tae-Young Kim^{1,2}, Seungwu Han³, Seung-Cheol Lee¹, Kwang-Ryeol Lee¹ and Doh-Yeon Kim²; ¹Future Technology Research Division, Korea Institute of Science and Technology, Seoul, South Korea; ²Department of Materials science and engineering, Seoul National University, Seoul, South Korea; ³Department of physics, Ehwa Womans University, Seoul, South Korea.

We investigated the effect of nitrogen on the carbon nanotube (CNT) growth by ab-initio calculation. Previous experimental work shows that nitrogen incorporation to the wall or cap enhances the growth rate of the carbon nanotube. In this study, two possible effects of the nitrogen incorporation were tested; the reduction of the strain energy of tubular graphite sheet or the reduction of the kinetic barrier for the CNT growth. Total energy calculation showed that the strain energy reduction caused by the nitrogen incorporation was not significant when the radius of CNT was larger than 3nm. Hence, this effect can be neglected in most cases of the CNT growth. A transition state calculation was employed for every step of carbon attachment to estimate the kinetic barrier for CNT growth. The kinetic barrier for carbon attachment for pure CNT was estimated to be 176meV for zigzag and 160meV for armchair growth edge. However, nitrogen incorporation to the carbon network significantly reduced the kinetic barriers in a certain nitrogen configuration. Furthermore, nitrogen incorporation changes the controlling step of the growth from zigzag to armchair growth. Local electron density revealed that nitrogen can reduce the bond strength of C-C or C-N bond, which would decrease the kinetic barrier for the carbon attachment.

10:15 AM *II3.5

Atomic Scale Design of Nanostructures. Jerry Bernholc^{1,2}, M. Buongiorno Nardelli^{1,2}, W. Lu¹, V. Meunier², S. Nakhmanson¹, W. G. Schmidt^{3,1}, S. Wang¹ and Q. Zhao¹; ¹NC State University, Raleigh, North Carolina; ²Oak Ridge National Laboratory, Oak Ridge, Tennessee; ³Friedrich-Schiller University, Jena, Germany.

Recent advances in theoretical methods and high performance computing allow for reliable first-principles predictions of complex nanostructured materials and devices. This talk will discuss three

examples: (i) Nanotube-cluster systems, which behave as effective chemical sensors whose electrical response changes dramatically upon adsorption of small molecules onto the metal clusters. (ii) Polarization and piezoelectric properties of BN nanotubes and BN-based polymers. We show that BN nanotubes are excellent nano piezoelectrics that could form the core of high-performance actuators and sensors, but have no spontaneous polarization. However, the predicted polymers offer 100% improvement in both ferro and piezoelectricity over those in current use. (iii) We demonstrate that reflectance anisotropy of a semiconductor surface or interface provides a *unique* signature of its atomic structure. The corresponding line shape can be obtained from first-principles calculations, leading to *unambiguous* identification of the structure and potentially enabling feedback-controlled growth of device structures with nearly monolayer resolution. A number of applications to III-V and Si surfaces will be discussed.

10:45 AM *II3.6

Density Functional Theory Calculations of the Electronic Properties of Single-Walled Carbon Nanotubes: Beyond the Local Density Approximation. Gustavo Scuseria and Veronica Barone; Chemistry, Rice University, Houston, Texas.

The calculation of the energy band gap of semiconducting materials has been a challenge since the early days of solid state physics. Density functional theory has been widely utilized to describe molecular and extended systems. Although the local spin density approximation works well for metallic systems, it tends to severely underestimate the energy band gap of semiconducting materials. The addition of electronic density gradient corrections to the exchange-correlation energy (GGA approximation) is not enough to overcome this difficulty. On the other hand, the Hartree-Fock (HF) approximation is not adequate for describing metallic systems and tends to drastically overestimate the band gap of semiconductors. Without employing more sophisticated and computationally expensive approximations, hybrid density functionals, which contain a portion of HF exchange, emerge as a natural choice to treat systems presenting an energy band gap. Particularly, the utilization of the recent developed screened exchange hybrid functionals[1] appears to be an excellent alternative that not only reproduces the experimental band gaps of semiconductors with good accuracy but also reduces the high computational cost of regular hybrid functionals.[2],[3] In this work, we present a systematic density functional theory study of the electronic properties of single-walled carbon nanotubes (SWNT) with diameters ranging from 3 to 5 Angstrom. For the first time, meta-GGA, hybrid, and screened exchange hybrid functionals have been utilized to compute energy band gaps in these narrow SWNT. [1] J. Heyd, G. E. Scuseria, M. Ernzerhof, J. Chem. Phys. 118, 8207 (2003). [2] J. Heyd, G. E. Scuseria, J. Chem. Phys. 118 (2) (2004). [3] V. Barone, J. Heyd, G. E. Scuseria, Chem. Phys. Lett, 389, 289 (2004).

11:15 AM II3.7

Formation and Migration of Soliton and Polaron in Conjugated Oligomers. Xi Lin¹, Ju Li² and Sidney Yip¹; ¹MIT, Cambridge, Massachusetts; ²Ohio State University, Columbus, Massachusetts.

The formations of soliton, polaron and bipolaron in polyacetylene and polypyrrole chains are characterized using large-scale quantum chemistry calculations, as density functional theory has been found to be incapable of describing the localizations. It is shown that the charge and carbon-backbone bond length alternation in the cores are generically coupled to soft vibrational modes of the oligomer chain, such as the carbon backbone bending in polyacetylene and the ring torsion in polypyrrole. Spin-paired bipolaron states in polypyrrole are found to be energetically preferable only in short polypyrrole chains, and become metastable with respect to spin-polarized polaron states in polypyrrole chains containing more than 6 pyrrole units. We have computed the interactions between these quasi-particles, and directly observed polaron and bipolaron lattices at high doping levels. The energetic barriers of translating soliton, polaron and bipolaron are calculated.

11:30 AM *II3.8

Carbon Nanotube Optics and Dynamics. Tobias Hertel, Physics and Astronomy, Vanderbilt University, Nashville, Tennessee.

The unique electronic structure of carbon nanotubes (CNTs) can be studied directly and in great detail using cw and time-resolved optical techniques but it can also be explored somewhat more indirectly, for example through the van der Waals (vdW) interaction as probed by inert adsorbates. Here, we first discuss some trends observed in the spectroscopy of CNTs in different environments where simple tight-binding calculations will guide our interpretation of optical spectra. Then we illustrate how carrier interactions with other carriers, phonons or impurities in CNTs become manifest through studies of the dynamics of photoexcited CNTs. Lastly, it will be

shown how the polarizability of CNTs can be probed indirectly through the vdW interaction with a variety of inert adsorbates.

SESSION II4:

Chair: D. Tomanek
Tuesday Afternoon, November 30, 2004
Room 204 (Hynes)

1:30 PM *II4.1

Structure and Mechanics of Composite Nanotubes.

David J. Srolovitz¹, Danxu Du¹, Mikhail I. Mendeleev¹, Samuel Safran² and Reshef Tenne²; ¹Mechanical & Aerospace Eng., Princeton University, Princeton, New Jersey; ²Materials and Interfaces, Weizmann Institute of science, Rehovot, Israel.

In this talk, we will examine two types of composite nanotubes. The first is a multiphase, nested nanotube structure (e.g., C/BN) and the second is a nanotube containing large intercalates (e.g., peas-in-a-pod structures). There are several distinct contributions to the energetics of these structures, including the internal and external surface energies, the energy of the interface between the different phases, the long range (van der Waals) interactions between interfaces, and elastic energies. For the case of a multiphase, nested nanotube, we perform energy minimizations to determine the equilibrium structures and present physical guidelines, quantitative theory and structure maps that show how materials and geometric parameters influence the stability of competing structures. For the peas-in-a-pod case, we examine the elastic interactions between peas mediated by the mechanics of the pod.

2:00 PM II4.2

Theoretical Investigation of the Mechanical Properties of Helical Nanosprings. Douglas S. Galvao¹ and Alexandre F. da

Fonseca²; ¹Applied Physics, UNICAMP, Campinas, SP, Brazil; ²Instituto de Fisica, USP, Sao Paulo, SP, Brazil.

The development of structures such as nanotubes and more recently nanowires, has attracted great attention from the scientific community due to the large range of possible applications and new physical phenomena. The great variety of electrical and mechanical properties presented by nanostructures can be exploited to generate new products and applications. Among these structures, helical nanosprings or nanocoils have attracted particular interest due to their remarkable mechanical properties. We report here a theoretical analysis for their mechanical properties in the Kirchhoff rod model. The Kirchhoff model has been extensively used to study the statics and dynamics of continuous rods. In this model the rod is seen as an assembly of short segments. Each segment is loaded by contact forces from the adjacent ones. The classical equations for the conservation laws of linear and angular momentum are applied to each segment in order to obtain a one-dimensional set of differential equations for the statics and dynamics of the rod in the approximation of the small curvature of the rod as compared to the radius of the local cross section. We have derived expressions that can be used experimentally to obtain nanospring Young's modulus and Poisson's ratio values. Another important result from our model is that intrinsic curvature increases the dynamical stability of the nanostructures and can explain why the presence of catalytic (that induce intrinsic curvature) is so important to grow nanostructures [1] [1] A. F. da Fonseca and D. S. Galvao, Phys. Rev. Let. V92 (2004) 175502.

2:15 PM II4.3

Scale-dependent Compliance Contribution Tensor of a Spherical Inhomogeneity. Larissa Gorbatiikh and Marina Popova; Mechanical Engineering, University of New Mexico, Albuquerque, New Mexico.

Mechanical properties of traditional composite materials may be improved through the appropriate use of small scale (nano-sized) inclusions in the fabrication, potentially leading to their unprecedented strength and elastic moduli. Classical theories of elasticity do not allow size-dependence in their solutions. For example, a pioneering work of Eshelby that currently serves as a fundamental solution for the entire field of composite materials cannot be used to study nano-sized inclusions and therefore needs to be re-examined. The effort of the present work is to develop an understanding of the role of size effects when predicting effective mechanical properties of materials with inclusions approaching small scales. In this work we re-visit the problem of a single spherical inhomogeneity by incorporating new effects into the elastic solution driven by surface/interface forces. We derive a compliance contribution tensor that characterizes the average strain change in the material due to the presence of the inhomogeneity and estimate elastic moduli of the effective medium. Dependence of the latter on the size of the inhomogeneity and the surface energy is a primary interest of this

study. The analysis is based on the recent developments in the area of nano-mechanics.

3:00 PM *II4.4

Self-Folding and Unfolding of Large Aspect Ratio Carbon Nanotubes. Markus J. Buehler, Yong Kong and Huajian Gao; Max Planck Institute for Metals Research, Stuttgart, Germany.

Carbon nanotubes (CNTs) constitute a prominent example of nanomaterials. In most studies on mechanical properties, the effort was concentrated on CNTs with relatively small aspect ratio of length to diameters. In contrast, CNTs with aspect ratios of several hundred can be produced with today's experimental techniques. We report atomistic-continuum studies of single-wall carbon nanotubes with very large aspect ratios subject to compressive loading. It was recently shown that these long tubes display significantly different mechanical behavior than tubes with smaller aspect ratios (Buehler et al., JEMT, 2004). We distinguish three different classes of mechanical response to compressive loading: While the deformation mechanism is characterized by buckling of thin shells in nanotubes with small aspect ratios, it is replaced by a rod-like buckling mode above a critical aspect ratio, analogous to the Euler theory in continuum mechanics. For very large aspect ratios, CNTs are found to behave like a wire that can be deformed in a very flexible manner to various shapes. Here we focus on the properties of such wire-like CNTs. Using atomistic simulations carried out over several nanoseconds time span, we observe that wire-like CNTs behave similarly as flexible macromolecules. The modeling reveals that they can form thermodynamically stable self-folded structures where different parts of the CNTs attract each other through van der Waals (vdW) forces. This self-folded CNT represents a novel structure not described in the literature. There exists a critical length for self-folding of CNTs that depends on the elastic properties of the tube. We observe that CNTs fold below a critical temperature, and unfold above a critical temperature. Surprisingly, we observe that self-folded CNTs with very large aspect ratios never unfold until they evaporate. The folding-unfolding transition can be explained by entropic driving forces that dominate over the elastic energy at elevated temperature. These mechanisms are reminiscent of the dynamics of bio-molecules like proteins. The different stable states of CNTs are finally summarized in a schematic phase diagram of CNTs. We also include studies of mechanical properties of bundles of CNTs, showing unique properties such as highly elastically anisotropic behavior.

3:30 PM II4.5

Multilayer adsorbates in oxide ceramics as two-dimensional nanomaterials: from experimental to modeling. Jian Luo¹, Yet-Ming Chiang² and Rowland M. Cannon³; ¹School of Materials Science and Engineering & COMSET, Clemson University, Clemson, South Carolina; ²Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts; ³Lawrence Berkeley National Laboratory, University of California, Berkeley, California.

Recent observation of 1-2 nanometer thick, surficial and intergranular films in Bi₂O₃-doped ZnO is briefly reviewed. The film thickness, corresponding to the Gibbsian excess of solute, decreases monotonically with decreasing temperature in the subsolidus range until vanishing at a lower dewetting temperature. With increasing temperature the films persist into the solid-liquid coexistence regime with gradual thickening upon heating until a complete wetting occurs. The equilibrium surficial and intergranular films can be understood to be the multilayer adsorption with ionic and covalent adsorbate-adsorbate bonds, where clear parallels exist to the theories of multilayer adsorption of simple gases, prewetting, and premelting. However, none of the existing theories treat the combined effects of ionic-covalent bonds, simultaneous surface segregation and disordering, space-charge, and dispersion interactions that are unique for ceramic adsorbates. A phase-field formalism is proposed for surficial films based on Carter and coworkers' intergranular film model as well as Cahn's prewetting model. While a forced gradient in orientation is drives the grain boundary disordering and stabilizes intergranular films, the orientation gradient is perhaps negligible in surficial films. Bulk phase free energy calculation methods, such as CALPHAD, can be incorporated into phase-field modeling. The stability of these nanoscale films doesn't follow bulk phase diagrams, but it is related to the bulk phase equilibria through the volumetric term in the phase-field model. In a second approach to better represent the adsorbate's atomistic nature, lattice gas models are modified for considering ionic-covalent adsorbates. Of particular interest is modifying the Besold-Moritsen model for interfacial melting and the Teraoka-Seto model for two-component gas adsorbates. In both schemes the lattice space is chosen to be smaller than the inter-atomic distance, and only a fraction of the lattice points is allowed to be occupied, thereby permitting ordering-disordered to be represented. The proposed lattice gas model may be an optimal intermediate method for modeling general (non-material-specific) surficial

adsorption behaviors in ceramics. On the one hand, it can be used to deduce the phase-field formalism by a mean-field approach and the Bishop and Carter's coarse-graining method. On the other hand, it approaches an atomistic model as the lattice distance shrinks to zero, if adopting realistic inter-atomic potentials. These oxide films exhibit nanoscale self-selecting thickness, as well as composition and partially-ordered structure that are neither observed nor stable as bulk phases, thereby representing a new class of two-dimensional nanomaterials with possible applications in microelectronics, catalysts, sensors, sintering and various nanotechnologies.

3:45 PM *II4.6

Large-Scale Atomistic Simulations of Hypervelocity Impact and Crack Propagation Under Compression.

Rajiv Kumar Kalia, Aiichiro Nakano and Priya Vashishta; Collaboratory for Advanced Computing and Simulations, University of Southern California, Los Angeles, California.

Large-scale molecular dynamics simulations involving several hundred million atoms have been performed on parallel computers to study hypervelocity impact damage of high-strength aluminum nitride film. Results reveal atomistic mechanisms that generate dislocations and micro-cracks at a rapidly advancing front of a structural phase transformation upon the arrival of an elastic rarefaction wave. We will also discuss simulations of wing-crack nucleation, growth, and healing in a confined pre-cracked silica glass.

4:15 PM II4.7

Nanoindentation of Ceramic Thin Films. Izabela Szulfarska, Rajiv Kalia, Aiichiro Nakano and Priya Vashishta; CACS, Univ. of Southern California, Los Angeles, California.

Atomistic mechanisms of nanoindentation of crystalline, amorphous and nanophase ceramic thin films have been studied by large-scale molecular dynamics simulations on parallel computers. In the crystalline 3C silicon carbide (SiC), atomistic mechanisms underlying the nanoindentation-induced amorphization have been investigated. The calculated load-displacement curve consists of a series of load drops, which are shown to reflect the crystalline structure and dislocation activities under the surface. Structural analyses reveal that the defect stimulated growth and coalescence of dislocation loops are responsible for the crystalline-to-amorphous transition. The shortest-path-ring analysis is effectively employed to characterize nanoindentation-induced structural transformations and dislocation activities. In amorphous SiC (a-SiC), the load displacement curve exhibits a series of load drops, reflecting the short-range topological order similar to crystalline 3C-SiC. In contrast to 3C-SiC, however, the load drops are irregularly spaced and less pronounced. The damage is spatially more extended than in 3C-SiC, and it exhibits long-range oscillations consistent with the indenter size. We will also present simulation results on the nanoindentation of nanophase SiC (n-SiC) as well as on other ceramics (Si₃N₄) and semiconductors (GaAs). Work supported by AFOSR: DURINT, ARL, ARO: MURI, DARPA: PROM, DOE, and NSF. Simulations were performed at DoD's Major Shared Resource Centers under DoD Challenge and CHSSI projects, and at the CACS and HPC at the University of Southern California.

4:30 PM II4.8

Origins of Longitudinal Supramolecular Traction in Nanotube Assemblies. Yu Lin¹, Yufeng Zhao², Luise S. Couchman³ and Boris I. Yakobson¹; ¹Department of Mechanical Engineering & Materials Science, Rice University, Houston, Texas; ²National Renewable Energy Laboratory, Golden, Colorado; ³Naval Research Laboratory, Washington, District of Columbia.

While the main mechanisms of intramolecular fracture in nanotubes appear to be elucidated and are being quantified further (see [1] as recent examples), yet the qualitative nature of intertubular traction is not understood. Here the notion of frictionless bearings seemingly conflicts with the load transfer in multiwall nanotubes or bundles. Smooth and incommensurate atomic layers provide no resistance to a relative glide of nanotubes in an array. Therefore a noticeable shear modulus in a bundle or an adhesion between the telescopically pulled nested layers of a multiwall tube must be attributed to imperfections. We analyze two classes of such defects. One is a concurrent presence of 5/7 cores in the adjacent walls in the coaxial tubes-essentially a penetrating edge dislocation line. Computations show that van der Waals forces in this warped area yield a noticeable axial traction, which scales with a tube length and can achieve significant magnitude over a series of such sites. As second alternative, we have investigated [2] energy, stability and kinetics of "Shottky interstitials" of carbon and other elemental (C, O, B, P) links, forming between the tubes. 2n-C (n=1,2,...,6) links are investigated systematically by finite temperature molecular dynamics, and the energies of certain configurations are calculated within density functional based tight-binding model. The strength of the links is measured by the

energy barriers that prevent them from being broken under applied shear, and the statistical theory allows us to relate molecular parameters with the macroscopic shear strength. 1. T. Dumitrica, T. Belytschko, and B. I. Yakobson, *J. Chem. Phys.* 118, 9485 (2003); T. Dumitrica and B.I. Yakobson, *Appl. Phys. Lett.* 84, 2775 (2004). 2. Y. Zhao, B. I. Yakobson, *Shottky Interstitials as Cross-links in Nanotube Arrays*, X26.011, Bulletin of the American Physical Society, March 2003 Meeting.

SESSION II5:

Chair: A. Balazs

Wednesday Morning, December 1, 2004

Room 204 (Hynes)

8:30 AM *II5.1

Self- and Directed-Assembly of One- and Two-Dimensional Nanomaterials from Anisotropic Amphiphilic Building Blocks. Sharon C. Glotzer, Departments of Chemical Engineering and Materials Science and Engineering, University of Michigan, Ann Arbor, Michigan.

The functionalization of nano building blocks, including nanospheres, nanorods, nanocubes, nanoplates, and nanoprisms, with biomolecular "handles" and organic tethers provides new possibilities for directing their self-assembly into complex structures for novel materials and devices. Currently, few demonstrated assembly approaches offer a comprehensive, predictable, and generally applicable scheme for the rational assembly of nanoparticles and nanostructured molecules into one- and two-dimensional ordered structures. We seek to develop an intuitive and general framework for predicting the assembly of nanoparticles functionalized at specific locations with oligomeric tethers or biomolecular ligands into complex structures [1-7]. In this regard, molecular simulation of model nano building blocks can yield insight into the conditions under which various target structures may be achieved. We present recent results of molecular simulations performed to study the self-assembly of strategically-functionalized nanocrystals and nanostructured molecules. We show how designing anisotropy in the interactions through tether and biomolecule functionalization and tuning thermodynamic parameters and architectural features of model nano building blocks can control aspects of local and global ordering of the nanoparticles, producing nanowires, nano-shells, nano-sheets, and nano-vesicles. We further investigate the stability of these one- and two-dimensional nanomaterials structures with respect to various fabrication limitations of the building blocks. [1] Z.L. Zhang and S.C. Glotzer, *Self-assembly of patchy particles*, *Nano Letters*, accepted. [2] Z.L. Zhang, M.A. Horsch, M.H. Lamm and S.C. Glotzer, *Tethered nano building blocks: Toward a conceptual framework for nanoparticle self-assembly*. *Nano Letters*, 2003. 3(10): p. 1341-1346. [3] T. Chen, M.H. Lamm and S.C. Glotzer, *Monte Carlo simulations of biomolecule-directed assembly of nano building blocks*, *J. Chem. Phys.*, in press. [4] X. Zhang and S.C. Glotzer, preprint. [5] E.R. Chan, X. Zhang, A.S. Keyes, C-Y Lee, M. Neurock and S.C. Glotzer, preprint. [6] M.A. Horsch, C.R. Iacovella, Z.L. Zhang and S.C. Glotzer, preprint. [7] C.R. Iacovella, M.A. Horsch, Z.L. Zhang and S.C. Glotzer, preprint. This work is supported by grants from the National Science Foundation (CTS-0210551), and the U.S. Department of Energy (DE-FG02-02ER46000 and DE-FG02-03-ER46094).

9:00 AM II5.2

Lack of Thermodynamic Signatures for a Phase Transition in Nanoconfined Poly(ethylene Oxide). Vikram K. Kuppala and Evangelos Manias; Materials Science and Engineering, Penn State University, State College, Pennsylvania.

Molecular Dynamics simulations are used to explore the phase transition behavior of severely confined poly(ethylene oxide)(PEO). Bulk and confined PEO systems are modeled in atomistic detail in an effort to comparatively illustrate their differences in thermodynamic signatures across a temperature range of 273-423K. Different indicators of a phase transition have been studied including statistical mechanical interpretations such as energy fluctuations structural features such as chain conformation measured via sequences of ordered backbone dihedrals, and dynamic factors such as diffusion coefficients. Bulk systems show a clear indication of a transition close to the experimentally determined melting point of pure PEO. In contrast, all the characteristics of a transition studied for the confined system show no evidence of a phase change across the same temperature range of study. This lack of a phase transition in nanoconfined PEO is attributed to the extreme spatial restriction imposed on the PEO chains by the adjacent surfaces and also to the strong coordination of the oxygen along the polymer backbone to the lithium cations present on the confining surface.

9:15 AM *II5.3

A Molecular Simulation Study of Self-association of Modified Buckyballs in Aqueous Solution. Grant D. Smith, Dmitry Bedrov and Liwei Li; Materials Science and Engineering, University of Utah, Salt Lake City, Utah.

C60 fullerenes (buckyballs) are insoluble in aqueous solution. Modification of buckyballs by grafting of low molecular weight chains of water soluble poly(ethylene oxide) (PEO) can solubilize buckyballs. By controlling the number of grafted chains, their molecular weight, and how the chains are distributed on the buckyball surface, it is possible to control the interaction between modified buckyballs and induce highly asymmetric interactions between them. As such asymmetric interactions can lead to a myriad of self-assembled structures and phases, chemical modification of buckyballs appears to be a promising route to obtaining nanoscale building blocks for novel self-assembled nanomaterials. I will discuss in detail the interaction of PEO modified C60 fullerenes in aqueous solution as obtained from atomistic molecular dynamics (MD) simulations, with emphasis on the water-induced interaction between buckyballs and how this depends upon PEO molecular weight, grafting density, and chain distribution. Based upon the potential of mean force between modified buckyballs obtained from these simulations as a function of separation and orientation, I will present a coarse-grained representation of the modified buckyballs that accurately reproduces the interaction between them, including solvent induced interactions and asymmetric interactions due to the distribution of PEO chains. Various structures and phases predicted by the coarse-grained model to be obtainable in solutions of PEO modified buckyballs will be discussed.

10:00 AM *II5.4

Simulations of the conduction of water, protons, ions, and polymers through carbon nanotubes. Gerhard Hummer, Laboratory of Chemical Physics, NIDDK, National Institutes of Health, Bethesda, Maryland.

Carbon nanotubes offer unique possibilities to probe the properties of confined fluids and to study the transport of molecules and ions through narrow molecular channels. Simulations of the flow of water, protons, ions, and biopolymers through individual nanotubes and nanotube membranes highlight key elements of different molecular translocation mechanisms. For instance, we could show that the proton diffusivity is about 40 times higher along one-dimensionally ordered water chains in (6,6) carbon nanotubes than in bulk water. Beyond possible technological applications, e.g., in nanofluidics and separation devices, studies of molecular flow through nanotubes has led to new insights into membrane transport in biological systems.

10:30 AM *II5.5

Automatic Self-Consistent Coarse-Graining of Polymer and Biomembrane Systems. Roland Faller, Chem Eng & Mat Sci, UC Davis, Davis, California.

A self-consistent systematic mapping procedure for polymer models is presented. It allows to efficiently derive mesoscale models with one interaction center per chemical repeat unit from atomistic models preserving the polymer identity. Different polymers in the melt and in solution at ambient conditions are investigated and the corresponding meso-scale models derived. Atomistic and coarse-grained results are compared to each other. Differences between models of the same polymer in various environments are pointed out. The meso-scale models could be simulated over a large variety of chain lengths and time-scales relevant for experimental comparison. Concerning static properties, we determined the persistence length of our systems and the scaling behavior of the radius of gyration. The latter was compared to experiments and the agreement is satisfactory. Furthermore, we find deviations from Rouse dynamics for polyisoprene at all chain lengths at ambient conditions. Additionally, a recent generalization of the technique to polymer blends is presented. We also discuss a related technique and its application to two dimensional structure formation in biomembranes. R. Faller, *D. Reith Macromolecules* 36 (2003) 5406 R. Faller, *Polymer* 45(2004) 3869

11:00 AM *II5.6

Shulgi Tablets for Computational Soft Nanotechnology. Johannes G.E.M. Fraaije, Leiden University, Leiden, Netherlands.

Computational Soft Nanotechnology lives in a multidimensional twilight zone. The task is to invent realistic computational models for a variety of nanoscopic surface modifications: the materials of choice are mixed formulations of flexible block copolymers, surfactants and colloids. Such modification are of relevance for applications as diverse as selective biosensors, antifouling coatings and cheap memorychips. In particular, we discuss the experimental and theoretical microphase diagram of soft surface layers. We conclude with a discussion of the Shulgi Tablets software package, a scripting/C++ library architecture which will enable, in an industrial

computational chemistry setting, the 'seamless' merging of a variety of field-particle models through advanced scripting protocols.

11:30 AM II5.7

A Uniform Methodology for the Design, Implementation and Verification of Efficient, Scalable, Large-scale Scientific Simulations based on the psi Calculus. James Reynolds¹ and Lenore R. Mullin²; ¹College of Nanoscale Science and Engineering, University at Albany, State University of New York, Albany, New York; ²Computer Science, University at Albany, State University of New York, Albany, New York.

The complexity inherent in software for large-scale scientific computational problems poses significant challenges and often demands the concerted effort of collaborative groups over multi-year development times. A new discipline is emerging to handle the complexity of large computational problems through the use of a systematic design protocol based on the rigorous mathematical formalism of the psi-calculus and Mathematics of Arrays. Success has been achieved through the application of these techniques to a number of algorithms that are ubiquitous across science and engineering disciplines, such as the Fast Fourier Transform (FFT), LU decomposition, matrix multiplication, time domain convolution, etc. This talk will provide an overview of these techniques and discuss algorithms arising in applications to large-scale density functional based electronic structure calculations.

SESSION II6:

Chair: S. Glotzer

Wednesday Afternoon, December 1, 2004
Room 204 (Hynes)

1:30 PM *II6.1

Using Nanoparticles to Create Self-Healing Films.

Anna Balazs, Chemical Engineering, University of Pittsburgh, Pittsburgh, Pennsylvania.

The need for viable materials for optical communications, display technologies and biomedical engineering is driving the creation of multilayer composites that combine brittle materials, such as glass, with moldable polymers. However, crack formation is a critical problem in composites where thin brittle films lie in contact with deformable polymer layers. Using computer simulations, we show that adding nanoparticles to the polymers yields materials in which the particles become localized at nanoscale cracks and effectively form patches to repair the damaged regions. Through micromechanics simulations, we evaluate the properties of these systems in the undamaged, damaged and healed states and determine optimal conditions for harnessing nanoparticles to act as responsive, self-assembled band-aids for composite materials. The results reveal situations where the mechanical properties of the repaired composites can potentially be restored to 75%-100% of the undamaged material. In an additional study, we investigate the benefits of coating substrates, which contain nanoscale defects, with nanoparticle-filled polymer films. In particular, we focus on surfaces that contain a nanoscopic notch and use simulations to determine the particle and polymer distribution on the damaged surface. The calculations reveal that a high volume fraction of relatively large particles are localized in the notch. Here, the polymer melt induces a depletion attraction between the particles and surface, and thereby drives the nanoparticles into the defect. The results also show that the stress concentration at the notch tip is significantly reduced due to the presence of the nanoparticles. The application of such nanocomposite coatings could potentially yield defect-free surfaces that exhibit enhanced mechanical, electrical or barrier properties.

2:00 PM II6.2

Multiscale Micromechanical Modeling of Polymer/Clay Nanocomposites. Nuo Sheng, Mary C. Boyce and David M. Parks; mechanical engineering, MIT, Cambridge, Massachusetts.

Polymer/clay nanocomposites can exhibit markedly enhanced mechanical properties at low fractions of clay. Traditional composite models cannot be directly applied to nanocomposites due to the hierarchical morphology of intercalated nanoclay and surrounding matrix. We developed a multiscale modeling approach to account for the hierarchical morphology through the use of an 'effective particle', defined to represent the inherently discrete clay as a basic element in continuum analysis; the geometry and properties of the 'effective particle' are determined from nano-scale characteristics of the clay structure. Special matrix morphology induced by the presence of the nanoclay (e.g., transcrystallization of semi-crystalline matrix) is taken into account by introduction of highly textured phases into numerical models. This modeling approach is employed to assess anisotropic elastic moduli and anisotropic thermal expansion coefficient of nanocomposites with various polymer matrices

(amorphous/semi-crystalline/elastomer, etc). FE Predictions are in good agreement with experimental data. Some interesting issues, such as influence of silicate sheet waviness on the end composite properties, and potential tradeoff when processing towards exfoliation, are explored as well.

2:15 PM II6.3

Atomistic Simulation of Organically Modified Montmorillonite. Hendrik Heinz^{1,2}, Hilmar Koerner³ and Barry L. Farmer¹; ¹Materials and Manufacturing Directorate, Air Force Research Laboratory, WPAFB, Ohio; ²Department of Mechanical and Materials Engineering, Wright State University, Dayton, Ohio; ³University of Dayton Research Institute, Dayton, Ohio.

Montmorillonite clay with trimethyloctadecylammonium ions (C18) is an important additive in polymer-clay nanocomposites. We describe an atomistic model of montmorillonite including physically justified atomic charges and a distribution of charge defects in agreement with statistical data based on ²⁹Si-NMR, suited for the simulation of inorganic-organic interfaces (integrated in the polymer consistent force field). Geometric deviations in unit cell parameters are less than 0.5 %. Molecular dynamics simulation of the surface structure of C18-montmorillonite shows that essentially a monolayer of C18 cations is formed on the surface. The lateral mobility of the surfactants on the surface increases at higher temperature. X-Ray diffraction data of both the natural and the organically modified montmorillonite show good agreement with simulated X-Ray diffraction data obtained from the computational models, and the origin of characteristic tails in the spectra is explained.

2:30 PM *II6.4

Fracture of Carbon Nanotubes and of Diamond Films.

George C. Schatz¹, Steven Mielke¹, Diego Troya¹, Lipeng Sun¹, Jeff Paci¹ and Ted Belytschko²; ¹Chemistry, Northwestern University, Evanston, Illinois; ²Mechanical Engineering, Northwestern University, Evanston, Illinois.

We use density functional theory and semiempirical electronic structure methods to study fracture of defected carbon nanotubes, and of doped and undoped ultrananocrystalline diamond films.

3:30 PM *II6.5

Filling Carbon Nanotubes: Predicted Effects on Mechanical Properties. Susan B. Sinnott, Materials Science and Engineering, University of Florida, Gainesville, Florida.

It is commonly accepted that opened carbon nanotubes can be readily filled by most materials. Here, computational simulations are used to explore the effect of filling on the mechanical properties of carbon nanotubes. In particular, classical many-body empirical potentials are used to consider the responses of individual carbon nanotubes and nanotube bundles that are filled with molecules, such as methane, fullerenes, and n-butane, to compression, tension, and shear. The results are contrasted to the responses of empty nanotubes and bundles. This work is supported by the NSF-funded Network for Computational Nanotechnology (EEC-0228390).

4:00 PM II6.6

Coarse-grained Molecular Dynamics of Carbon Nanotube Filled Epoxy Based Nanocomposites. Kelly L. Anderson, Barry L. Farmer and Richard A. Vaia; MLBP, AFRL, Dayton, Ohio.

Meso-scale simulations are employed to elucidate the coupling of interaction constraints to the structural evolution of low dimensional nanocomposites. Using the Kremer-Grest coarse-grained bead-spring model, the intercalation of epoxy monomers into bundles of nanorods was simulated. Coarse-graining the molecular system to represent specific epoxy monomers and bundles of single-walled nanotubes required matching the spatial and temporal regimes of both the epoxy and nanotubes to spherical beads that represent both uncured and cured epoxy as well as nanorods. Beginning with an intercalated, exfoliated or de-mixed system, curing of the epoxy monomers in the presence of the nanorods was undertaken using a distance dependent reaction methodology to examine the influence of nanoscale fillers on the curing process. Network formation and resultant mechanical behavior near the nanofiller is influenced by the presence of nanorods.

4:15 PM II6.7

Molecular Dynamics Simulations of Mechanical Properties of Carbon Nanotube/Polymer Nanocomposites with Controllable Microstructure and Distribution. Jihua Gou and Krishna Anumakonda; Department of Mechanical Engineering, University of South Alabama, Mobile, Alabama.

Carbon nanotubes have large interfacial area per volume and hold extraordinary mechanical, electrical as well as thermal properties. Therefore, the properties of polymer composites could be enhanced by

adding carbon nanotubes into polymer matrices. However, it is critical to obtain a fundamental understanding of the processing-structure-property relations of carbon nanotube/polymer composites. In this research, the predicative models for the mechanical properties of nanocomposites with controllable microstructure and distribution of carbon nanotubes have been developed based on molecular dynamics simulations. The effects of aspect ratios of nanotubes on the mechanical properties of nanocomposites have been examined. The mechanical properties have also been calculated for the nanocomposites with controllable distributions, including varied concentrations of nanotubes, gradient concentrations of nanotubes, and orientations of nanotubes in the composites. The establishment of these models will enable the nanoscale design of advanced nanocomposites.

4:30 PM *II6.8

Defect Management and Morphology Changes in Carbon Nanostructures. David Tomanek, Physics and Astronomy Department, Michigan State University, East Lansing, Michigan.

Due to their structural flexibility, carbon nanotubes and related nanostructures show an unprecedented capability of healing themselves at defect sites. The combination of *abinitio* density functional electronic structure calculations with molecular dynamics simulations is a powerful tool to demonstrate the ability of narrow nanotubes to heal out vacancies at high temperatures and in the photo-excited state [1]. Photo-excitations can be used to identify [2] and even non-destructively remove other defects [3], including chemisorbed oxygen. Large-scale morphology changes in sp^2 bonded carbon nanostructures can be initiated at Stone-Wales defects, and may propagate throughout the structure by a sequence of Generalized Stone-Wales transformations. This process may cause large-scale morphology changes, including fusion of nanotubes [4] and fullerenes [5]. Such reactions can be most efficiently modeled by computer simulations on a new generation of massively parallel supercomputers. [1] Yoshiyuki Miyamoto, Savas Berber, Mina Yoon, Angel Rubio, David Tomanek, Can Photo Excitations Heal Defects in Carbon Nanotubes? Chem. Phys. Lett. (2004). [2] Yoshiyuki Miyamoto, Angel Rubio, Savas Berber, Mina Yoon, David Tomanek, Theoretical Identification of Stone-Wales Defects in Nanotubes, Phys. Rev. BR **69**, 121413 (2004). [3] Yoshiyuki Miyamoto, Noboru Jinbo, Hisashi Nakamura, Angel Rubio, and David Tomanek, Photosurgical Deoxidation of Nanotubes (submitted for publication). [4] Mina Yoon, Seungwu Han, Gunn Kim, Sangbong Lee, Savas Berber, Eiji Osawa, Jisoon Ihm, Mauricio Terrones, Florian Banhart, Jean-Christophe Charlier, Nicole Grobert, Humberto Terrones, Pulickel M. Ajayan, David Tomanek, The zipper mechanism of nanotube fusion: Theory and Experiment, Phys. Rev. Lett. **92**, 075504 (2004). [5] Seungwu Han, Mina Yoon, Savas Berber, Noah Park, Eiji Osawa, Jisoon Ihm, and David Tomanek, Microscopic Mechanism of Fullerene Fusion (submitted for publication).

SESSION II7: Poster Session
Chair: G. Goldbeck-Wood
Wednesday Evening, December 1, 2004
8:00 PM
Exhibition Hall D (Hynes)

II7.1

Reconstruction of silicon surfaces: a stochastic optimization problem. Cristian Ciobanu^{1,2} and Cristian Predescu³, ¹Division of Engineering, Brown University, Providence, Rhode Island; ²Division of Engineering, Colorado School of Mines, Golden, Colorado; ³Chemistry, University of California Berkeley, Berkeley, California.

Over the last two decades, scanning tunnelling microscopy (STM) has become one of the most important ways to investigate the structure of crystal surfaces. STM has helped achieve remarkable successes in surface science such as finding the atomic structure of Si(111) and Si(001). For high-index Si surfaces the information about the local density of states obtained by scanning does not translate directly into knowledge about the positions of atoms at the surface. A commonly accepted strategy for identifying the atomic structure is to propose several possible models and analyze their corresponding simulated STM images for a match with the experimental ones. However, the number of good candidates for the lowest-energy structure is very large for high-index surfaces, and heuristic approaches are not likely to cover all the relevant structural models. In this article, we take the view that finding the atomic structure of a surface is a problem of stochastic optimization, and we address it as such. We design a general technique for predicting the reconstruction of silicon surfaces with arbitrary orientation, which is based on parallel-tempering Monte Carlo simulations combined with an exponential cooling. The advantages of the method are illustrated using the Si(105) surface as example, with two main results: (a) the correct single-step rebonded structure [e.g., Fujikawa et al., Phys. Rev. Lett. **88**, 176101 (2002)] is

obtained even when starting from the paired-dimer model [Mo et al., Phys. Rev. Lett. **65**, 1020 (1990)] that was assumed to be correct for many years, and (b) we have found several double-step reconstructions that have lower surface energies than any previously proposed double-step models.

II7.2

A Theoretical Study of Single-Wall Carbon Nanotubes Functionalization: Reaction Mechanisms and Raman Characterization. Xiaofeng Frank Duan¹, Brahim Akdim² and Ruth Pachter^{1,2}, ¹Aeronautical Systems Center Major Shared Resource Center for High Performance Computing, WPAFB, Ohio; ²Air Force Research Laboratory, Materials & Manufacturing Directorate, WPAFB, Ohio.

In order to gain a fundamental understanding of reaction mechanisms in functionalized single-wall carbon nanotubes (SWCNTs), and of the changes in the Raman modes in such systems, we report a theoretical study employing density functional theory (DFT) calculations. In particular, because control by chemical functionalization, using water-soluble diazonium salts, has recently demonstrated specific electronic structure tailoring (Strano et al., Science, 2003), we examined the reaction pathways of a C(5,5) SWCNT model, functionalized with a 4-chloro-phenyl functional group. Our results show that a charge-transfer-complex mechanism is the most probable reaction pathway, consistent with the experimental observation. Furthermore, we examined theoretically the experimentally observed Raman breathing mode (RBM) upshift in carboxy-functionalized SWCNTs (Kuzmany et al., Synthetic Metals, 2004).

II7.3

Ag Nanowires Deposited on Silicon Steps Studied by the Density Functional Theory. Anna Maria Mazzone, IMM, Sezione di Bologna, CNR, Bologna, Italy.

There is currently a considerable interest for nanoscale devices. Among currently discussed structures, one-dimensional metallic chains deposited on a semiconductor substrate show interesting electronic properties, oscillating between conductor and insulator. Ag/on/Si is a central topic in surface science and the interest for this systems has stimulated efforts for the fabrication and characterization of Ag nanowires deposited on silicon. Recent studies on the highly vicinal Si(5,5,12) show that surface steps can be advantageously used as a template for nanowires growth, though for the Ag/Si system there is an unusual coupling between the wire and the states of the surface. This study has been performed to gain insight into these effects. Therefore the Density Functional theory at GGA level and a cluster model of the exposed surface have been applied to structures formed by linear chains of Ag atoms deposited onto monolayer steps on Si(100). The calculations illustrate the effects of the geometrical parameters of the deposited system (i.e the step geometry and the length of the wire) on the wire geometry, electronic configuration and phonon response as well as the related effects on step surface states.

II7.4

A Quantum Mechanical Study of CO Adsorption onto SnO₂ Grains and Wires. Anna Maria Mazzone, IMM, Sezione di Bologna, CNR, Bologna, Italy.

The purpose of this study is to gain insight into the gas-adsorbing properties of SnO₂ nanosized materials and the is based on Hartree-Fock and Density Functional theories. The structures considered are nanocrystalline grains and nanowires with a realistic size and shape. In fact, according to experiments, the shape of the grains is columnar or spongy whereas nanowires have a linear, plated form. The maximum dimension is in the range 2-4nm and all structures retain the rutile lattice of the bulk phase. The adsorbed system is formed by the SnO₂ nanostructure and by a CO molecule. The calculations describe preferred adsorption sites, the structure of the deposited molecule and its effects on the electronic structure, charge and polarizability of the absorbing medium. The focus of the calculations is on the difference between nanograins and nanowires and literature results on CO adsorption on the flat surfaces of crystalline SnO₂ are also discussed.

II7.5

First-Principles Optical Cross-Sections for Single-Walled Carbon Nanotubes. Shagoto Nandi^{2,1}, Shelly L. Elizondo¹ and John W. Mintmire¹, ¹Department of Physics, Oklahoma State University, Stillwater, Oklahoma; ²Department of Computer Science, Boston University, Boston, Massachusetts.

Using a first-principles local-density functional (LDF) method, we have carried out theoretical calculations for the optical absorption properties of single-walled carbon nanotubes. Our motivation is influenced by recent interests in utilizing optical absorption and Raman data to characterize the structure of carbon nanotubes.

Bachilo, et al. [1] have recently reported results from spectrofluorimetric studies, in which photoluminescence spectra were obtained for varying photoexcitation wavelengths. The experimental results were interpreted in terms of the first and second van Hove optical transitions theoretically expected for various nanotube species, with photoluminescence peaks occurring for specific combinations of absorption and emission wavelengths then assigned to specific (n,m) nanotube structures. The results for the ratio of optical excitation to emission energies is plotted for each peak versus the peak's excitation wavelength and are compared with results obtained extended tight-binding model calculations. [2] In the current work, we have used first-principles LDF calculations to examine the optical cross-sections of various nanotubes, taking into account polarization effects. In earlier work, we and others have demonstrated that carbon nanotubes should have an anisotropic optical response. [3,4] Our results indicate that polarization effects could play an important role in the interpretation of earlier photoluminescence experiments. [1] This work was supported by the US Office of Naval Research, the DoD HPCMO CHSSI program through the Naval Research Laboratory, the Oklahoma NASA EPSCoR program. SN acknowledges support from the NSF REU program at Oklahoma State University. [1] S.M. Bachilo, M.S. Strano, C. Kittrell, R.H. Hauge, R.E. Smalley, R.B. Weisman, *Science* **298**, 2361 (2002). [2] S. Reich, J. Maultzsch, C. Thomsen, P. Ordejon, *Phys. Rev. B* **66**, 035412 (2002). [3] J.W. Mintmire, C.T. White, *Synthetic Metals* **77**, 231 (1996). [4] S. Tasaki, K. Maekawa, T. Yamabe, *Phys. Rev. B* **57**, 9301 (1998).

II7.6

Effects of Surface Stoichiometry on Electronic Structures of Metals Adsorbed on TiO₂(110). Kazuyuki Okazaki¹, Yoshitada Morikawa², Satoshi Ichikawa¹, Shingo Tanaka¹ and Masanori Kohyama¹; ¹Materials Science Research Group, National Institute of Advanced Industrial Science and Technology, Ikeda, Osaka, Japan; ²Institute of Scientific and Industrial Research, Osaka University, Ibaraki, Osaka, Japan.

Catalytic properties of metal particles supported on TiO₂ depend on the kind of metal. Therefore, we have theoretically investigated the electronic structures of metals, such as Au and Pt, adsorbed on the rutile TiO₂(110) surface based on the density functional theory. We used the *ab initio* pseudopotential method and a periodic slab model separated by a vacuum region of 19.8 Å. Moreover, we have considered three types of surfaces with the different stoichiometry and defects; the stoichiometric surface, the surface formed by removing the bridging-oxygen atoms (Ti-rich surface), and the surface formed by removing the bridging-oxygen and sixfold Ti atoms (O-rich surface) in order to investigate the effects of the stoichiometry of TiO₂(110). We examined the Au or Pt adsorption on the on-top site above the bridging-oxygen and the on-top site above the fivefold Ti atom for the stoichiometric surface, on the vacant site formed by removing the bridging-oxygen atoms for the Ti-rich surface, and the vacant site formed by removing the sixfold Ti atoms for the O-rich surface. All the calculations were carried out using the program package STATE (Simulation Tool for Atom TEchnology). For both Au and Pt, the adhesive energies between the metal and TiO₂(110) for the non-stoichiometric, the Ti-rich and O-rich, surfaces are larger than that for the stoichiometric surface. Especially, the adhesive energy for the O-rich surface is considerably large because of the strongly hybridization between the *d* orbitals of metal and the *p* orbitals of oxygen and large electrons transfer from the metal atom to the oxygen atom. It can be said that some non-stoichiometry or defects at TiO₂ substrates are essential for the stable adhesion of metal particles on TiO₂ substrates in the catalysts. For each surface stoichiometry, the adhesive energies between Pt and TiO₂(110) are much larger than those between Au and TiO₂(110). This is because charge transfers and orbital hybridization between Pt and TiO₂(110) are larger than those between Au and TiO₂(110). It can be considered that the difference of the interaction between the metals and the substrate is closely concerned with the difference of catalytic properties between the Au/TiO₂ and Pt/TiO₂ systems.

II7.7

Computational Studies of Si and Ru Complexes Bound to Carbon Nanotubes. Jordan Poler^{1,2}, Tom DuBois^{1,2} and Tom A. Schmedake^{1,2}; ¹Chemistry, UNC Charlotte, Charlotte, North Carolina; ²Center for Optoelectronics and Optical Communications, UNC Charlotte, Charlotte, North Carolina.

We will report our studies of the quantum mechanical calculations of novel Si and Ru organometallic complexes, either covalently or "mechanically" bound to carbon nanotubes. Using derivatives of Ru2+[tris(phenanthroline)], Si0[tris(phenanthroline)], Si2+[tris(phenanthroline)], and Si4+[tris(phenanthroline)] we have designed several useful motifs for assembling single walled carbon nanotubes (SWNT), and for studying the electronic, optical and magnetic properties of these assemblies. Initial Calculations using Hartree Fock and Density Functional Theory show that the cis-

isomers of the silicon zero and silicon 2+ systems bound to the SWNTs via a phenazine bridge is more stable than the trans- isomer. Moreover, these systems are paramagnetic and seem to result in magnetic behavior which may enable actuation and sensing with the nanotubes assemblies. Further studies of the mixed metal/mixed valence multimers of the organometallic derivatives indicate an interesting electronic communication between and along the SWNTs. These results indicate potential applications in information technology and solar energy conversion.

II7.8

Monte Carlo Simulation of Nanocomposites. Alejandro D. Rey¹ and Majid Ghiass²; ¹Chemical Engineering, McGill University, Montreal, Quebec, Canada; ²Chemical Engineering, McGill University, Montreal, Quebec, Canada.

A lattice Monte Carlo simulation is performed to investigate microstructural processes in polymer-carbon nanotube composites. Size, aggregation and distribution of filler particles are also investigated. Self-avoiding random polymer chain motions including end bead reptation and rotation, kink jump and crankshaft motions are applied in conjunction with the Metropolis algorithm. The effect of particle-particle and polymer-particle interactive energies on structural features are investigated. The conformational information serves as an input to predict mechanical, electronic properties.

II7.9

Electronic Transport in Low-Dimensional Nanomaterials. Vicenta Sanchez¹ and Chumin Wang²; ¹Departamento de Física, Facultad de Ciencias, Universidad Nacional Autónoma de México, México D.F., México; ²Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México, México D.F., México.

The ac and dc electrical conductances of nanotubes, nanotapes and nanowires at zero temperature are studied by means of the Kubo-Greenwood formula [1]. For single-wall nanotubes, a uniform distribution of 2G₀ steps are obtained in dc conductance spectra, where G₀=2e²/h is the conductance quantum, as recently observed in carbon nanotubes [2]. This fact could be understood as a consequence of the degeneracy introduced by the periodic boundary condition in the cross section of nanotubes, as confirmed in nanotapes, where regular G₀ steps are observed in their dc conductance spectra. For the case of nanowires, the dc conductance is also quantized, except that the steps have a variation of height of nG₀ depending on the degeneracy of eigenvalues. On the other hand, the ac conductance reveals a transition from one- to two-dimensional behavior when the cross-section area of nanotubes or nanotapes increases. Finally, the quantized dc conductance spectrum becomes a devil's stair if the perpendicular subspace of the system is quasiperiodic. This work has been partially supported by CONACyT-41492F and UNAM-IX122704. Computations were performed at Bakliz of DGSCA, UNAM. [1] V. Sanchez and C. Wang, *J. Non-Cryst. Solids* **329**, 151 (2003). [2] A. Urbina, I. Echeverria, A. Perez-Garrido, A. Diaz-Sanchez, and J. Abellan, *Phys. Rev. Lett.* **90**, 106603 (2003).

II7.10

Self-Diffusion Mechanisms in Two-Dimensional Crystals in Metals. Gennady Mikhailovich Poletaev, Mikhail Dmitrievich Starostenkov and Julia Vladimirovna Patzeva; General Physics Department, Altai State Technical University, Barnaul, Russian Federation.

It is known that there are several diffusion mechanisms in metals: exchange two-atomic exchange cyclic, crowdion, vacancy and interstitial mechanism of displacement. The major mechanism is vacancy mechanism. It is very difficult to evaluate the activation energy and contribution of every mechanism into the process of diffusion in a real experiment. The method of molecular dynamics allows to study the mechanism of self-diffusion in details. The paper is concerned with the research of self-diffusion mechanisms in two-dimensional crystals of Ni, Al, Cu metals by the method of molecular dynamics. The packing of two-dimensional metals in a computer model was corresponded to the plane [111] of FCC lattice. Morse pair potentials and Finnis-Sinclair multipartial potentials were used in the researches. Different self-diffusion mechanisms were studied. Activation energies of the mechanisms, the contribution of every mechanism into diffusion process in the dependence on temperature were calculated. It was found, that vacancy mechanism (the vacancy was formed by Shottki method) and the mechanism of the formation and annihilation of Frenkel pairs made major contribution into self-diffusion in two-dimensional metals. The second mechanism is exchange cyclic mechanism, but it contains from three to several tens of atoms in the cycle. Frenkel pair forms in the crystal in the result of the crossing of thermal crowdion displacements. It is worth to note, that this mechanism in some two-dimensional metals, for example Al, makes even bigger contribution than vacancy Shottki mechanism. The other diffusion mechanisms influence on self-diffusion

in two-dimensional metals not so gritty.

II7.11

Diffusion Mechanism at the Grain Boundaries in 2D Metals. Gennady Mikhailovich Poletaev, Roman Yuryevich Rakitin and Mikhail Dmitrievich Starostenkov; General Physics Department, Altai State Technical University, Barnaul, Russian Federation.

The present paper is concerned with the research of diffusion mechanism at the grain boundaries in two-dimensional metals by the method of molecular dynamics. The diffusion of atoms was studied on the example of three metals: Ni, Al, Cu. The packing of two-dimensional crystals was corresponded to the plane [111] of FCC lattice. The researches were made, using two types of the potentials of interatomic interaction: Morse pair potentials and multipartial Finnis-Sinclair potentials. The metals under study were heated up to the temperatures, corresponded from 0.3 to 0.95 relatively to the melting temperature. It was found, that leading diffusion mechanism at the grain boundaries of two-dimensional metals was the result of interaction of grain boundary dislocation pairs. The creep of dislocation pairs in opposite sides was observed in the experiments. The rugged atomic row of one dislocation was lengthened at the expense of shortening of the other dislocation atomic row. In this connection, the chain of the displaced atoms was observed in the directions, connecting the nuclei of two dislocations. The inverse displacements of atoms (the return of atoms in the initial positions) were observed. One of the important elements of similar mechanism is the appearance of the vacancy in the chains of the displaced atoms. The trajectory of the vacancy migration from one nucleau to the other one can have ring reserved elements, which are the cause of the appearance of ring exchange displacements of atoms at the boundary. The diffusion mechanism is nearly the same for highangle grain boundaries. In this case it can be interpreted as the interaction of the pairs of point defects (vacancies and interstitial atoms). The chains of the displaced atoms from the areas of pressure (interstitial atom) to the areas of tension (vacancy) appear in the process of thermal movements of atoms as in the case of lowangle boundaries. Besides the mechanism, the dependences of the coefficient of diffusion at the grain boundaries in the dependence on temperature, mutual orientation of grains, free volume, energy of grain boundaries were studied.

II7.12

Ab-initio Study of Redox Effects on Atomic and Electronic Structure of 4,4'-Terphenyldithiol. Kazuyuki Uchida, Hiroyuki Kageshima and Hiroshi Inokawa; NTT Basic Research Laboratories, Atsugi, Japan.

Recently, it was experimentally observed that Au-electrodes bridged by 4,4'-terphenyldithiol shows I-Vsd(Vg) characteristics as a single-electron transistor (SET) with strong gate effects, while the mechanism behind them has not been clarified yet. As the I-V_{sd}(V_g) characteristics of the system as a SET is affected by the discrete energy levels of the nano-scale single-electron island, it is significant to realize the atomic and electronic structure of the island. We performed ab-initio calculations based on the density-functional theory in order to obtain the optimized structures of 4,4'-terphenyldithiol molecules under several redox states. We found that the rotation angle between two phenyls is finite when the molecule is electrically neutral, and that the rotation angle is reduced by electron or hole doping. We also found that the thiol is in the same plane as the phenyl to which it is connected when the molecule is neutral or oxidized, and that the C-S-H plane becomes perpendicular to the phenyl plane when the molecule is reduced. The structural relaxation, accompanied by the energy gain of ~ 100meV, cannot be neglected in the low temperature observations. The intervals of the discrete energy levels were large enough to affect that of the Coulomb oscillation of the SET. It is concluded that the intervals of the Coulomb oscillation can be affected by discrete energy levels of the molecule, which are modified by the structural deformation induced by carrier doping, in other words, reduction and oxidation. The influences of the connections between the electrode and the molecule on the atomic and electronic structures of the system are also discussed.

II7.13

Spectra and structure of phonon vibrations of BN nanotubes. Pokropivny Vladimir¹, Gubanov Victor², Covrigin Sergey² and Partch Richard³; ¹IPMS NASU, Kiev, Ukraine; ²Taras Shevchenko National University, Kiev; ³Clarkson University, Potsdam, New York.

Boron nitride nanotubes synthesized by carbothermal method have been studied by Raman spectroscopy. A number of single-walled BN nanotubes of arm-chair and zig-zag configuration with open and closed ends are calculated by ab initio, RHF, PM3, STG and other quantum chemistry methods. Calculated infra-red and Raman active spectra were compared with original experimental and recently obtained literature data. Vibration structure of whispering modes gallery, especially radial A1 breathing and E2g ellipsoidal modes, are

animated and investigated in more detail. Application for hypersound transducer in tera-hertz range device is discussed.

II7.14

Abstract Withdrawn

II7.15

Laser-Induced Coherent Breathing Phonons and Directed Fragmentation of Carbon Nanotubes. Traian Dumitrica¹, Martin E. Garcia², Harald O. Jeschke² and Boris I. Yakobson¹; ¹Rice University, Houston, Texas; ²Freie Universitat Berlin, Berlin, Germany; ³Goethe-Universitat, Frankfurt/Main, Germany.

We show the ability of coherent phonons to forcibly drive precise ultrafast transformations in carbon nanotubes. Performing molecular dynamics simulations based on a microscopic electronic model, which also accounts for the interaction with an external e.m. field, we obtain that the laser induced ultrafast structural changes differ dramatically from the thermally induced ones. In the ultrafast prethermal regime, we show that bond weakening and a simultaneous excitation of three coherent phonons modes, localized in the spherical caps (one mode) and cylindrical nanotube body (two main modes), lead to a selective cap opening. We proceed to analyze bond-perturbation distribution as a result of interference pattern of the excited vibrations, and investigate possibility of nanotubes cleavage in the non-cap locations. Our finding is of a broader fundamental interest since it provides a unique way of manipulating lattice structures and shapes at the nanoscale level. The transformation achieved here, of CNT cap opening with little loss of material, is a challenging technological issue motivated for example by the perspective of nano-confinement of molecular species inside CNTs. T. Dumitrica, M.E. Garcia, H.O. Jeschke, and B.I. Yakobson, Phys. Rev. Lett. 92, 117401 (2004).

II7.16

Normal modes of vibration of carbon nanotubes doped with nitrogen. Jorge Ramon Soto, Jordi Austrich, Renela Maria Valladares, Alexander Valladares, Maria Luisa Marquina, Raul Espejel and Alipio Calles; Departamento de Fisica, Facultad de Ciencias, UNAM., Mexico D.F., Mexico.

The conducting properties of carbon nanotubes can be changed by doping with nitrogen. There exists an enormous interest in modifying the conducting properties of organic and inorganic, single and multi-wall nanotubes, through doping, since their modified transport properties can be exploited in electronic nano devices such as diodes, transistors and super resolution displays. In order to characterize these systems, in this work we study the changes in the raman and infrared spectra as a function of nitrogen content and possible different geometries. We use a first principles approach, with periodic boundary conditions. We observe the symmetry breaking of the raman and infrared peaks as a frequency shift compared with the pristine carbon nanotubes to calculate the phonon spectra. These results are contrasted with experimental results and based on our calculations we propose possible doped nanotube structures to fabricate nano-devices.

SESSION I18:

Chair: L. Davis

Thursday Morning, December 2, 2004
Room 204 (Hynes)

8:30 AM *I18.1

Ultrathin Metal Films on Oxides: Ferroelectric Boundary Conditions and Surface Chemistry. Andrew M. Rappe, Department of Chemistry, University of Pennsylvania, Philadelphia, Pennsylvania.

Oxide-supported metals play an important role as catalysts, and oxide-metal electrode interfaces are a key feature of ferroelectric devices. In this talk, we discuss the oxide-metal interface and its influence on metal surface chemistry and bulk oxide properties. Using DFT, we model ultrathin Pt films supported on Al₂O₃ and on ferroelectric ABO₃ perovskites. We relate the oxide-metal interface chemistry to the increasing reactivity with decreasing size of supported metal nanoclusters. Monolayer Pt shows enhanced CO adsorption on either O-terminated or Al-terminated Al₂O₃, and we relate this directly to the polarity of the underlying oxide. By contrast, bilayer Pt shows dramatically reduced chemisorption energies on O-terminated Al₂O₃. This result is indeed a nanoscale effect as the chemisorption energies return to their bulk values by four layers. We demonstrate that Pt thin films can act as perfect metal electrodes for ferroelectric oxides, allowing for the existence of electric polarization in ultrathin ferroelectric films. We examine the influence of the oxide-metal interface on the Pt layer and the oxide. We also discuss prospects for changing the adsorptive and catalytic properties by the polar effect in the ferroelectric thin film. The author would like to acknowledge vital contributions to this work by Alexie M. Kolpak,

Valentino R. Cooper, Na Sai, and Yashar Yourdshahyan. This work was supported by the Air Force Office of Scientific Research, the Office of Naval Research, the Laboratory for Research on the Structure of Matter, and the DoD HPCMO.

9:00 AM *IIS.2

One-Dimensional Structures at Oxide Surfaces.

Peter V. Sushko¹, Paolo E. Trevisanutto¹, Alexander L. Shluger¹, Oliver Diwald², Martin Sterrer³ and Erich Knozinger²; ¹Physics and Astronomy, University College London, London, United Kingdom; ²Institut für Materialchemie, Technische Universität Wien, Wien, Austria; ³Department of Chemical Physics, Fritz-Haber-Institute of the Max-Planck-Society, Berlin, Germany.

Steps at oxide and other surfaces can serve as 1-D charge or exciton channels. In particular, the recent experiments clearly demonstrate that selective photo-excitation of 4-coordinated step sites on MgO nano-particles leads to a formation of several types of oxygen hole can be general for a range of materials where electronic states of quasi 1-D surface defects are separated from other surface states both spatially and energetically. Stepped surfaces of oxides are particularly promising candidates since the electronic properties of oxide ions strongly depend on their coordination. To elaborate this concept further, in this presentation we use an embedded cluster approach to correlate the local atomic structure of the surface topological features and their electronic properties. The method combines a quantum-mechanical treatment of a "site of interest" with a classical treatment of the remaining part of the crystalline or amorphous lattice [2]. The calculations of optical absorption energies, ionisation potentials and electron affinities of surface point defects, steps, corners and kinks on MgO nano-particles demonstrate the existence of a hierarchy of electron states. The step optical excitation energy is 5.6 eV and is very different from that for the bulk (7.8 eV), surface terrace (6.2 eV), or surface corner (4.6 eV). Combining the experimental and theoretical results we demonstrate the existence of various electron traps at the surface. These are ranging from deep positively charged oxygen vacancies, with electron affinities of 3.5 - 5 eV, to 3-coordinated cations (shallow traps) with electron affinities of 0.5 - 1.5 eV [3]. Similar hierarchy exists for the hole traps. We suggest that the selective excitation of steps results in the exciton or hole transfer towards terminating corner sites where several processes can take place: i) formation of an oxygen hole centre, ii) formation of a corner site exciton or iii) formation of a corner neutral vacancy with simultaneous desorption of an oxygen atom. Studying the energy and charge transfer to molecules adsorbed at step and kink sites could elucidate the mechanism of this transfer. 1. O. Diwald, M. Sterrer, E. Knozinger, P. V. Sushko, A. L. Shluger, J. Phys. Chem., v.116, p.1707, (2002). 2. M. Sterrer, O. Diwald, E. Knozinger, P. V. Sushko, A. L. Shluger, J. Phys. Chem. B, v.106, p.12478, (2002). 3. P. V. Sushko, A. L. Shluger, C. R. A. Catlow, Surf. Sci., v.450, p.153, (2000); P. V. Sushko, J. L. Gavartin, A. L. Shluger, J. Phys. Chem. B, v.106, p.2269, (2002).

9:30 AM IIS.3

Additivity of Bond Strengths at Heterovalent Interfaces.

Helen H. Farrell and Randall A. LaViolette; Materials Science, INEEL, Idaho Falls, ID, Idaho.

We have investigated the additivity of interfacial cohesive energies, on a per-bond-pair basis, at heteroepitaxial interfaces using first-principles, density functional theory calculations. Though our ultimate goal is to characterize III-V/II-VI interfaces in general, we have concentrated on the ZnSe(100)/GaAs(100) system to reduce the effects of strain introduced by lattice misfits. We have studied three general categories of heterojunctions; those with only Ga-Se bonding, those with only Zn-As bonding, and those with a mixture of Ga-Se and Zn-As bonding. In the last category, we have looked at the effects of ordering in the interfacial layer. Specifically, we have considered several different variations in interfacial stoichiometry that are conceptually based on the heteroepitaxial growth of ZnSe(100) on the so-called beta-2 surface reconstruction of GaAs(100). The resulting differences will be discussed in terms of bond strength, interfacial charge neutrality and strain. We have also studied the effects induced by the presence of vacancies in the vicinity of the interface, and will discuss these on the same terms as above. The charge balance at the interface is a powerful determinant in governing whether the growth will be 2D and planar, as is ideal for heteroepitaxy, or 3D leading to island formation that can be used to generate self-assembled nanostructures at the interface. The relationship between charge balance, bond strength and these two growth modes will be also be discussed.

9:45 AM IIS.4

First Principles Evaluation of Ideal Strength of Si

Low-Dimensional Structures. Akihiro Kushima, Yoshitaka Umeno and Takayuki Kitamura; Engineering Physics and Mechanics, Kyoto University, Kyoto, Japan.

The ideal strength was originally defined as the stress or strain at which unstable deformation occurs in a perfect crystal lattice under homogeneous deformation, which is the ultimate strength of the material. There have been a good number of researches investigating the ideal strength because it is a fundamental mechanical property of the material and is important for understanding the intrinsic strength of the material itself. Most of the analyses on the ideal strength have been conducted on single crystals with three dimensional periodicity in the viewpoint of investigating basic properties of the materials. However, it is well known that the mechanical strength of materials depends on their structures. Therefore, investigating the ideal strength of the bulk structure only is not enough to understand the mechanical property of such materials. The structured materials can be created by the combination of two-dimensional, one-dimensional, and zero-dimensional structures, the low-dimensional structures. Simple low-dimensional structures, such as nano-films, nano-wires, and nano-dots with defect-free ideal structures can provide us with the fundamental mechanical property of the structured materials. Evaluating the mechanical strength of low-dimensional structure is important in designing nano-scale electronic and mechanical devices. In this point of view, the definition of the ideal strength must be expanded to include the strength of ideal structures because it provides us with fundamental strength of the structured materials. In this study we conducted tensile simulations of Si low-dimensional structures by first principles calculations to investigate the strength of atomic structured materials of Si. For the two-dimensional structure, we provide three Si nano-films with different thicknesses of 0.82nm, 1.36nm, and 1.91nm (6, 10, and 14 atomic layers, respectively) to examine how the thickness of the film affects the mechanical property. The elastic coefficients and the ideal strengths of the Si thin films are 108GPa and 9.60GPa for 6 atomic layers, 142GPa and 11.5GPa for 10 layers, and 149GPa and 13.5GPa for 14 layers, respectively. They are small compared to those of single crystal, and become closer to the bulk values, which are 160GPa and 15.8GPa, respectively, as the thickness increases. For one-dimensional structure, we investigated the strength of Si nano-wire with square-shaped cross section consists of four Si atoms under axial tension. We found the ideal strength of Si nano-wire to be 5.1nN at the strain of 0.125. For zero-dimensional structure, we selected Si cluster with trigonal bipyramid shape consists of 6 atoms. Tensile strain is applied by displacing top and bottom atoms of Si cluster. The peak strength was 5.6nN at the strain of 0.30.

10:15 AM *IIS.5

Computational Tools for Helical Nanostructures.

John W. Mintmire¹ and Carter T. White²; ¹Department of Physics, Oklahoma State University, Stillwater, Oklahoma; ²Chemistry Division, Naval Research Laboratory, Washington, District of Columbia.

One-dimensional nanostructures such as inorganic nanowires and nanotubes represent potential materials for key components of future electronic, optoelectronic, and nanoelectromechanical systems. They will also serve as important model systems to demonstrate quantum-size effects in nanostructured materials. Understanding the properties of these nanostructures is essential to the development of devices based on their use, and substantial progress has been made in the synthesis of Si, Ge, GaAs, InP semiconductor nanowires as well as with a range of metal oxides. Typical semiconductor nanowires are synthesized with diameters ranging from 10-50 nm, although recent experiments report the synthesis of silicon nanowires with diameters as small as 1 nm. We are currently developing a scalable and portable suite of programs for calculating the first-principles electronic structure, total energy, and energy derivatives of quasi-one-dimensional nanostructures with screw symmetry, allowing us to treat carbon nanotubes, silicon and silica nanowires, as well as a range of biomolecular materials such as DNA, etc. This approach considers the helical symmetry of these particular materials and calculates the electronic structure using local Gaussian-type orbitals within a one-dimensional local-density functional band-structure approach. A nanowire can be described by a unit cell containing a finite number of atoms and a screw operation acting on that unit cell. We discuss how this approach has been adapted to a parallel environment, and present some results for double-walled carbon nanotubes and semiconductor nanowires. This work was supported by the US Office of Naval Research, the DoD HPCMO CHSSI program through the Naval Research Laboratory, and the Oklahoma NASA EPSCoR program.

10:45 AM IIS.6

Alkyl Passivated Si Dots: A First Principles Study.

Fernando Agustin Reboledo and Giulia Galli; Physics & Adv. Technologies, Lawrence Livermore National Lab, Livermore, California.

We have carried out a series of ab-initio calculations to investigate the

changes in optical properties of Si clusters as a function of surface passivation. In particular, we have compared hydrogen passivated dots with those having alkyl groups at the surface. We find that, while on clusters with reconstructed surfaces a complete alkyl passivation is possible, steric repulsion prevents full passivation of Si dots with unreconstructed surfaces. In addition, our calculations show that stability of alkyl passivated clusters depend on the length of the carbon chains. Alkyl passivation weakly affects optical gaps of silicon quantum dots, while it substantially affects ionization potentials and electron affinities. The number of bound unoccupied states of the clusters also changes significantly as the passivation is changed from H to alkyl radicals. On the basis of our results we propose that alkyl terminated quantum dots could be eventually size selected taking advantage of the change of the ionization potential with the size of the cluster.

11:00 AM I18.7
Density Functional Theory Study of Platinum Core-Shell Nanoclusters. Jianguo Yu and Ju Li; Materials Science and Engineering, Ohio State University, Columbus, Ohio.

Density functional theory (DFT) calculations are used to study the structural, electronic and vibrational properties of platinum 13- and 55-atom clusters. Icosahedral, fcc, hcp geometries are considered. It is found that the icosahedral structure is not the most favored, in contrast to DFT results in less directionally-bonded Cu and Au clusters. We use spatial and angular-momentum projected density of states to analyze the difference in electronic structure and bonding between core and shell atoms. For comparison, the results for the hollow clusters are also studied. We then study the effect of alloy substitution at core and shell sites, in both 13- and 55-atom clusters. Thermodynamic preference for segregation is estimated.

11:15 AM I18.8
Contaminants in Suspended Gold Nanowires: An Ab Initio Molecular Dynamics Study. Sergio B. Legoas², Varlei Rodrigues³, Daniel Ugarte^{1,3} and Douglas S. Galvao¹; ¹Applied Physics, UNICAMP, Campinas, SP, Brazil; ²Departamento de Física, UFAM, Manaus, AM, Brazil; ³LNLS, Campinas, SP, Brazil.

Gold metallic nanowires have attracted great scientific interest in the last years due to new observed phenomena such as quantum conductance and the existence of unexpected long interatomic distances (3.0-5.0 Angstroms) in suspended atomic chains. Based on experimental data from high resolution transmission electron microscopy (HRTEM) and theoretical calculations from ab initio density functional methods we have proposed [1] that the origin of these anomalously interatomic distances could be the result of carbon contamination during sample manipulation. The large Au-Au distance would be in reality an Au-C-Au structure. More recently other authors based on zero-temperature calculations have proposed that hydrogen instead of carbon should be the most probable contaminant. Our results from ab initio molecular dynamics calculations using the DMOL code [2] show that for non-zero temperatures (more realistic to simulate the experimental conditions) hydrogen has to be ruled out and carbon atoms remain the best candidate for contaminants. [1] S.B. Legoas, D.S. Galvao, V. Rodrigues, and D. Ugarte, Phys. Rev. Lett. v.88, 076105 (2002). [2] DMOL3 package, <http://www.accelrys.com>.

11:30 AM I18.9
Coherency Limits in Epitaxial Nanowire Quantum Dots. Elif Ertekin¹, Daryl C. Chrzan² and Timothy Sands^{3,4}; ¹Materials Science and Engineering, Univ. of California, Berkeley, California; ²Materials Science and Engineering, Univ. of California, Berkeley, California; ³School of Materials Engineering, Purdue University, West Lafayette, Indiana; ⁴School of Electrical and Computer Engineering, Purdue University, West Lafayette, Indiana.

The recently developed nanowire heterostructures provide a new venue for exploring the properties of interfaces and new opportunities for exotic material integration. An intriguing characteristic of nanowire heterostructures is that, due to their one-dimensional geometry and boundary conditions, they relieve mismatch strain more effectively than epitaxial thin-film systems. Thus, materials with large lattice mismatch can be coherently integrated. Here, we study the coherency limits at equilibrium of nanowire heterostructure for the particular case of quantum dots emmedded in a nanowire matrix. This nanowire quantum dot structure is interesting for many applications; for example, a bandgap-tuned InGaN/GaN system may be useful as a white light source. We develop a critical thickness/radius model to predict the circumstances under which misfit dislocations will form. A numerical, variational approach is used to describe the stress and strain fields within the heterostructured nanowire containing the quantum dot. We assume that at the interface, the overlayer and underlayer are coherently mapped onto each other, and that the strain fields decay exponentially with distance from the interface. Strain partitioning is permitted in this model, as the total mismatch is

accommodated by strains in the quantum dot as well as the matrix. The degree of partitioning depends on the quantum dot thickness: for longer quantum dots, the mismatch should be accommodated evenly; for smaller h, the quantum dot will be strained to match the matrix. The variational approach we use here is assessed by comparison to finite element results, and we note that in the limiting case of large quantum dots, the decay constants obtained are consistent with the value that we previously obtained for the single nanowire heterostructure. Finally, we employ a Matthews-Blakeslee approach to studying the coherency limits in the quantum dot nanowires: we allow the mismatch to be accommodated partially by misfit dislocations. The total energy of the coherent system is compared to that of a dislocated system, the critical point being that at which the dislocated system becomes energetically favorable. These results indicate that quantum dot structures can coherently accommodate large mismatch strains, relative to thin-film epitaxy as well as to single heterojunction nanowires that we considered previously. Therefore, appropriate nanowire geometries enable systems of relatively large lattice mismatch to be accommodated coherently, thus opening the door to novel materials integration. Hence, nanowire quantum dot structures may be useful for realizing new devices that have traditionally been inaccessible due to defected interfaces.

11:45 AM I18.10
Spatial Current Distribution Around a Single Impurity in Nanowire. Rui Jun Wang¹, Hui He² and Wei Yang¹; ¹College of Physics Science and Technology, University of Petroleum (East China), Dongying, ShanDong, China; ²College of Machinery and Electronic Engineering, University of Petroleum (East China), Dongying, ShanDong, China.

The electron current distribution around a single impurity in a planar quantum wires is studied in this paper. Two-dimensional nanowire is a kind of important structure about real devices. By using the theory of scattering the model is defined. In electron waveguide, electrons are confined by hard-wall potential to the wire of constant width and an impurity is inserted into the wire. The influence of the impurity is as a delta potential, so the Hamiltonian is defined, and the wave function around the impurity and the transmission through the impurity is obtained exactly. This allows us to calculate the spatial current density within the quantum wire. In this paper the first and the second subband in transverse are propagating modes and the evanescent state is considered to the transport. The current distribution shows that it is quite different for the attractive (donorlike) and the repulsive (acceptorlike) impurity potential. By plotting the spatial distribution of current density we find that attractive scatters have a dramatic result. When the strength of delta function potential is 3 fev.cm2 (note: above of the fev.cm2 represent fev times square of cm), the influence is small, there are not any vortices, and when it is changed to 5 or 7 there have more clear vortices around the impurity. While the impurity is in the middle of wire, four vortices is occurred with symmetric around the impurity atom, and only one vortex if impurity in other position. When reduce the width of the planar strip the vortices are from four to two. The pictures of current density show also that the first subband and the second subband have important difference. There are many vortices for the first subband only and for the second subband only not only the impurity in the middle of the strip but also in any other position of the strip. To repulsive potential it has little influence with the different width and arbitrary position in free strength of delta function potential. It is clear that the vortices are caused by quantum-mechanical inference between elastic scattering states and it is accentuated by evanescent states, which have a stronger effect in the case of attractive scatters owing to the formation of quasidonor states. We find that it that the vortices are resulted in localized magnetic moments, and it is a very interesting thing.

SESSION I19:
 Chair: C. White
 Thursday Afternoon, December 2, 2004
 Room 204 (Hynes)

1:30 PM *I19.1
Thermal conductivity of nanowhiskers and nanowires: insights from theory. Natalio Mingo, NASA-Ames Center for Nanotechnology, Moffett Field, California.

Recently, it has been possible to measure the thermal conductivity of single nanowires [1]. From a theoretical point of view, phonon transport through 30-100 nm thick crystalline wires (nanowhiskers), and through very thin (sub-10 nm) nanowires, poses some attractive problems. It is known that the lattice thermal conductivity of sub-100 nm thick whiskers is considerably reduced with respect to that of the same material in bulk form, due to phonon boundary scattering [1,2]. However, it is far from obvious how much thermal conductivity reduction one can expect for each particular material. By means of

computer calculations and theoretical analysis, I will show that in zincblende binary compounds the amount of reduction when going from bulk to nanowhisker is directly related to the mass ratio of the constituent atoms [3]. This fact has interesting consequences. For example, even though the room temperature lattice thermal conductivity of bulk InP is higher than that of GaAs, a 30 nm wide GaAs whisker is expected to have almost 50% higher thermal conductivity than an InP nanowhisker of the same thickness. Some technological implications follow, for example, for nanocomposite thermal conductivity, nano-device heat dissipation, and for nanowire based thermoelectric refrigeration. In particular, it will be shown why III-V semiconductor nanowhiskers are expected to be better suited for thermoelectric applications than II-VI nanowhiskers. In the case of phonon transport through very thin nanowires, I will address the transition from ballistic to diffusive regimes as a function of nanowire length, from a Green's function perspective. In addition, I will discuss the problem posed by long wavelength longitudinal acoustic phonons, and we will see how an exact solution of the phonon Boltzmann equation, beyond the relaxation time approximation, gives us important insights. [1] Li, D., Wu, Y., Kim, P., Shi, L., Yang, P., and Majumdar, A. (2003). Appl. Phys. Lett. 83, 2934; Shi, L., Qing Hao, Choongho Yu, Mingo, N., Xiangyang Kong, and Wang, Z. L. (2004). Appl. Phys. Lett., 84, 2638; [2] Mingo, N., (2003). Phys. Rev. B, 68, 113308; [3] Mingo, N. and Broido, D. Manuscript in preparation.

2:00 PM I19.2

Thermoelectric modeling of Si-Si1-xGex core-shell nanowires. Ming Yeung Tang¹, Mildred S Dresselhaus^{1,2}, Hohyun Lee³ and Gang Chen³; ¹Electrical Engineering, MIT, Cambridge, Massachusetts; ²Physics, MIT, Cambridge, Massachusetts; ³Mechanical Engineering, MIT, Cambridge, Massachusetts.

Thermoelectrics have always been attractive for power generation and cooling because of power reliability and environmentally friendly issues. However, this concept remains non-competitive due to the limitation in the efficiency of available thermoelectric materials and device designs. In the 1990s, Hicks and Dresselhaus predicted the possibility of a dramatic enhancement in thermoelectric performance based on the special behavior of low dimensional materials. This enhancement is mainly due to the increase in quantum confinement effects, the increase in carrier density of states at specified energies, and the increase in phonon interface scattering for low dimensional structures. Nanowires and core-shell nanowires are 1D systems that exemplify low dimensional materials. It is expected that a core-shell nanowire structure would have a higher thermoelectric performance than a nanowire structure due to an increase in number of interfaces. The interfaces introduced must be such that phonons are readily scattered but not the electrons. Theoretical studies have been carried out to better understand the transport properties of a single Si-Si1-xGex core-shell nanowire. The nanowire consists of Si as the core material with a shell layer of a Si1-xGex alloy. The diameter of the core-shell nanowire in the model ranges from 5nm to 50nm. A decrease in thermal conductivity is shown theoretically for this configuration due to the increase in interface phonon scattering. No significant reduction in either electrical conductivity or Seebeck coefficient is expected for the nanowire, and hence, ZT of this system is expected to increase. The effect of the core diameter, the shell thickness, the total core-shell diameter, and the shell alloy composition on ZT will be presented. Experimental realization of this model will also be discussed.

2:15 PM I19.3

Surface Phonon-Polariton Mediated Heat Conduction in Nano-Scale Thin Films. Dye-Zone Abraham Chen, Arvind Narayanaswamy and Gang Chen; Mechanical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts.

It is well-known that the thermal conductivities of nanostructures such as thin films and nanowires are significantly reduced below their corresponding bulk values due to surface and interface scattering of the heat carriers. As a result, using nanostructures to improve thermal conductivity is difficult. However, there are applications which require the use of nanostructures for other important functionalities, which would benefit from an improved ability to transport heat flux. Examples include the use of nanostructures for increased performance in microelectronic and photonic devices, the enhanced mechanical properties of nanocomposites, and the rheological behavior of thermal interface materials. Towards this end of increasing the thermal conductivity of nanostructures, we investigated the heat-carrying capability of surface phonon-polaritons. Our study based on kinetic theory shows that in nano-scale thin films, the in-plane heat flux carried by surface phonon-polaritons can exceed the heat flux carried by phonons. We also found that the equivalent thermal conductivity due to surface phonon-polaritons increases with decreasing film thickness, offsetting the reduction in thermal conductivity due to the increased scattering of the phonons.

2:30 PM I19.4

Modeling the phonon specific heat in low-dimensional nanostructures. Christopher Dames¹, Bed Poudel², Zhifeng Ren² and Gang Chen¹; ¹Mechanical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts; ²Physics, Boston College, Chestnut Hill, Massachusetts.

For effective device design it is important to understand how the basic thermal properties of low-dimensional nanostructures differ from those of bulk materials. To further this understanding we have recently measured the specific heat of crystalline TiO2 anatase nanotubes of 2.6 nm wall thickness, 10 nm outside diameter, and 500 nm length. The measurements show that the specific heat of the nanotubes is within 30% of bulk anatase at 90 K, but begins to exceed bulk significantly below 50 K, and diverges even more strongly below 3 K to exceed bulk by a factor of 25 at 1.5 K. These observations can be partly understood as a phonon size effect as more and more long-wavelength modes are cut off at lower temperatures, reducing the effective dimensionality. A simple model for the phonon dispersion relation in isotropic, elastic, continuum nanostructures predicts a transition from bulk to two-dimensional behavior when the characteristic thermal wavelength becomes comparable to the wall thickness. A further transition from two-dimensional to one-dimensional behavior is expected when the wavelength becomes comparable to the nanotube circumference. Well below the Debye temperature, the transition criteria is that the product of the length scale and the temperature should be roughly 50 - 100 nm*K, depending on the speed of sound. While this model can explain certain features of the measured specific heat, several shortcomings will be identified, and alternatives suggested.

3:15 PM *I19.5

Electron Image States and Control of Molecules in Suspended Arrays of Metallic Nanotubes. Petr Kral^{1,2}, Dvira Segal^{1,2}, Brian E. Granger³, H. R. Sadeghpour³, Moshe Shapiro^{1,2} and Ioannis Thanopoulos^{1,2}; ¹Chemical Physics, Weizmann Institute of Science, Rehovot, Israel; ²Chemistry and Physics, University of British Columbia, Vancouver; ³ITAMP, Harvard-Smithsonian Center for Astrophysics, Cambridge, Massachusetts.

Recently, electronic "Tubular Image States" (TIS) were predicted to form and experimentally observed above suspended metallic nanotubes [1]. For angular momenta $l > 6$, these Rydberg-like molecular states are highly detached from the material surfaces. We discuss the formation and control of TIS-bands in one and two-dimensional arrays of suspended nanowires, which could be used in building of electron waveguides, filters and storage places. We also show how one can control by external fields molecules adsorbed on surfaces of nanotubes, arranged in arrays or ropes. Catalytic properties of proteins, enzymes and other bio-molecules could be varied in vivo [2]. [1] B. E. Granger, P. Kral, H. R. Sadeghpour and M. Shapiro, Phys. Rev. Lett. 89, 135506 (2002); D. Segal, B. E. Granger, H. R. Sadeghpour, P. Kral and M. Shapiro, submitted; M. Zamkov, N. Woody, S. Bing, H.S. Chakraborty, Z. Chang, U. Thumm and P. Richard, submitted. [2] P. Kral, Chem. Phys. Lett. 382, 399. (2003); I. Thanopoulos and P. Kral, submitted.

3:45 PM I19.6

Quantitative Analysis of Electronic Properties of Carbon Nanotubes by Scanning Probe Microscopy: from Atomic to Mesoscopic Length Scales. Sergei V. Kalinin¹, V. Meunier², C.

Staii³, A. T. Johnson³, J. Shin^{1,4}, Arthur P. Baddorf¹ and R. J. Harrison²; ¹Condensed Matter Sciences Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee; ²Computer Sciences Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee; ³Department of Physics and Astronomy, The University of Pennsylvania, Philadelphia, Pennsylvania; ⁴Department of Physics and Astronomy, The University of Tennessee, Knoxville, Tennessee.

Scanning Probe Microscopy (SPM) techniques are the key to real space imaging of electronic transport properties, including the electrostatic potential distribution and local field effects, in low-dimensional systems. Despite the wealth of experimental data, the interpretation of SPM data to extract the local electronic properties of 1D systems such as carbon nanotubes requires quantitative analysis of the tip-nanotube interactions. We present here a new approach to quantitatively interpret SPM which treats the interaction between the probe and the system using a combination of first principles density functional calculations and continuum electrostatics modeling. In addition, an original approach for experimental measurement of the tip radius of curvature from the electrostatic SPM data is presented. Within this approach, we can quantitatively describe, for the first time, the capacitive tip-surface interactions and predict the magnitude of the tip gate effect in nanoscale systems, such as carbon nanotubes, oxide nanobelts and semiconductor nanowires, permitting quantitative determination of electronic properties of atomic defects in these systems. The various aspects of the model are applied to a number of

recently acquired and published images of nanotube circuits with varied back gate voltages, and the interpreting power of the approach is demonstrated. Research was sponsored by the U.S. Department of Energy, under contract DE-AC05-00OR22725 with UT-Battelle, LLC and by the National Science Foundation grant DMR-0072998. Research performed as a Eugene P. Wigner Fellow (SVK).

4:00 PM **II9.7**

Designs and Relative Stability of Multicomponent Nanowires.

Ming Hua, Traiana Dumitrica, Veronica Barone and Boris I.

Yakobson; Rice University, Houston, Texas.

Along with carbon nanotubes, nanowires-seamless solid rods with nanometer size widths and micrometer lengths-represent critical parts of molecular electronics. Computations of ground state energies permit stability analysis and design of thermodynamically favorable one-dimensional structures, e.g. of Si [1], through generalization of the Wulff construction. However, for multicomponent wires, the usually computed average cohesive energies carry no clear information about their relative stability at different stoichiometries. We present energies mapped as a function of molar composition for several important nanowires, with constituent elements of C, Si, Me (various metals). In one important example, we propose the thinnest (2,2) and (3,0)-using standard fullerene nanotube notation-metal endohedral nanotubes of silicon, compute their stability and possible transitions, as well as correspondence and comparison with thicker metal-silicide wires and with the bulk disilicide. Proposed approach allows quantitative stability comparison of Si-C, B-N, C-B-N tubes, and other emerging nanowires of current interest, by direct calculations of their formation energies at arbitrary conditions (i.e. chemical potentials). 1. Y.Zhao and B.I.Yakobson, *Phys.Rev.Lett.*, **91**, 035501 (2003).

4:15 PM **II9.8**

Exciton Confinement in Molecular J-aggregate Quantum

Wires. Pavlos G. Lagoudakis¹, Melanie M. de Souza¹, Florian

Schindler¹, Thomas A. Klar¹, John M. Lupton¹, Jochen Feldmann¹, Jakob Wenus² and David G. Lidzey²; ¹Physics and CeNS, Maximilians-Universitat Munchen, Munich, Germany; ²Physics and Astronomy, The University of Sheffield, Sheffield, United Kingdom.

Resonant Rayleigh scattering from self-assembled one-dimensional molecular J-aggregate wires reveals a distinct dependence of the exciton energy on the width of lateral confinement. Our observations provide strong experimental evidence of exciton quantisation in self-assembled molecular wires. We describe our results in terms of centre-of-mass motion quantization of the J-band excitons, which is in agreement with the observed energy dependence. While single semiconducting macromolecules, such as polymers or aggregates of molecular dyes, exhibit properties of natural quantum wires, little is known about quantum wire effects in crystalline macromolecular assemblies. Interestingly, macromolecular aggregates of cyanine dyes, under certain conditions, self-assemble to form ostensible one-dimensional structures. Scanning electron microscopy and X-ray diffraction measurements have revealed that these structures resemble electrical wires since they are formed from fibrillation of ordered macromolecular aggregates surrounded by a cladding of probably less ordered molecular assemblies. Here, we present experimental evidence of exciton confinement in self-assembled J-aggregate wires of cyanine dyes. We have developed a systematic way of producing thin gelatine films with embedded molecular cyanine J-aggregate elongated structures (wires) of variable lengths. We used scanning electron microscopy to characterise the structural configuration of the J-aggregate wires, and we observed that the width of these structures varies systematically along the wire. Resonant Rayleigh scattering from individual wires revealed a distinct dependence of the J-band exciton energy on the width of the lateral confinement. We interpret the observed energy dependence in terms of a lateral quantisation of the centre-of-mass motion of the exciton in the wire, since the influence of the lateral confinement on the wave function of the correlated relative motion of the electron and hole is negligible in wide wires. Delocalisation of the exciton wave function is attributed to strong inline dipole-dipole coupling, which is further supported by the experimentally observed alignment of the exciton dipole moments in the direction perpendicular to the wire. By considering reduced active wire widths compared to the physical widths measured with scanning electron microscopy, we find that this simple model is in good agreement with the experiment. The rescaling of the active wire width by a constant factor is ascribed to an inactive shell covering the molecular J-aggregates due to static disorder introduced from uncoupled monomers and interface interactions with the gelatine matrix.

4:15 PM **II9.9 TRANSFERRERD TO II9.8**