Microelectronics Journal 39 (2008) 208–221

Microelectronics Journal

www.elsevier.com/locate/mejo

Multiscale modeling with carbon nanotubes

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Received 24 February 2006; received in revised form 8 June 2006; accepted 13 June 2006
Available online 28 August 2006

Abstract

Technologically important nanomaterials come in all shapes and sizes. They can range from small molecules to complex composites and mixtures. Depending upon the spatial dimensions of the system and properties under investigation computer modeling of such materials can range from equilibrium and non-equilibrium quantum mechanics, to force-field-based molecular mechanics and kinetic Monte Carlo, mesoscale simulation of evolving morphology, and finite-element computation of physical properties. This brief review illustrates some of the above modeling techniques through a number of recent applications with carbon nanotubes: nano electromechanical sensors (NEMS), chemical sensors, metal–nanotube contacts, and polymer–nanotube composites.

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Keywords: DFT (density functional theory); Molecular modeling; NEGF (nonequilibrium Green's function); Mesoscale modeling; Nanotubes; Sensors; Nanocomposites; NEMS (nanoelectromechanical sensors)

1. Introduction

More than 15 years after its initial discovery, carbon nanotubes (CNTs) [1] continue to be one of the hottest research areas in all of science and engineering. The interest is driven by the possibility of several commercial applications [2–6], including: Field emission-based flat panel displays, transistors, quantum dots, hydrogen storage devices, structural reinforcement agents, chemical and electromechanical sensors, nanoscale manipulators, probes, and tweezers. At the same time, the highly regular atomic structure of CNTs and the large degree of structural purity makes it accessible to accurate computer modeling using a variety of theoretical techniques. In fact, ever since the discovery of CNTs it has provided a fertile ground for theoretical simulations and analysis. The prediction of the dependence of CNT's electronic structure on its chirality [7–9] came within a year of the initial experimental discovery [1]. Since then there have been a huge number of theoretical investigations [10–18] of growth mechanisms, structure and energetics of topological defects, mechanical and electrical response to various kinds physical perturbation, field-emission from tips of metallic CNTs, electronic effects of doping and gas adsorption, chemical reactivity, interaction with polymers, capillary effects, CNT–metal contacts, H- and Li-storage, thermal conductivity, encapsulation of organic and inorganic material, optical properties, as well as intrinsic quantum effects like quantized conductance, Coulomb Blockade, Aharonov–Bohm effect, Kondo effect, and so on. Computational approaches used in the above work include solving diffusion equations, QM simulations (density functional theory, tight-binding, and semi-empirical methods), classical molecular dynamics, kinetic Monte Carlo, Genetic algorithms, and Green's-function-based electronic transport theory. This paper illustrates several of the above theoretical techniques through a few recent modeling studies of CNTs. In the following, we provide a brief overview of the theoretical techniques, which is followed by separate sections detailing each application example.

2. Theoretical techniques: a brief overview

2.1. Density functional theory (DFT)

In principle, all chemical information of any nanostructure can be obtained if one could solve the Schrödinger

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0026-2692/$ - see front matter © 2006 Elsevier Ltd. All rights reserved.
doi:10.1016/j.mejo.2006.06.003

wave equation for all relevant electrons of the system. Ideally, all one should require as an input are the positions and element identity of all atoms describing the nanostructure. Such computational methods are called ab initio or first-principles methods [19]. The Schrödinger equation of an interacting system of electrons cannot be solved analytically, and involves a number of physically motivated approximations and clever numerical tricks. The most well accepted formalisms can be broadly classified into two types: those based on the Hartree–Fock method [20], and those based on the DFT [21]. Due to better scaling with the number of electrons, DFT is quickly becoming the first-principles technique of choice in technologically important problems. DFT is based on a theorem due to Hohenberg and Kohn [22], which states that all ground state properties are functions of the total electronic charge density $\rho(\boldsymbol{r})$. The total energy of an electron gas can be written as a sum of the kinetic, potential (electrostatic), exchange and correlation energies. A practical implementation of this formalism into computer programs was made possible by the local density approximation (LDA) of Kohn and Sham [23], which recast the many-electron problem into a problem of single electrons moving in an average field of the other electrons and ions. The basic formalism has stood the test of time, although important subsequent developments on gradient corrections to the LDA and the exchange-correlation functional have increased the accuracy of DFT significantly. There are several different DFT codes available commercially, differing primarily in the choice of the basis functions in which the electronic wave functions are expanded, and the scheme of integration. For the work reported here, we used the DFT code DMol^3 [24]. In the present work all electrons in the system were considered explicitly, and the electronic wave functions were expanded in a double-numeric polarized (DNP) basis set. The calculations employed a “medium” integration grid, and a gradient-corrected exchange-correlation functional due to Perdew, et al. [25].

2.2. Classical molecular mechanics

Some of the applications discussed here, especially electromechanical sensing and polymer–CNT composites involve long nanotube structures with several hundred to a few thousand atoms. First-principles DFT calculations on systems of such size is prohibitively expensive. An explicit treatment of electrons is also unnecessary in situations where no making or breaking of chemical bonds occur in the process of interest. In such cases one uses classical molecular mechanics (MM) employing interatomic interactions or force fields, which are parameterized analytical functions of the atomic positions only [26]. For the polymer–CNT composite system, we used a class II force field COMPASS [27], developed primarily for condensed organic systems. For NEMS applications, on the other hand, a metallic AFM tip was modeled by a needle made up of Li atoms (Li was chosen to ensure a metallic system with the fewest number of electrons, thus reducing the computational load). Interactions in such a system were described by the universal force field (UFF) [28], which is rules-based and has a broader coverage of the periodic table. In order to explore possible re-arrangement of chemical bonds in a localized region one often cuts a small model out of the original structure, and relaxes it with a quantum mechanical (QM) method of choice. Such a hybrid QM/MM method using DMol^3/UFF was employed in the NEMS application, as discussed below in Section 4.1.

2.3. Electronic transport modeling—non-equilibrium Green’s function

Electromechanical and chemical sensors typically operate by changing electrical conductance of the active device when subjected to a mechanical perturbation or upon the absorption of a chemical species. Mesoscopic electron transport through molecular wires is best described by an energy-dependent transmission function $T(E)$, which strongly depends on the (discrete) electronic levels of the molecular wire (in our case, a nanotube), the levels in the (usually metallic) leads or electrodes, and broadening of the electronic levels in the wire due to chemical coupling to the electrodes [29–33]. Such physics is most conveniently described under the formalism of non-equilibrium Green’s function (NEGF). The starting point is the Green’s function of an *isolated* system at an energy E, which is defined by

$$(E\,S_{ij} - H_{ij})G^{\mathrm{R},jk} = \delta_i^k, \tag{2.1}$$

where δ_i^{k} is the Kronecker delta, and $S_{ij} = \langle i|j\rangle and H_{ij} = \langle i|H|j\rangle$ are the overlap and Hamiltonian matrix elements between electronic states i and j, respectively. However, we are interested in systems in which a nanoscale region is coupled with two semi-infinite electrodes at the two ends (the so-called *two-probe* system). In such a system, the coupling to the electrodes (mathematically expressed in terms of the so-called *self-energy* matrices Σ) modifies Eq. (2.1) to the form:

$$(E\,S_{ij} - H_{ij} - \sum\nolimits_{\mathrm{L},ij} - \sum\nolimits_{\mathrm{R},ij})G^{\mathrm{R},jk} = \delta_i^k, \tag{2.2}$$

where $\Sigma_{\mathrm{L,R}}$ are the retarded self-energies of the left and the right semi-infinite contacts. The transmission at each energy is then found [29–33] from :

$$T(E) = G^{\mathrm{R},ij}\Gamma_{\mathrm{L},jk}G^{\mathrm{A},kl}\Gamma_{\mathrm{R},li}, \tag{2.3}$$

where $\Gamma_{\mathrm{L,R}} = i(\Sigma^{\mathrm{R}}_{\mathrm{L,R}} - \Sigma^{\mathrm{A}}_{\mathrm{L,R}})$ are the couplings to the left and right leads and the superscripts R and A represent retarded and advanced quantities, respectively. Finally, the total conductance of the tube is computed using Landauer–Büttiker formula [29–33]:

$$G = \frac{2e^2}{h}\int_{-\infty}^{\infty} T(E)\left(-\frac{\partial f_o}{\partial E}\right)\mathrm{d}E, \tag{2.4}$$

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