Published in final edited form as:

J Comput Electron. 2005 April ; 4(1-2): 161–165. doi:10.1007/s10825-005-7130-9.

Screening of Water Dipoles Inside Finite-Length Armchair Carbon Nanotubes

Yan Li,

*Beckman Institute, University of Illinois at Urbana-Champaign, Urbana, IL 61801, USA,
yanli@uiuc.edu*

Deyu Lu,

Beckman Institute, University of Illinois at Urbana-Champaign, Urbana, IL 61801, USA

Klaus Schulten,

Beckman Institute, University of Illinois at Urbana-Champaign, Urbana, IL 61801, USA

Umberto Ravaioli, and

Beckman Institute, University of Illinois at Urbana-Champaign, Urbana, IL 61801, USA

Slava V. Rotkin

Department of Physics, Lehigh University, Bethlehem, PA 18015, USA

Abstract

The electronic structure and dielectric screening of finite-length armchair carbon nanotubes are studied with both tight-binding and *ab initio* methods. Good agreement is found in the band gap oscillation patterns and dielectric constants, which validates the tight-binding method as a reliable and fast approach to describe the screening effect of carbon nanotubes. For an illustration, our method is applied to a system consisting of a short (6,6) nanotube filled with six water molecules. Substantial screening of the water dipoles through the nanotube is observed. This polarization effect should have an important influence on the permeation of water and other biomolecules inside carbon nanotubes.

Keywords

carbon nanotubes; finite-length; dielectric screening; molecular transport; polarizable channel

1. Introduction

One-dimensional nanostructures based on single-walled carbon nanotubes (SWNTs) may lead to exciting applications in material science and biology. For example, such structures are good candidates for nano-scale channels transporting water, protons, ions or polymers. Filling of the hydrophobic interior of narrow SWNTs by water molecules has been recently demonstrated both theoretically [1] and experimentally [2]. However, the SWNTs studied in molecular dynamics (MD) simulations are usually modeled as non-polar channels interacting with the ambient environment through a short-ranged van der Waals potential, while little attention is paid to the polarizable nature of the SWNTs. Unlike many biological channels, SWNTs are highly polarizable due to their delocalized π -electrons, which respond effectively to external electric fields [3].

Recent density functional theory (DFT) calculations carried out on a short SWNT water channel demonstrate substantial screening of water dipoles [4]. However, the finite-size effect on the dielectric response is not well characterized and the high computational cost makes DFT inapplicable to larger systems, for instance, including thousands of atoms. A fast and reliable

algorithm to capture the polarization effect of SWNTs for realistic biological applications is thus in high demand. In this paper, we demonstrate that a self-consistent third-nearest-neighbor tight-binding (third-NN TB) method reproduces the principal electronic features and dielectric behavior of finite-length SWNTs in reasonable agreement with advanced *ab initio* methods, but at a much lower computational cost. Our method is then applied to a short (6,6) SWNT water channel. For six water molecules inside the SWNT, we evaluate the dipole screening from the SWNT and the resulting Coulomb interaction energy. We propose that the polarization effect of SWNTs is an important factor in determining the filling and permeation properties of the nanotube channel that needs to be accounted for in MD simulations.

2. Model and Methods

The system under study consists of finite-length (6,6) armchair SWNT segments with both ends saturated by hydrogen atoms. The C-C and C-H bond lengths are fixed at $d_{CC} = 1.440$ Å and $d_{CH} = 1.090$ Å. The electronic properties of the SWNTs are calculated by using both an *ab initio* (B3LYP level of theory [5] with 6-31G* basis sets in the Gaussian 03 package [6]) and a semi-empirical (self-consistent third-NN TB) method. The third-NN TB model employs parameters derived in [7] with $\gamma_0 = -2.97$ eV, $\gamma_1 = -0.073$ eV, $\gamma_2 = -0.33$ eV, which are the first-, second- and third-NN hopping integrals respectively. We find that inclusion of non-zero overlapping integrals increases the overall asymmetry of the electron band and hole band, while exerting little influence on the low energy properties. A difference of about 5% is found for both the band gap and the dielectric constant. For the sake of simplicity, we neglect the overlapping integrals in the following TB calculation. The Hamiltonian, which includes the Coulomb interaction from a non-uniform charge distribution, is solved iteratively to ensure the self-consistency of total charge and potential.

For these two methods, we compare the computed HOMO (highest occupied molecular orbital)/LUMO (lowest unoccupied molecular orbital) gap and the dielectric response as a function of tube length. The dielectric behavior is studied by turning on a uniform electric field along the nanotube axis and extracting resulting changes of the Mulliken atomic charges [8], from which the electrostatic potential profile and dielectric constant are calculated. Our preliminary *ab initio* calculation shows that the screening ability of the optimized structure is slightly decreased [9], while the main conclusions in this paper remain valid.

3. Results and Discussion

Band Gap Oscillation

Infinitely long armchair SWNTs are metallic, but a finite HOMO/LUMO gap opens when their length is shortened. The band gaps computed with TB and B3LYP methods are plotted in Fig. 1 as a function of the tube length, i.e., the number of carbon sections with spacing equal to $\sqrt{3}d_{CC}/2$. As one can see, the two curves exhibit similar oscillation patterns, but the TB band gap is systematically lower than the B3LYP band gap by ~ 1 eV at short length. This is primarily due to the fact that TB parameters used here were derived by fitting the band structure of graphite to DFT results [7], while the latter is generally known for systematically underestimating the band gap. On the other hand, the B3LYP method, a hybrid DFT variant, is expected to give an improved evaluation of the band gap by using a mixture of Hartree-Fock exchange with DFT exchange-correlation functional. Neglecting the curvature effect in our TB model also causes a slight difference in the occurrence of band gap minima. However, as we shall see below, the dielectric behavior, one of the most essential properties for carbon nanotubes in technical uses, agrees quantitatively well for both methods.

Dielectric Response

The dielectric properties of SWNTs can be characterized by defining the dielectric constant $\varepsilon = V_{ext}/V_{tot}$, where V_{ext} and V_{tot} are the external and total electrostatic potential on the SWNT surface. The parallel dielectric constant for infinitely long armchair nanotubes diverges, i.e., $\varepsilon_{\parallel} \rightarrow \infty$, and decreases rapidly when the length is reduced to a few nm [3]. Shown in Fig. 2 is the total electrostatic potential on a short (6,6) SWNT segment in response to an external electric field of $E = 0.0257 \text{ V/\AA}$ applied along the tube axis. The potential profiles calculated from both the third-NN TB method and B3LYP method agree generally, except at the edges (indicated by “C1” and “C12”), where a steeper change in the potential is observed in the TB results. This is due to the sharp termination in the all- π electron approximation used in the model. The dielectric constants extracted from the middle region of the potential profiles are $\varepsilon_{\parallel}^{TB} \approx 5.23$ and $\varepsilon_{\parallel}^{B3LYP} \approx 5.09$, respectively.

The parallel dielectric constant of short SWNTs of 4–12 sections is evaluated and plotted in Fig. 3. Both computational methods show similar oscillations with respect to number of sections in reasonable agreement with each other. The inset of Fig. 3 demonstrates the linear increase of $\varepsilon_{\parallel}$ with tube length computed from the third-NN TB model.

Dipole Screening

For applications of carbon nanotubes as artificial channels in biological environments, it is important to know how the polarizable wall of a nanotube responds to molecules near or inside it, especially charged or polar molecules. Fig. 4 depicts the dielectric response of a short (6,6) SWNT of 12 sections to an external dipole $\mu_0 \sim 2.35$ Debye, consisting of two equal charges of opposite sign ($|Q| = +0.834 \text{ e}$) separated by a distance $d = 0.586 \text{ \AA}$ along the tube axis. The values of Q and d are defined to mimic the water dipole of the TIP3P water model ($2Q_H = -Q_O = +0.834 \text{ e}$, $d_{OH} = 0.957 \text{ \AA}$, $\theta_{HOH} = 104.52^\circ$). μ_0 is effectively screened by the induced charges ρ^{ind} on the SWNT when positioned near the tube center ($z = 0$), with the ratio $\mu^{tot}/\mu_0 \sim 10\%$, where $\mu^{tot} = \mu_0 + \sum_i \rho_i^{ind} z_i$. The screening becomes weaker as μ_0 moves towards the tube edge ($z/L = 0.5$) and μ^{ind} flips its sign when μ_0 moves outside the tube and results in an effective attraction to the external dipole. This feature may affect the entering probability of dipole molecules like water into the SWNT channel. The magnitude of the electrostatic Coulomb interaction energy between μ_0 and the induced charges on the SWNT is also plotted in Fig. 4, showing an increase from zero to its maximum magnitude $\Delta U \sim 21 \text{ meV}$ as μ_0 moves toward the tube center. The gain in energy resulting from the SWNT polarization should affect the ordering of dipoles inside nanotubes.

To illustrate the polarization effect in a “real” transport problem, we take a snapshot from a classical MD simulation of a SWNT water channel (see Fig. 5) and use our TB model to evaluate the polarization effect of the nanotube [3]. The simulated (6,6) nanotube is $13.4 \text{ \AA}$ long with 12 sections and $8.2 \text{ \AA}$ in diameter. The six water molecules form a single file subject to the confinement of the tube interior, and their dipole moments are preferably aligned along the tube axis. During the 1 ns simulation, the total dipole moment of the confined water molecules is 13.48 ± 1.28 Debye, with an axial component of -11.54 ± 1.31 Debye. For the given snapshot, the total water dipole moment is 12.23 Debye. The electrostatic field of the water dipoles polarizes the nanotube and induces a charge distribution on the nanotube surface as shown in Fig. 5. The resulting effective counter-dipole leads to a much smaller net dipole of only 5.24 Debye (see Table 1). A similar screening effect has been observed earlier in an *ab initio* calculation [4].

The Coulomb energy gained from the interaction between the confined water and the image charges on the SWNT is evaluated to be $\sim 6 \text{ k}_B\text{T}$. It is known that filling of the hydrophobic

nanotube interior is highly sensitive to the interaction strength between water molecules and the nanotube [1]. With the polarization effect of the SWNT taken into consideration, the above filled state becomes energetically more favorable.

It has been proposed that the transport of water and/or ions can be enhanced by functionalizing the SWNT or applying an electric field along the SWNT [10,11]. In these situations, the dielectric response from the image charges on the SWNT may modify the local or global electric fields and needs to be included in the whole electrostatic system. Another factor that could influence the molecular transport arises from the charge transfer occurring between the s orbitals of the terminating hydrogen atoms and the σ orbitals of edge carbon atoms. We estimate the partial charge on each H atom to be $\delta q \sim +0.14$ e at B3LYP level of theory from both Mulliken and electrostatic potential (ESP) population analysis, while the negative partial charges on C atoms decay towards the tube center. This charge redistribution contributes significantly to the electric field near the tube edges [9] and the local dipole moments imposed by these partial charges may influence the entering and ordering of charged or polar molecules. Work is in progress to study the molecular transport in short polarizable SWNTs by combining MD simulations [12] with our computational scheme.

4. Conclusion

We have studied the length dependence of the electronic properties and dielectric behavior of finite-length armchair SWNTs within a self-consistent TB description, which agrees well with *ab initio* results. The polarization effect for short SWNTs is further illustrated by computing the induced charges and dipole moments of a (6,6) SWNT segment in the presence of external dipoles. Substantial screening is found and the Coulomb interaction energy between the external dipoles and the image charges on the SWNT turns out to be significant. We believe our self-consistent TB description provides a fast and reliable method to compute the SWNT polarization which may be essential for designing SWNT channels.

Acknowledgements

This work was supported by NSF grants CCR 02-10843, CCR 01-21616, MCB 02-34938, EEC-0228390, by NIH grant P41-RR05969, by the ARMY DURINT contract SIT 527826-08 and by DoE grant DE-FG02-01ER45932, computer time provided by the National Resource Allocations Committee (MCA93S028).

References

Elements of this work have been summarized in an extended abstract published by IEEE.

1. Hummer G, Rasaiah JC, Noworyta JP. Nature 2001;414:188. [PubMed: 11700553]
2. Kolesnikov AI, Zanotti JM, Loong CK, Thiyagarajan P, Moravsky AP, Loutfy RO, Burnham CJ. Phys Rev Lett 2004;93:035503. [PubMed: 15323833]
3. Lu D, Li Y, Rotkin SV, Ravaioli U, Schulten K. Nano Lett. to be published
4. Mann DJ, Halls MD. Phys Rev Lett 2003;90:195503. [PubMed: 12785955]
5. Becke AD. J Chem Phys 1993;98:5648.
6. Frisch, MJ., et al. Gaussian 03. Gaussian Inc.; Wallingford, CT: 2004.
7. Reich S, Maultzsch J, Thomsen C, Ordejón P. Phys Rev B 2002;66:035412.
8. Although Mulliken charges are not fit to and in many circumstances do not match the electrostatic potential, we find in our case the *change* in Mulliken charges to reproduce the *change* in electrostatic potential fairly well.
9. Lu D, Li Y, Rotkin SV, Ravaioli U, Schulten K. unpublished
10. Joseph S, Mashl RJ, Jakobsson E, Aluru NR. Nano Letters 2003;3:1399.
11. Vaitheeswaran S, Rasaiah JC, Hummer G. J Chem Phys 2004;121:7955. [PubMed: 15485258]

12. Zhu F, Schulten K. Biophys J 2003;85:236. [PubMed: 12829479]

Figure 1. Band gap variation of a (6,6) nanotube as a function of tube length computed by two different methods.

Figure 2.
The total electrostatic potential on a (6,6) SWNT segment with 12 sections (C1-C12) in a uniform axial field.

Figure 3. Dielectric constant of a (6,6) nanotube as a function of tube length from two different computation methods.

Figure 4.

The effective screening ratio μ_{tot}/μ_0 (in squares) and the gain in Coulomb interaction energy ΔU (in circles) vs. the distance of the external dipole to the tube center. The distance is scaled by the tube length L and the dashed line ($z/L = 0.5$) indicates the right end of the SWNT.

Figure 5. The summed induced charges (squares) of each section of the nanotube for a system configuration shown in the background (see text for details)[3]. Water molecules outside the nanotube are not shown for clarity.

Table 1

Dipole moments (in units of Debye) of a water-filled (6,6) CNT segment by the third-NN TB calculation.

H ₂ O wire length	μ_x	μ_y	μ_z	$ \mu $
6 (no CNT)	2.13	-0.54	-12.03	12.23
6 (with CNT)	0.43	-0.12	-5.22	5.24