NANO LETTERS

2003
Vol. 3, No. 8
1001−1005

Oscillatory Behavior of Double-Walled Nanotubes under Extension: A Simple Nanoscale Damped Spring

José L. Rivera,[†,‡] Clare McCabe,[§] and Peter T. Cummings*[,∥,⊥]

Department of Chemical Engineering, University of Tennessee, Knoxville, Tennessee 37996-1508, Department of Chemical Engineering, Colorado School of Mines, Golden, Colorado 80401, Department of Chemical Engineering, Vanderbilt University, Nashville, Tennessee 37235-1604, and Chemical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831-6110

Received March 19, 2003; Revised Manuscript Received April 28, 2003

ABSTRACT

Computer simulations of double-walled carbon nanotubes show that if the inner nanotube is pulled out part of the way and then released, then the inner tube exhibits damped oscillatory behavior at gigahertz frequencies. A simple mathematical model, formulated in terms of macroscopic ideas of friction, is shown to predict the observed behavior to a high degree of accuracy.

Introduction. Carbon nanotubes, which can be thought of as sheets of graphite rolled up into cylinders, occupy a unique place in nanoscience and nanotechnology. They are relatively easily synthesized,[1] have an extraordinary range of properties (e.g., they can be metallic or semiconducting, depending on the structure of the nanotube as characterized by the chiral vector (n, m)[2,3]), are the strongest material known to man,[4] and are fundamental building blocks in many nanosystems. Because of their ready synthesis and characterization, they have become the test bed of theoretical and computational approaches to nanoscience and technology. In particular, numerous ab initio electronic structure calculations and atomistic molecular dynamics simulations have been performed on carbon nanotubes and their variants (e.g., decorated nanotubes). In the work reported below, we employ the Dreiding model[5] for single-walled carbon nanotubes (SWCNTs) that includes a model for the carbon−carbon van der Waals interaction as well as bond stretching, bond-angle stretching, torsional, and coupled bond and bond-angle stretching potentials. The Dreiding potential model was refined for carbon materials by Guo et al.,[6] who fitted the potential parameters to experimental lattice parameters, elastic constants, and phonon frequencies of graphite. This model has been employed to study the structure, energy, and mechanical and vibrational properties of single-walled carbon nanotubes[7] and doped nanotubes,[8] to predict packing structures and cohesive energies of C_{60} and C_{70} fullerenes,[6] and to simulate the performance of graphitic radial nanobearing systems.[9]

Most synthetic routes to carbon nanotubes result in multiwalled carbon nanotubes with diameters ranging from ∼1.4 to 100 nm,[10] but double-walled carbon nanotubes (DWCNTs) can now be produced in small amounts through a heating process of nanotubelike structures,[11] and non-carbon nanotubes can be produced en masse using a plasma-arc method.[12] Ruoff and workers performed experiments on DWCNTs in which they attached a DWCNT to a substrate and then pulled on the inner nanotube via an atomic force microscope (AFM) tip, thus measuring the resistance to the sliding motion of one tube inside the other.[13,14] They measured a steady-state resistance of 0.08−0.3 MPa,[13] which is consistent with values measured in our simulations of the same experiment (reported below). There is considerable interest in the sliding behavior of carbon nanotubes, partially because of the relationship to the sliding of flat surfaces in which a number of studies suggest that sliding resistance is greater for commensurate surfaces (or sliding in a commensurate direction) than for incommensurate surfaces (or sliding in an incommensurate direction)[15,16] and that friction between two molecularly smooth surfaces is due to impurities adsorbed on the surfaces, which would otherwise be superlubricating.[17,18] Specifically, in the case of nanotubes, on the basis of corrugation calculations, Kolmogorov and Crespi[19] reported shear strengths on the order of few megapascal for

* Corresponding author. E-mail: peter.cummings@vanderbilt.edu.
† University of Tennessee.
‡ Current address: Universidad Michoacana de San Nicolas de Hidalgo, Facultad de Ingenieria Quimica, Morelia 58060, Michoacan, Mexico.
§ Colorado School of Mines.
∥ Vanderbilt University.
⊥ Oak Ridge National Laboratory.

10.1021/nl034171o CCC: $25.00
Published on Web 05/23/2003

commensurate systems, and for incommensurate systems, the shear strength is very low but ill-defined. The results led Kolmogorov and Crespi to conclude that sliding MWCNs constitute the smoothest unary solid−solid interfaces known, with the energetic barrier to interlayer sliding in defect-free nanotubes being independent of nanotube length and comparable to that for a single unit cell of crystalline graphite. Their calculation was inspired by the experimental measurements by Cumings and Zettl[12] on DWCNTs, which demonstrated ultralow friction between sliding carbon nanotube surfaces and led to the suggestion that DWCNT could be used as 0.1−1 GHz oscillators; this has very interesting possible electromechanical device applications. Additionally, they measured a shear strength of less than 0.66 MPa and a sliding shear resistance of less than 0.43 MPa. Zheng and Jiang[20] developed a theoretical model of the DWCNT systems studied by Cumings and Zettl and predicted an oscillation frequency of 0.15 GHz. Similar results to those of Kolmogorov and Crespi were reported by Damnjanovic et al.[21]

Here we provide a brief report on molecular dynamics "experiments" on DWCNTs of varying lengths and diameters in which we pull the inner nanotube out of the outer nanotube to several different distances and allow the nanotube to retract and subsequently oscillate. We find that the oscillation is damped (hence acting like a nano-shock-absorber) and can be predicted by a very simple mechanical model that takes into account the sliding friction between the surfaces. We find that the oscillation is around 1 GHz, consistent with prior experimental and theoretical calculations. A more detailed account of our results will be published in the future (Rivera, J. L; McCabe, C.; Cummings, P. T. To be submitted for publication).

Methods. Our implementation of the Guo et al. potential model[6] was tested through the study of vibrational[22] and elastic[23] properties of SWCNTs. This potential model reproduces the values reported by Yao and Lordi[22,23] for vibrational frequencies and elastic constants using the universal force field (UFF).[24] The simulations were carried out at constant temperature using a reversible multiple time step algorithm that has been tested previously on nanoscale systems;[25] the slow time step used was 2.21 fs. The system sizes varied from 2600 to 21 000 carbon atoms. The code was parallelized using force decomposition; production runs were performed on the IBM SPs at the Center for Computational Sciences at Oak Ridge National Laboratory and at the National Energy Research Supercomputing Center at Lawrence Berkeley Laboratory.

Results. The main focus of this study is DWCNs in which the inner nanotube has a chiral conformation (7, 0) and the outer nanotube has a chiral conformation (9, 9); we denote such a DWCN as (7, 0)/(9, 9). We simulated several axial lengths (12.21, 24.56, 36.92, 49.27, and 98.24 nm) at 298.15 K. For these systems, the inner and outer shells had the same axial length. To investigate the impact of differences on the lengths of the inner and outer nanotubes, another set of simulations were performed keeping the inner length at 12.21 nm and using axial lengths for the outer nanotube with −30 to +40% increments with respect to the inner nanotube axial length. The effect of temperature was studied for the system with an axial length of 12.21 nm in the range of temperature from 275 to 450 K. The effect of larger intershell separation was studied using the system with a chiral conformation (7, 0)/(10, 10) and lengths from 24.56 to 49.27 nm at 298.15 K. Commensurate systems were studied using the chiral conformation (5, 5)/(10, 10) with axial lengths from 12.21 to 49.27 at 298.15 K.

Except for the simulations of (5, 5)/(10, 10) DWCNs, the DWCNs were chosen to be incommensurate systems[26] that should exhibit very low and ill-defined shear strengths.[19] From the initial configuration (fully retracted), the nanotubes were pulled apart to a separation with an overlapped area involving at least 6 Å in the axial direction. This procedure is similar to the experiment of Cummings and Zetl.[12] After this initial displacement, the nanotubes were allowed to move freely, so the separation of the nanotubes' centers of mass executed damped oscillation motion in the axial direction, and we simulated this process until the amplitude of the oscillation was less than 1 Å; for the largest system, around 4.5 ns of simulation was needed.

Shear Resistance. As part of the testing and evaluation of our codes, we performed a series of simulations of incommensurate DWCNTs [(7, 0)/(9, 9)] with periodic boundary conditions in the axial direction (corresponding to an infinitely long carbon nanotube) to measure the resistance to motion as a function of sliding velocity. For these simulations, a constant translation velocity was imposed on the nanotubes by adding it to their thermal velocity. After 100 ps of equilibration, frictional forces were calculated over a period of 500 ps. This simulation is similar to the Ruoff et al. experiments[13,14] and is comparable to the theoretical calculation of Kolmogorov and Crespi.[19] We find that the shear resistance is dependent on the sliding velocity, varying from less than 0.03 MPa at a sliding velocity of 100 m/s to 0.12 MPa for a sliding velocity of 1000 m/s and exhibiting a plateau at 0.06 MPa for sliding velocities in the range of 250−750 m/s. These values for the shear resistance are similar in order of magnitude to that measured by Ruoff and co-workers[13,14] and are suitably low, in accordance with the prediction of Kolmogorov and Crespi.[19]

Oscillatory Motion of Incommensurate DWCNTs. Results for equal-length (7, 0)/(9, 9) DWCNTs of varying lengths L are shown in Figure 1. By fitting the simulation results, the initial frequency of oscillation, f_0, is found to be inversely proportional to length, $f_0 \cong A/L$, with $A = 198$ GHz nm. This functional dependence is consistent with the theoretical prediction of Zheng and Jiang,[20] which for the special case of equal-length inner and outer nanotubes yields

$$f = \frac{1}{4}\sqrt{\frac{c_1 \Pi}{\Delta}}\frac{1}{L} \tag{1}$$

Δ is the initial extrusion as a faction of L, c_1 is a variable that depends on the number of shells and their intershell separation, and Π is an average value for the van der Waals interactions that depends only on the number of shells in

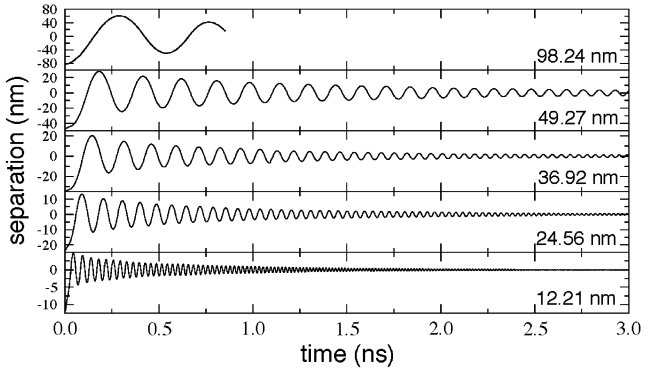

Figure 1. Separation of the centers of mass of (7, 0)/(9, 9) DWCNTs as a function of time at 298.15 K. The initial separation corresponds to pulling out the inner nanotube until it overlaps the outer nanotube by 0.3 nm.

the core. The Zheng and Jiang analysis assumes a constant frequency of oscillation, and we see from Figure 1 that the frequency of oscillation increases with time, consistent with a viscous dissipation of the oscillatory motion. Notice also from our empirical fit that the initial frequency of oscillation is in the gigahertz range.

We have analyzed the forces normal and tangential to the oscillatory motion for several of the DWCNT simulations. A typical result is shown in Figure 2. The relative constant magnitude of these two forces suggests that we can derive a simple model for the oscillatory motion of the DWCNTs. If z is the distance between the centers of mass of the two nanotubes in a DWCNT, then Newton's equation gives

$$\frac{d^2z}{dt^2} = \frac{F}{m} \tag{2}$$

We identify the axial force as the restoring force generated by van der Waals forces, F_{vdw}, and we additionally propose that the normal force can give rise to a relatively constant friction force, F_{fr}. Hence, during the course of one cycle, starting at the minimum separation, we can identify four regions labeled I−IV in Figure 2a. In the four regions, our differential equation then becomes

$$\begin{aligned}
&\text{I:} && \frac{d^2z}{dt^2} = \frac{1}{m}(F_{vdw} - F_{fr}) && \text{IC: } \frac{dz}{dt} = 0 && z < 0 \\
&\text{II:} && \frac{d^2z}{dt^2} = \frac{1}{m}(-F_{vdw} - F_{fr}) && \text{IC: } \frac{dz}{dt} > 0 && z = 0 \\
&\text{III:} && \frac{d^2z}{dt^2} = \frac{1}{m}(-F_{vdw} + F_{fr}) && \text{IC: } \frac{dz}{dt} = 0 && z > 0 \\
&\text{IV:} && \frac{d^2z}{dt^2} = \frac{1}{m}(F_{vdw} + F_{fr}) && \text{IC: } \frac{dz}{dt} < 0 && z = 0
\end{aligned} \tag{3}$$

where IC indicates the initial condition at the start of each region. To solve eq 3, we assume that F_{vdw} and F_{fr} are constants. The solution in each region is then a simple

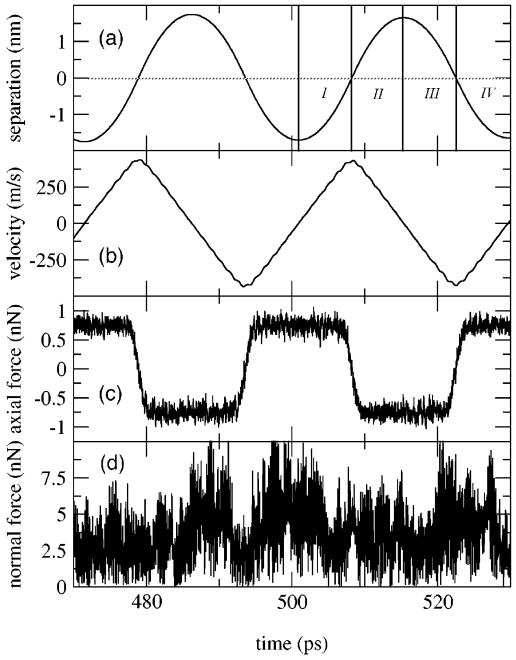

Figure 2. (a) Relative separation and (b) relative velocity of the centers of mass of 12.21-nm (7, 0)/(9, 9) DWCNTs as a function of time; (c) axial force and (d) normal force experienced by the inner nanotube as a function of time. All results are at 298.15 K.

quadratic function of time with constants determined by the initial conditions for each region. This is an extremely simple model that is equivalent to a spring with a restoring force and a constant friction. By solving this equation over successive cycles, we generate the displacement as a function of time. For example, for the (7, 0)/(9, 9) DWCNT of length 24.56 nm, we find by averaging F_{vdw} and F_{fr} over the period from 0.2 to 2.5 ns that $F_{vdw} = 1.05$ nN and $F_{fr} \cong 2.44 \times 10^{-2}$ nN. Notice that the frictional force is 2 orders of magnitude less than the van der Waals driving force and at this simplest level of approximation is assumed to be independent of the relative velocity of the nanotubes. Although in principle F_{fr} depends on the relative velocity of the nanotubes, given the small magnitude of F_{fr} we find that the assumption of a velocity-independent F_{fr} is sufficient for the purposes of this simple model. Using fixed values for F_{vdw} and F_{fr} for each DWCNT, we predict the oscillatory behavior to a remarkably high degree of accuracy, as shown in Figure 3. In each case, the model is fixed to reproduce just one point on the simulation curves—the height and position of the third peak. (The one exception is the 98.24-nm DWCNT for which we have only two peaks of simulated displacements; in this case, the single fitted point is the position and magnitude of the first minimum.) The model is then propagated forward and backward in time to give the model curves shown in Figure 3. This simple model has difficulty at very short times (i.e., the first cycle, where the distortion of the nanotubes makes F_{vdw} and F_{fr} strongly time-dependent). Likewise, at long times there is evidence of a frequency mismatch, which is consistent with the values of F_{vdw} and F_{fr} slowly changing over time. To model the oscillatory motion of the DWCNTs over the entire range of

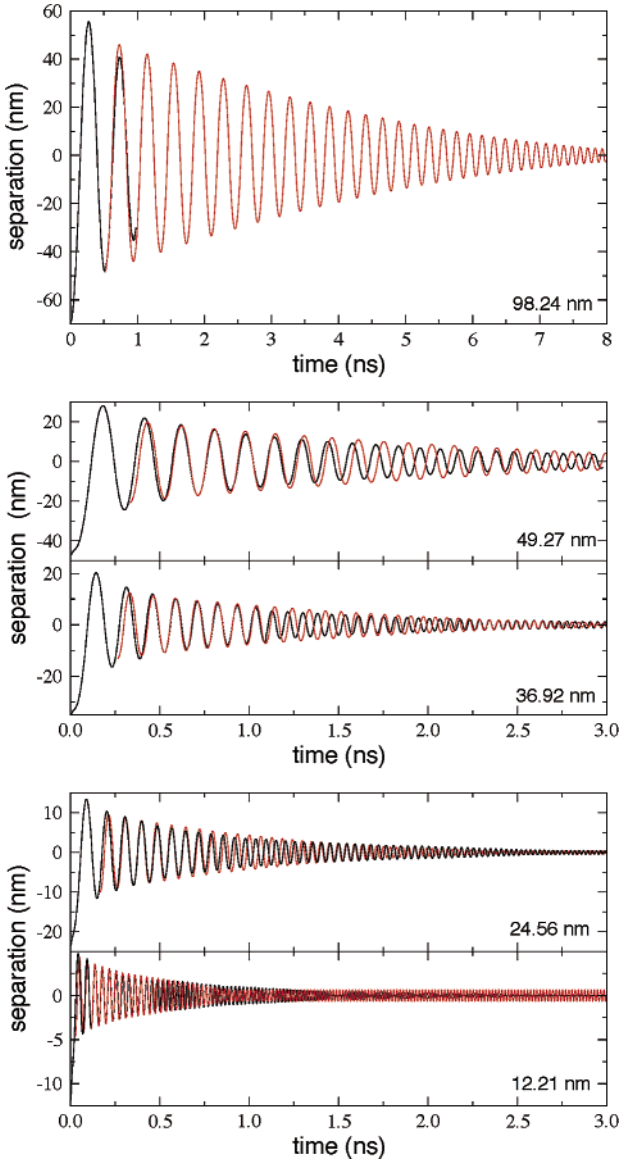

Figure 3. Relative separation for (7, 0)/(9, 9) equal-length DWCNTs as a function of time for various lengths at 298.15 K as shown in each panel. The simulation results are shown as black solid lines, and the results from the simple mechanical model of eq 3 are shown as red solid lines.

time, the assumption of constant F_{vdw} and F_{fr} must be abandoned, leading to a model that must be solved numerically. Results obtained with this more sophisticated model represent a minor improvement over those obtained with the simple model given here and will be reported in a more detailed publication (Rivera, J. L.; McCabe, C.; Cummings, P.T. To be submitted for publication). We have also investigated the dependence of these results on the relative length of the DWCNTs, and these data will also be reported in the more detailed publication.

We have also performed simulations on another incommensurate equal-length DWCNT system, (7, 0)/(10, 10). Qualitatively similar results, shown in Figure 4, are obtained and are equally well described by the simple model that we have introduced in this paper. As in the (7, 0)/(9, 9) case, the frictional force is several orders of magnitude smaller

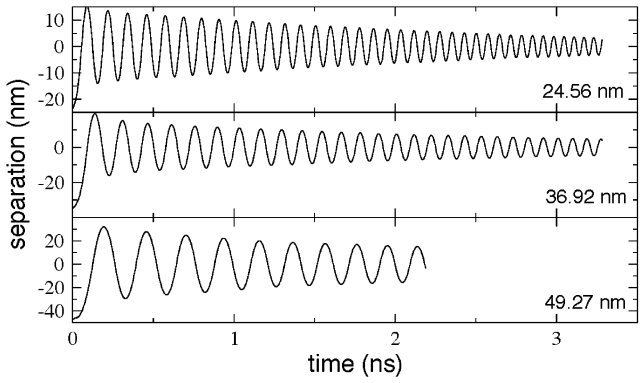

Figure 4. Separation of centers of mass of (7, 0)/(10, 10) DWCNTs as a function of time at 298.15 K. The initial separation corresponds to pulling out the inner nanotube until it overlaps the outer nanotube by 0.3 nm.

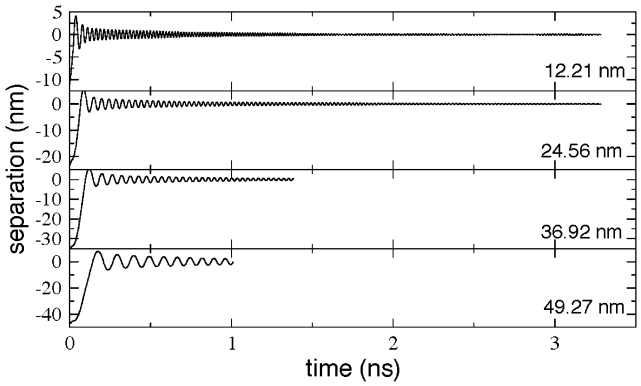

Figure 5. Separation of the centers of mass of (5, 5)/(10, 10) DWCNTs as a function of time at 298.15 K. The initial separation corresponds to pulling out the inner nanotube until it overlaps the outer nanotube by 0.3 nm.

than the van der Waals force, leading to long-lived and slowly decaying oscillations.

From our visualizations of the molecular dynamics simulations, we concluded that thermal fluctuations affecting the diameter of the inner and outer nanotubes are primarily responsible for the frictional forces in the DWCNTs. This would lead to the hypothesis that increasing temperature should lead to higher frictional forces and hence to a more rapid decay in the oscillatory behavior. To test this hypothesis, we performed simulations on the 12.21-nm (7, 0)/(9, 9) DWCNTs at temperatures ranging from 270 to 450 K. As a function of increasing temperature, we observed a monotonic decrease in the time taken for the amplitude of oscillation to decay to less than 0.4 nm, thus confirming our hypthesis.

Oscillatory Motion of Commensurate DWCNTs. According to the theoretical predictions described in the Introduction, we should expect to see rather different behavior in commensurate DWCNTs because in this case we expect a much larger frictional resistance to motion. In the same way as for the incommensurate DWCNTs, we performed simulations of oscillatory motion for equal-length (5, 5)/(10, 10) commensurate DWCNTs induced by pulling them apart until the nanotubes overlapped by only 0.3 nm. The results for various-length DWCNTs are shown in Figure 5. Clearly, the

motion is more rapidly damped, consistent with a much larger frictional resistance. Additional analysis of the commensurate nanotubes will be reported in a more detailed publication (Rivera, J. L.; McCabe, C.; Cummings, P. T. To be submitted for publication).

Conclusions. We have performed extensive molecular dynamics simulations of the oscillatory motion of DWCNTs resulting from pulling the inner nanotube out and releasing it. We investigated both incommensurate and commensurate DWCNTs of the same and different lengths at 298.15 K and in one case at temperatures ranging from 270 to 450 K. Our results are consistent with various prior theoretical predictions and confirm our hypothesis that the frictional forces result from thermal fluctuations in the conformation of the nanotubes. We also demonstrated that the motion of the DWCNTs can be modeled to a high degree of fidelity by a simple mechanical model that views the DWCNT system as equivalent to a block on a surface (experiencing constant frictional drag) attached to an unusual kind of spring—one that exerts a constant (rather than displacement-dependent) restoring force on the block. The fact that these DWCNTs can be described by such a simple model opens up the possibility that one can design DWCNTs to have specific mechanical properties with rather simple design tools.

Acknowledgment. This research was supported by the Division of Chemical Sciences, Geosciences, and Biosciences, Office of Basic Energy Sciences, U.S. Department of Energy. The research reported here was performed by J.R. in partial fulfillment of the doctoral degree in chemical engineering at the University of Tennessee. Calculations were performed at the Center for Computational Sciences at Oak Ridge National Laboratory, the National Energy Research Supercomputing Center at Lawrence Berkeley Laboratory, and on the SinRG cluster at the University of Tennessee, supported by NSF grant EIA-9972889.

Note Added after ASAP Posting. This article was released ASAP on 5/23/2003 with an incomplete version of Figure 3. The corrected article was posted on 7/10/2003.

References

(1) Iijima, S. *Nature* **1991**, *354*, 56−58.
(2) Baughman, R. H.; Zakhidov, A. A.; de Heer, W. A. *Science* **2002**, *297*, 787−792.
(3) Collins, P. C.; Arnold, M. S.; Avouris, P. *Science* **2001**, *292*, 706−709.
(4) Zhao, Q. Z.; Nardelli, M. B.; Bernholc, J. *Phys. Rev. B* **2002**, *65*, 144105.
(5) Mayo, S. L.; Olafson, B. D.; Goddard, W. A.*J. Phys. Chem.* **1990**, *94*, 8897−8909.
(6) Guo, Y.; Karasawa, N.; Goddard, W. A. *Nature* **1991**, *351*, 464−467.
(7) Gao, G.; Cagin, T.; Goddard, W. A. *Nanotechnology* **1998**, *9*, 184−191.
(8) Gao, G.; Cagin, T.; Goddard, W. A. *Phys. Rev. Lett.* **1998**, *80*, 5556−5559.
(9) Tuzun, R. E.; Noid, D. W.; Sumpter, B. G. *Nanotechnology* **1995**, *6*, 64−74.
(10) Ding, R. G.; Lu, G. Q.; Yan, Z. F.; Wilson, M. A. *J. Nanosci. Nanotechnol.* **2001**, *1*, 7−29.
(11) Bandow, S.; Takizawa, M.; Hirahara, K.; Yudasaka, M.; Iijima, S. *Chem. Phys. Lett.* **2001**, *337*, 48−54.
(12) Cumings, J.; Zettl, A. *Science* **2000**, *289*, 602−604.
(13) Yu, M.-F.; Lourie, O.; Dyer, M. J.; Moloni, K.; Kelly, T. F.; Ruoff, R. S. *Science* **2000**, *287*, 637−640.
(14) Yu, M.-F.; Yakobson, B. I.; Ruoff, R. S. *J. Phys. Chem. B* **2000**, *104*, 8764−8767.
(15) Tamura, H.; Tsujimichi, K.; Yamano, H.; Shiota, K.; Kubo, M.; Fahmi, A.; Miyamoto, A. *Appl. Surf. Sci.* **1997**, *119*, 335−340.
(16) Wenning, L.; Müser, M. H. *Europhys. Lett.* **2001**, *54*, 693−699.
(17) Donnet, C.; Martin, J. M.; Le Mogne, T.; Belin, M. *Tribol. Int.* **1996**, *29*, 123.
(18) He, G.; Müser, M. H.; Robbins, M. O. *Science* **1999**, *284*, 1650−1652.
(19) Kolmogorov, A. N.; Crespi, V. H. *Phys. Rev. Lett.* **2000**, *85*, 4727−4730.
(20) Zheng, Q.; Jiang, Q. *Phys. Rev. Lett.* **2002**, *88*, 045503.
(21) Damnjanovic, M.; Vukovic, T.; Milosevic, I. *Eur. Phys. J. B* **2002**, *25*, 131−134.
(22) Yao, N.; Lordi, V. *J. Appl. Phys.* **1998**, *84*, 1939−1943.
(23) Yao, N.; Lordi, V. *Phys. Rev. B* **1998**, *58*, 12649−12651.
(24) Rappe, A. K.; Casewit, C. J.; Colwell, K. S.; Goddard, W. A.; Skiff, W. M. *J. Am. Chem. Soc* **1992**, *114*, 10024−10035.
(25) Procacci, P.; Darden, T.; Marchi, M. *J. Phys. Chem.* **1996**, *100*, 10464−10468.
(26) Damnjanovic, M.; Milosevic, I.; Vukovic, T.; Sredanovic, R. *Phys. Rev. B* **1999**, *60*, 2728−2739.

NL034171O