Computational design of carbon nanotube electromechanical pressure sensors

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We investigate electronic transport properties of single-walled carbon nanotubes (SWNT’s) under hydrostatic pressure, using first-principles quantum transport calculations aided by molecular-dynamics simulation and continuum mechanics analysis. We demonstrate a pressure-induced metal-to-semiconductor transition in armchair SWNT’s, which provides a basis for designing nanoscale tunable pressure sensors.

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Recent advances in computational algorithms and supercomputers have brought us into a new era of computational modeling and simulation. Computation has emerged as an additional method for scientific research in parallel to experiment and theory, not only used for elucidating experiments but also as an effective method for designing new materials and devices prior to their existence. One example is the computational design of the super-hard material of boron nitride demonstrated by Cohen et al.1,2

So far, computational design has mostly focused on predicting new materials, using first-principles total-energy calculations. Here, we demonstrate an example of another repertoire of computational design to predict device structures, using first-principles quantum transport (QT) calculations.

The correlation between mechanical and electrical properties of carbon nanotubes has led to the exploration of nanotube-based electromechanical devices. For example, computations have shown that radial deformation can induce electrical transitions in single-walled carbon nanotubes (SWNT’s).3–6 However, in these earlier studies, the radial deformation is caused by artificially squashing the tube, a process that is difficult to quantify and control for designing devices. Here, we investigate the mechanical and electrical properties of SWNT’s under hydrostatic pressure, using first-principles QT calculations aided by molecular dynamic (MD) simulations and continuum mechanics analysis. We demonstrate that hydrostatic pressure can induce radial deformation and hence electrical transition of SWNT, through a physical process that can be readily quantified and controlled. It provides a unique and promising basis for creating nanoscale tunable pressure sensors.

The transport properties of armchair SWNT’s under different pressures, including the current-voltage (I-V) curves, are calculated using a newly developed formalism7 that combines the Keldysh nonequilibrium Green’s function (NEGF) (Refs. 8–10) with pseudopotential-based real-space density-functional theory (DFT).7,11 The main advantages of this NEGF-DFT approach are: (i) a proper treatment of the openboundary conditions for the device system as required for quantum transport under external bias potentials; (ii) an atomistic treatment of the electrodes; and (iii) a self-consistent calculation of the charge density via NEGF thereby incorporating the effects of both the scattering and bound states present in the system.

In order to carry out self-consistent DFT analysis of the nanotube systems under the nonequilibrium transport condition, we calculate the electron charge density matrix \( \hat{\rho} \) via the NEGF (Refs. 8,9) \( G^< \),

\[
\hat{\rho} = -\frac{i}{2\pi} \int dE G^<(E),
\]

where \( G^< \) is obtained by using the Keldysh equation, \( G^< = G^R \Sigma^< G^A \). Here \( G^R/A \) is the retarded/advanced Green’s function of the device that we calculate by direct matrix inversion; \( \Sigma^< \) is the self-energy representing injection of charge from the electrodes,8–10 which is obtained from self-energies \( \Sigma^L \) and \( \Sigma^R \) arising from coupling to the left and right nanotube electrodes, respectively, and the Fermi distribution functions of these electrodes. With the density matrix we carry out DFT interactions in the usual fashion until numerical convergence up to \( 10^{-3} \) eV. The bias potential enters the self-consistent real-space solution of the Hartree potential, its important effect is naturally included in the NEGF \( G^<(E) \). We use a s, p, d real-space atomic basis set7,11,12 in the DFT analysis, where atomic cores are treated by the standard nonlocal norm conserving pseudopotential scheme.13

After DFT self-consistency is reached, the I-V curve is obtained as8

\[
I = \frac{2e}{h} \int_{\mu_{\text{min}}}^{\mu_{\text{max}}} dE (f_l - f_r) T(E,V_b),
\]

where \( \mu_{\text{min}} \) (\( \mu_{\text{max}} \)) is the smaller (larger) of the chemical potentials of the left and right reservoirs; \( T(E,V_b) \) is the transmission coefficient at energy \( E \) and bias potential \( V_b \),8,10

\[
T(E,V_b) = 4 \text{Tr} [\text{Im}(\Sigma^R)G^R \text{Im}(\Sigma^A)G^A].
\]

It is emphasized that the functions inside the trace in Eq. (3) are all functions of bias potential \( V_b \), as the current is calculated from a self-consistent analysis.

MD simulations were first performed to obtain the equilibrium structures (shapes) of nanotubes under hydrostatic pressure, which are used as input atomic structures for QT calculations. The pressure induces a series of mechanical shape transitions, as shown in Fig. 1 for a (10,10) armchair
FIG. 1. MD simulated equilibrium shapes (cross sections) of a
(10,10) SWNT at pressures of (a) 0, (b) 1.55, (c) 1.75, and (d) 2.2 GPa.

SWNT. It first transforms the tube from a circle to an ellipse
at a critical transition pressure of \( P_1 \approx 1.55 \) GPa [Fig. 1(b)],
and then from an ellipse to a dumbbell at a pressure of \( P_2 \)
\( \approx 1.75 \) GPa [Fig. 1(c)].

Detailed analyses\(^\text{14,15}\) show that the first shape transition
from circle to ellipse is physically well defined, driven by a
competition between compression and bending of the tube
under pressure. Above a critical pressure (\( P_1 \)), it becomes
easier to bend (increasing the curvature) than to compress
(reducing the perimeter) the tube. This leads to a spontaneous
shape instability, transforming the tube from an isotropic
circular shape to an anisotropic elliptical shape. Microscopi-
cally, it reflects the fact that it costs less energy to change
bond angle than bond length, as evidenced from our MD
simulations.\(^\text{14,15}\) For this reason, the radial modulus
(hardness) of the tube decreases by two orders of magnitude upon
the first transition at a well-defined transition pressure.\(^\text{14}\)
Continuum mechanics calculations\(^\text{14}\) show that the transition
pressure \( P_1 \) scales with the tube radius inversely in a third-
power law, \( P_1 \approx \frac{3D}{R_0^3} \), where \( R_0 \) is the original tube radius
at zero pressure and \( D \) is flexural rigidity, a constant related to
the modulus and Poisson ratio of the tube. Thus, the larger
the tube, the sooner the transition. The dependence of \( P_1 \) on
\( R_0 \) is shown in Fig. 2.

The second shape transition from ellipse to dumbbell is
not physically well defined. It is actually caused by the
geometric constraints, while the physical properties (such as
hardness) of the tube are the same for the two different
shapes (ellipse vs dumbbell). As the tube continues to shrink
(reducing its cross-sectional area) under pressure, after the first
transition it tends to reduce the overall curvature of the tube
(maximizing bending) but maintain the length of its perimeter
(minimizing compression).\(^\text{15}\) (In contrast, before the first
transition, the tube shrinks under pressure by reducing its
radius, i.e., perimeter.) In doing so, it must eventually trans-
form into a dumbbell shape, giving rise to the second shape
transition. This is consistent with a mathematical theorem\(^\text{16}\)
that an enclosed boundary with fixed perimeter and con-
strained curvature will adopt a dumbbell (peanut) shape to
have the minimum area. The second transition pressure (\( P_2 \))
can be simply calculated as

\[
P_2 = P_1 - B_2 \ln \left( \frac{A_2}{A_1} \right),
\]

where \( A_2 \) and \( A_1 \) are the tube cross-sectional area at the
transition pressures of \( P_2 \) and \( P_1 \), respectively. \( B_2 \) is the
radial modulus of the tube after the first transition, which
approximately equals to \( 3D/R_0^3.\)^\text{17}\) Geometrically, \( A_2 \) corre-
sponds to the point where the curvature becomes zero at the
middle of the flattened area [normal to \( y \) direction, as shown
in Fig. 1(c)]. Geometric analysis using the variational theo-
rem shows that\(^\text{17}\) the ratio of \( A_2 \) over \( A_1 \) turns out to be a
universal constant, \( A_2/A_1 \approx 0.819 \), independent of tube ra-
dius. Thus, we have \( P_2 \approx 1.2P_1 \). This universal relation is
further confirmed by MD simulations,\(^\text{17}\) as shown in Fig. 2.

The pressure induced SWNT shape transition in turn in-
duces an electrical transition.\(^\text{3–6}\) Figure 3 shows QT calcu-
lations of the conductance versus energy at four different
pressures, for the (10,10) SWNT. The equilibrium conductance
is defined as \( G = G_0 T(E, V_b = 0) \). Here \( G_0 = 2e^2/h \) is the
conductance quantum. For the original armchair nanotubes at
\( P = 0 \) there are two bands crossing Fermi energy \( E_f \) (Refs.
18, 19) therefore \( G = 2G_0 \) at \( E = E_f = 0 \). Experimentally, by
making good electrical contact to SWNT, such a high con-
ductance has been recently obtained. Away from \( E = E_f \), \( G(E) \) shows the familiar quantized step-like structure; each time another electronic band of the SWNT is “cut” by the energy \( E, G \) increases by a unit of \( G_o \). This step-like structure correlates perfectly with the band structure of the tube.

As pressure increases, the tube first transforms into an elliptical shape, breaking the original circular symmetry. The breaking symmetry lifts the degeneracy of the electronic energy bands. Consequently, the conductance curve displays extra steps at \( 4G_o \), as shown in Figs. 3(b)–3(d). The energy width of the extra steps increases with increasing pressure [from Fig. 3(b) to Fig. 3(d)], as the splitting of the degeneracy-lifted bands increases, due to larger structural deformation. As pressure further increases to 2.2 GPa, a noticeable qualitative change in conductance curve occurs. The conductance around Fermi energy drops by two orders of magnitude to zero, as shown in Fig. 3. This indicates that the tube undergoes a metal-to-semiconductor transition, which opens a band gap of \( \sim 0.12 \) eV. Figure 4 shows the \( I-V \) curve calculated by using Eq. (2) for the dumbbell tube at 2.2 GPa. It displays typical semiconductor \( I-V \) characteristics, in qualitative contrast to the linear behavior of the original metallic tube.

The metal-to-semiconductor transition for the dumbbell tube at 2.2 GPa is caused by a combined effect of the interaction between the two flattened areas [normal to \( y \) direction, as shown in Fig. 1(d)] of the dumbbell tube and a spontaneous breaking of mirror symmetry about \( y \) axis, which makes the two equivalent sublattices in the SWNT physically distinguishable. The onset of transition can be estimated at the minimum distance between the two flattened areas, \( d \), is short enough so that atoms from the two flattened areas start to interact with each other (forming new bonds), as indicated in Fig. 1(d). The corresponding transition pressure \( (P_3) \) can be calculated, similar to \( P_2 \), as

\[
P_3 = P_1 - B_3 \ln(A_3/A_1),
\]

where \( A_3 \) is the tube cross-sectional area at \( P_3 \). By using the minimum distance \( d \) between the two flattened area of 2.6 Å, the cutoff length of C-C interaction, we can also numerically estimate the ratio of \( A_3 \) over \( A_1 \) for different tube size from MD simulations. It is found that it varies slightly from 0.6 to 0.3 for armchair tubes ranging from (6,6) to (50,50). The dependence of \( P_3 \) on \( R_0 \) is shown in Fig. 2.
In conclusion, using first-principles quantum transport calculations aided by MD simulations and continuum mechanics analysis, we demonstrate a reversible pressure induced shape transition for armchair SWNT’s, which in turn induces a reversible electrical transition from metal to semiconductor. Based on these findings, we propose a designing idea of nanoscale tunable electromechanical pressure sensors. Exploration of other forms of carbon nanotubes, such as those with different chiralities, multiwalled tubes, and bundle of tubes, will broaden the perspective of this potential application. Furthermore, the physical mechanism underlying the pressure induced shape transition is not limited either to carbon tubes or to nanoscale tubes. Therefore, the principles we demonstrate here can be extended to other kinds of nanotubes as well as to microtubes or macrotubes, with a broad range of potential applications.

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14 D.Y. Sun et al. (unpublished).
15 MD simulations show that after the first transition, the bond length remains constant while the bond angle decreases with increasing pressure for both elliptical and dumbbell tubes.