# PRESSURE-INDUCED INTERLINKING OF CARBON NANOTUBES

Carbon nanotubes, originally discovered as by products of fullerene synthesis, are now considered to be the building blocks of future nanoscale electronic and mechanical devices. It is therefore desirable to have a good understanding of their electronic and mechanical properties and the interrelations between them. In particular, single wall carbon nanotubes (SWNT) provide a system where the electronic properties can be controlled by the structure of the nanotubes and by various deformations of their geometries[1,2]. The physical properties can also be altered by intertube interactions between nanotubes packed in hexagonal lattices, as so called "nanoropes".
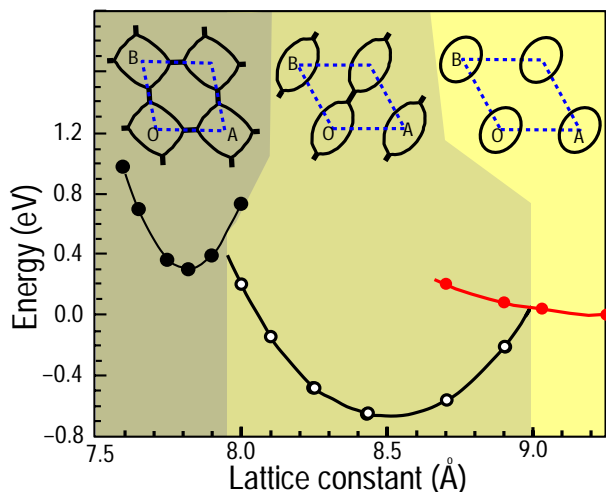
The intertube interactions in nanoropes can be probed by applying external pressure to vary the intertube distance. For fullerenes, such high pressure studies have yielded many interesting results including new compounds such as the pressure-induced polymeric phases of C_{60}. It is, therefore, of interest to inquire if similar covalent-bonding can occur between the nanotubes in a rope. This could have important consequences for nanoscale device applications and composite materials that require strong mechanical properties since nanoropes consisting of inter-linked SWNT will be significantly stronger than nanoropes composed of van der Waals packed nanotubes.
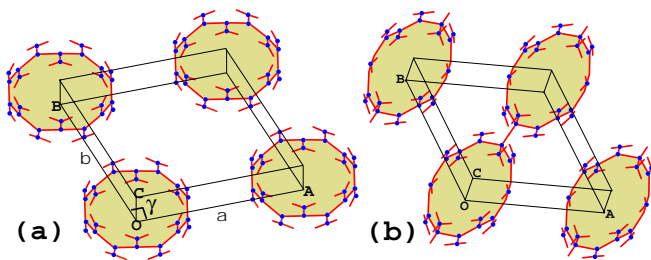
We investigated possible new pressure-induced ground state structures for (n,0) nanotube ropes from first-principles total energy calculations using the pseudopotential method within the generalized gradient approximation (GGA)[1]. For simplicity, we model the nanoropes as a hexagonal lattice of nanotubes with one nanotube per unit cell. The pressure dependence of the lattices of nanotubes was determined by calculating the total energy as a function of nanotube separation (i.e. a and b) while the other parameters, including atom positions, c, and γ are optimized. We observe that (7,0) nanotubes become elliptically distorted with applied pressure (i.e. decreasing nanotube-nanotube distance). At a critical pressure, we observe a structural phase transformation from the van der Waals nanotube lattice (as shown in Fig.1 a) to a new lattice in which the nanotubes are interlinked along the [110] direction, where the strain of the nanotube is largest (Fig.1(b)). The covalent bonding between nanotubes is therefore the result of curvature-induced re-hybridization of the carbon orbitals. The same structural transformation was observed for the other (n,0) nanoropes.

To quantitatively study the bonding mechanism, we calculated the total energies of the different phases as a function of the lattice constant (i.e. applied pressure). The result for (7,0) nanotubes is summarized in Fig.2. The energies of the vdW and the one dimensional interlinked phases cross each other at about a = 9.0 Å with an energy barrier of only 46 meV/unitcell (552 K). The pressure required to attain this lattice constant is only about 0.3 GPa for the vdW phase, indicating that polymerization of vdW (7,0) nanoropes could occur at modest pressures and temperatures. Once the interlinked phase is reached, the energy barrier required to break the bonds and obtain free nanotubes is about 0.7 eV (25 meV/atom), which is comparable to that of 1D polymerized C_{60} molecules (20 meV/atom).


FIGURE 1. Optimized structures of the vdW (7,0) (a), and one dimensional interlinked (7,0) (b) nanotube lattices. The interlinked structure shown in (b) has lower energy than vdW packed (7,0) nanotubes shown in (a).

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Figure 2. Planer lattice constant variation of the total energy of (7,0) nanotube ropes in three different phases. Inset shows the view of the structures along c-axis. The zero of energy was taken to be the energy of vdW packing of the nanotubes.

Fig.2 also shows that another interlinked phase of (7,0) nanotubes becomes the ground state for lattice parameter smaller than 8.0 Å. In this new phase the nanotubes are interlinked along both a- and b-axes (see Fig.3(a)). This two dimensional interlinked structure is about four times stiffer than the 1D interlinked phase and sixteen times stiffer than the vdW nanoropes.

We observe that applying even higher pressures yields more complicated and denser phases for many of the nanoropes studied here (see Fig.3). For (9,0) nanoropes, we find that the nanotubes are interlinked along three directions forming a hexagonal network. The length of the intertube bond, d_{C-C} = 1.644 Å, is significantly elongated for a sp^3 C-C bond. The two dimensional interlinked phase of (7,0) nanotubes is further transformed to a denser structure at 30 Gpa with a band gap of 2 eV (Fig.3(c)). By comparison, (6,6) nanotubes do not form an interlinked structure up to a pressure of 60 GPa. Rather the nanotubes are hexagonally distorted such that the local structure of the nanotube faces is similar to that in graphite sheets (Fig.3(d)). Furthermore, releasing the pressure yields the original structure, indicating that the distortion is purely

elastic. The structural changes clearly have strong effects on the electronic properties[2] and therefore should be detected in the pressure dependence of various transport properties of nanoropes.
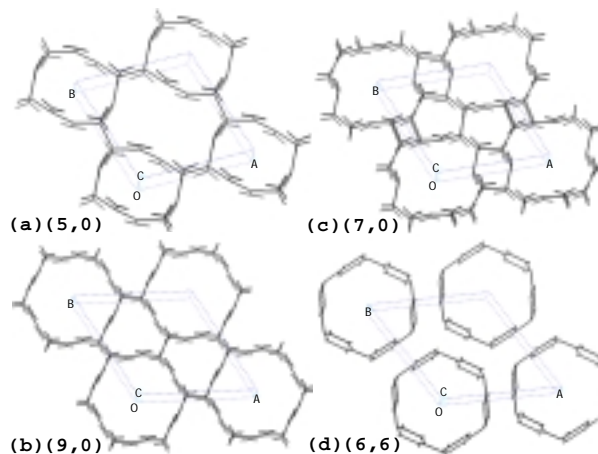
Figure 3. Various high density phases of carbon nanotubes.(a) Two dimensional interlinked structure of (5,0) nanotubes, consisting of rectangularly distorted nanotubes interlinked on a 2D network. (b) A hexagonal network of (9,0) nanotubes, (c) A very dense structure of (7,0) nanotubes obtained under 30 GPa pressure. (d) The optimized structure of (6,6) nanotubes under P=53 GPa.

The new pressure-induced, high density phases[1] reported here may provide a way of synthesizing novel carbon base materials with interesting physical properties. For example interlinking of the nanotubes may improve the mechanical performance of composites based on these materials. The change in the band gap of a SWNT with applied pressure can be exploited to realize various quantum devices on a single nanotube with variable and reversible electronic properties[2]. It will be an experimental challenge to confirm the structures predicted here. A difference INS spectrum of two identical samples; one treated with pressure and the other not, may give some evidence for the new phases.

[1] T. Yildirim, O. Gulseren, C. Kilic, and S. Ciraci, Phys. Rev. B 62, pg. xxx (15 November, 2000).
[2] C. Kilic, S. Ciraci, O. Gulseren, T. Yildirim, Phys. Rev. B Rapid Comm. (15 October, 2000).