Self-assembly and electronic structure of bundled single- and multi-wall nanotubes

David Tománek

*Department of Physics and Astronomy and Center for Fundamental Materials Research,
Michigan State University, East Lansing, Michigan 48824-1116, USA*

Abstract. Detailed growth mechanism of single-wall nanotube bundles and of multi-wall nanotubes of carbon is investigated using *ab initio* and parametrized calculations. Our results show that single-wall tubes grow only in presence of a catalyst, whereas multi-wall tubes, stabilized at the growing edge by a covalent "lip-lip" interaction, may form in a pure carbon atmosphere. The individual tubes in these systems are likely to exhibit a low-frequency twisting motion. The weak, partly anisotropic inter-wall interaction, present in single-wall nanotube bundles and in multi-wall nanotubes, may cause significant changes in the density of states near the Fermi level.

Introduction

Carbon nanotubes, consisting of graphite layers wrapped into seamless cylinders, have been produced in the carbon arc and by laser vaporizing graphite [1–6]. Both single-wall and multi-wall systems have been observed that are up to a fraction of a millimeter long, yet only nanometers in diameter. Absence of defects and chemical inertness suggests that these molecular conductors should be ideal candidates for use as nano-wires.

The present study has been motivated by several open questions. First, the formation of single-wall nanotubes from lightly doped graphite and of multi-wall nanotubes from pure graphite is unusual in view of the fact that spherical finite-size isomers, or graphite and diamond in the bulk, are the most stable modifications of carbon. Also, the spherical counterparts of nanotubes, fullerenes such as C_{60}, have been shown to spin within the C_{60} solid, whereas spinning or twisting of individual tubes within a bundle or a multi-wall tube has not been discussed so far. Our particular interest in tube rotations results from the fact that both the spinning/twisting motion and the electronic structure of these systems depends strongly on the anisotropy of the inter-tube interaction. We suggest the onset of "orientational melting" at T^* as one possible explanation of the unusual temperature dependence of resistivity in nanotube bundles, which show a transi-

tion from non-metallic to metallic behavior when changing the sign of $d\rho/dT$ at $T^*\approx 50 - 100$ K.

These questions are addressed using a combination of *ab initio* and parametrized techniques. To obtain the total energy of nanotubes in perfect lattices or of fragments near the tube end, we use the Density Functional Formalism with a plane wave basis for the solid [7] and a numerical basis for the fragments [8]. Band structure details are studied using a parametrized Linear Combination of Atomic Orbitals (LCAO) formalism, with parameters described in Ref. [9]. The inter-tube interaction is described in analogy to the inter-ball interaction in the doped C_{60} solid [10]. Up to $102,400$ k-points in the irreducible Brillouin zone are used to determine the electronic structure of ordered nanotube lattices, the "ropes" [7].

Formation Mechanism

It is generally agreed that the most stable carbon isomers should be chains and rings for up to $N\approx 20 - 30$ atoms, and closed single-wall fullerenes for tens to hundreds of atoms [9,11–13]. Only beyond several hundred atoms should one observe a transition to spherical multi-layer "onions" [14,15]. Hence, reaction kinetics during the condensation of carbon atoms from the vapor is expected to play a crucial role in the formation of nanotubes.

Formation of Single-Wall Nanotube Ropes

The nucleus of a growing nanotube is a short cylinder that is capped on one side and open on the other side [5,8]. The system consists of carbon atoms forming hexagonal rings, six of which have been substituted by pentagonal rings. Substitution of more hexagons by pentagons (up to twelve) would gradually close the tube to a fullerene capsule; a system with less than six pentagons in the structure would resemble a cone with an increasing exposed edge. With a given number of atoms, the half-closed tubule may be either long and thin, thus minimizing the "dangling-bond" energy at the open edge, or short and fat, thus minimizing the strain energy in the cylinder. The equilibrium will lie in-between; as a matter of fact, the equilibrium diameter increases very slowly, only with the cube root of the number of atoms N. The tube diameter will eventually be frozen at a critical size estimated to be few hundred atoms under synthesis conditions; then, the rate associated with global structural rearrangements will no longer be competitive with the growth rate. For systems containing few hundred carbon atoms, the equilibrium diameter lies close to 1.4 nm, that of a (10,10) "armchair" tube [5].

Nanotube closure will necessarily be initiated by substituting pentagonal rings for hexagons at the growing edge. It has been shown in Ref. [8] that pentagon formation can be prevented catalytically by transitions metals atoms, such as Ni or Co, adsorbed at the growing edge. These metal atoms have the ability to enter a forming pentagon, with essentially no activation barrier, to form a metallacycle

and thus to "masquerade" as carbon atoms. In the next step, the metal atom in the hexagonal ring is substituted by a carbon atom. This completes the formation of a hexagon at the defect-free edge of a nanotube.

Short tubes are likely to coalesce as they grow. The attractive inter-wall interaction will attempt to maximize the contact area between adjacent tubes, thus yielding a triangular lattice (a "rope") of nanotubes, observed in Ref. [5].

Formation of Multi-Wall Nanotubes

In absence of metal atoms at the growing edge, which would inhibit dome closure, a different mechanism has to be invoked to explain the growth of carbon nanotubes rather than their energetically favored spherical counterparts. In the first stage of the aggregation process, as in the case of single-wall nanotubes, we expect the formation of a graphitic hemisphere containing six pentagons. While this half-dome is being formed, a second "layer" may aggregate rapidly on this pre-formed graphitic template. This is expected especially if the carbon vapor is very dense, which is the case when focussed laser pulses are used [16].

It has been shown in Ref. [17] that the inter-wall gap at the edge of the double-dome is likely to be bridged by carbon atoms which establish a covalent "lip-lip" interaction, thus saturating eventual dangling bonds. Under this scenario, growth would occur by accretion of carbon at the stabilized edge. In presence of the strong "lip-lip" interactions, which maintain a constant inter-wall separation, eventual tube closure now would involve a concerted addition of pentagons in the inner and outer wall. This is unlikely to occur, and thus we expect the double-dome not to close, but rather to continue growing by adding hexagonal rings, as a double-wall tube. The efficiency of the "lip-lip" interaction mechanism to keep a double-wall nanotube from closing at high temperatures has been confirmed by *ab initio* Car-Parrinello calculations [18].

Electronic Structure of Single-Wall Nanotube "Ropes"

The interaction between adjacent nanotubes in a bundle or "rope" is, same as in the C_{60} solid, not completely isotropic about the tube axis. Individual (10,10) tubes are expected to librate about their axis with a relatively low frequency of $50 - 60$ cm^{-1}, close to the observed (but not identified) 41 cm^{-1} infrared-active mode [19]. Even though the activation barrier for free rotation is only $\lesssim 4$ meV *per atom*, individual tubes are not expected to rotate rigidly due to their high total mass. Since the rigidity of nanotubes is limited, finite segments are more likely to twist about the tube axis. The twisting motion is likely to be accompanied by displacement of orientational dislocations that have been frozen in during the assembly of the "ropes".

Inter-tube interactions in the ropes have been shown to modify the electronic structure of individual tubes by opening a pseudo-gap near the Fermi level [7,20,21].

With the onset of orientational melting, one would expect the pseudo-gap to smear out, thus significantly increasing the conductivity of the system.

Inter-tube coupling leads to an increase in the density of states by $\approx 7\%$ outside the pseudo-gap. An even larger increase in the density of states, namely by a factor of ≈ 12 with respect to the pristine system, is predicted for the potassium doped system with the composition KC_8, in agreement with the observed conductivity increase by a factor of $10 \sim 20$ [22].

Electronic Structure of Multi-Wall Nanotubes

Inter-wall interaction in a multi-wall nanotube may cause similar changes in the electronic structure near the Fermi level as the inter-tube interaction in "ropes" of nanotubes described above [23,24]. Our calculation for the (5,5)@(10,10) double-wall tube [25] suggests that due to inter-tube coupling, the density of states near E_F increases by $\approx 3\%$. The value of the rotational barrier *per atom* in this system is somewhat smaller than in nanotube "ropes", in agreement with results for the same system published in Ref. [26]. Off-axis displacements of $\lesssim 0.1$ Å in multi-wall tubes cost essentially no energy. For the particular (5,5)@(10,10) double-tube, we expect librational modes to occur at $\omega_{in} \approx 31$ cm^{-1} for the inner tube and $\omega_{out} \approx 11$ cm^{-1} for the outer tube, depending on which of these tubes is pinned. As in the case of nanotube "ropes", we expect segments of individual tubes to exhibit a twisting motion rather than the entire tubes to rotate rigidly. We also expect an orientational melting transition to occur in multi-wall nanotubes, close to or below the temperature expected in single-wall nanotube "ropes".

Summary and Conclusions

Ab initio and parametrized calculations have been used to show that under specific conditions, carbon atoms condense to form nanotubes. Whereas single-wall tubes form only in presence of an atomically dispersed transition metal catalyst, it is the covalent "lip-lip" interaction at the growing edge that prevents multi-wall tubes from closure even in absence of such a catalyst. The attractive inter-wall interaction stabilizes not only multi-wall nanotubes, but causes also single-wall tubes to pack into ordered "ropes". This interaction induces additional band broadening by ≈ 0.2 eV, and opens up a pseudo-gap at E_F in the "ropes". Due to their large inertia, individual nanotubes do not rotate as a whole. Finite tube segments are rather expected to exert a local twisting motion. Orientational dislocations, which were frozen in during the formation of the "ropes", lower the activation barrier for tube rotations and hence the orientational melting temperature of the "ropes".

REFERENCES

1. S. Iijima, Nature **354**, 56 (1991).
2. S. Iijima and T. Ichihashi, Nature **363**, 603 (1993).
3. D.S. Bethune, C.H. Kiang, M.S. de Vries, G. Gorman, R. Savoy, J. Vazquez, R. Beyers, Nature **363**, 605 (1993).
4. R.E. Smalley, Mat. Sci. Eng. B **19**, 1 (1993).
5. A. Thess, R. Lee, P. Nikolaev, H. Dai, P. Petit, J. Robert, C. Xu, Y. H. Lee, S. G. Kim, D. T. Colbert, G. Scuseria, D. Tománek, J. E. Fisher, and R. E. Smalley, Science **273**, 483 (1996).
6. M.S. Dresselhaus, G. Dresselhaus, and P.C. Eklund, *Science of Fullerenes and Carbon Nanotubes* (Academic Press, San Diego, 1996).
7. Young-Kyun Kwon, Susumu Saito, and David Tománek (submitted for publication).
8. Young Hee Lee, Seong Gon Kim, and David Tománek, Phys. Rev. Lett. **78**, 2393 (1997).
9. D. Tománek and Michael A. Schlüter, Phys. Rev. Lett. **67**, 2331 (1991).
10. M. Schlüter, M. Lannoo, M. Needels, G.A. Baraff, and D. Tománek, Phys. Rev. Lett. **68**, 526 (1992).
11. K.S. Pitzer and E. Clementi, J. Am. Chem. Soc. **81**, 4477 (1961).
12. G. von Helden, N. Gotts, and M.T. Bowers, Nature **363**, 60 (1993).
13. J.M. Hunter, J.L. Fye, E.J. Roskamp, M.F. Jarrold, J. Phys. Chem. **98**, 1810 (1994).
14. D. Ugarte, Nature **359**, 707 (1992); Europhys. Lett. **22**, 45 (1993).
15. D. Tománek, W. Zhong, and E. Krastev, Phys. Rev. B **48**, 15461 (1993).
16. Ting Guo, Pavel Nikolaev, Andrew G. Rinzler, David Tománek, Daniel T. Colbert, and Richard E. Smalley, J. Phys. Chem. **99**, 10694 (1995).
17. Young-Kyun Kwon, Young Hee Lee, Seong-Gon Kim, Philippe Jund, David Tománek, and Richard E. Smalley, Phys. Rev. Lett. **79**, 2065 (1997).
18. J.-C. Charlier, Alessandro De Vita, Xavier Blase, and Roberto Car, Science **275**, 646 (1997).
19. W. Holmes, J. Hone, R. Mallozzi, J. Orenstein, P.L. Richards, and A. Zettl (private communication).
20. J.-C. Charlier, X. Gonze, and J.-P. Michenaud, Europhys. Lett. **29**, 43 (1995).
21. P. Delaney, H.J. Choi, J. Ihm, S.G. Louie, and M.L. Cohen, Nature **391**, 466 (1998).
22. R.S. Lee, H.J. Kim, J.E. Fischer, A. Thess, and R.E. Smalley, Nature **388**, 255 (1997).
23. Ph. Lambin, L. Philippe, J.C. Charlier, and J.P. Michenaud, Comp. Mat. Sci. **2**, 350 (1994).
24. Ph. Lambin, J.C. Charlier, and J.P. Michenaud, in *"Electronic Properties of Novel Materials"*, edited by H. Kuzmany, J. Fink, M. Mehring and S. Roth (World Scientific, Singapore, 1994), p. 130.
25. Young-Kyun Kwon and David Tománek (unpublished).
26. J.C. Charlier and J.P. Michenaud, Phys. Rev. Lett. **70**, 1858 (1993).