

## Nanotube-substrate interactions: distinguishing carbon nanotubes by helical angle

Aleksey N. Kolmogorov and Vincent H. Crespi

*Department of Physics and Materials Research Institute, The Pennsylvania State University, 104 Davey Lab, University Park, PA, 16802-6300*

Monika H. Schleier-Smith and James C. Ellenbogen

*Nanosystems Group, The MITRE Corporation, McLean, VA 22102-7508*

(August 27, 2003)

We investigate the interaction of a carbon nanotube with a graphite substrate, using an interlayer potential that explicitly treats the registry dependence of the interaction. We also take into account that carbon-carbon bond-lengths in nanotubes differ slightly from those in flat graphite, so that the naively commensurate angular orientations for the tube with respect to the substrate lattice are destroyed. In these conditions, the interaction of a one-dimensional tube with a two-dimensional substrate leads to an unusual registry phenomenon not visible in standard layer-on-layer growth: the system develops favorable orientations which clearly are incommensurate.

62.20.Qp, 61.48.+c

Carbon nanotubes [1] are gaining prominence as potential components of future nanoelectronic and nanomechanical systems [2]. This is primarily because of their exceptional electronic [3] and mechanical [4] properties, both of which can be strong functions of the wrapping indices  $(n, m)$  that define the helicity of the nanotube. These indices define the tube's circumference in graphitic lattice coordinates; an  $(n, m)$  tube wraps at a helical angle of  $\theta_0 = \tan^{-1}(\sqrt{3}m/(2n+m))$  to the hexagonal rows of graphite [5]. Because of the great sensitivity of nanotube properties to structure, many envisioned applications will require a means to separate nanotubes on the basis of the ultimate distinction in structure, namely differences in  $(n, m)$ . Here we describe the physical basis of one potential means for doing so.

Post-synthesis separation into metal and semiconducting components already has been demonstrated [6,7] to complement the reasonably good control of the average diameter for as-grown tubes [8–11]. Such separations based on electronic response are attractive for electronics applications, since they target directly the relevant materials property. However, a wider range of applications might be opened up if tubes could be separated more precisely, e.g. by their helical pitch. This structural property, which reaches directly at the fundamental  $(n, m)$  distinction, is finer grained than the metal/semiconductor distinction.

Experimental observations of spontaneous nanotube alignment on graphite suggest that nanotubes have a registry-dependent interaction with an underlying graphitic lattice [12]. Preliminary calculations [13] show sharp peaks every 60 degrees in the tube/graphite binding as a function of angle  $\theta$  measured about an axis perpendicular to the substrate. Here we refine these important preliminary results and demonstrate that the energy selectivity is five to ten times stronger than previously suspected. In addition, we demonstrate that the

preferred tube-graphite orientations are not limited to commensurations. Surprisingly, many *incommensurate* orientations are also favorable, even in the realistic case of slightly different C-C bond lengths for the tube and substrate. These unexpected incommensurate lock-in angles arise from finite-size effects perpendicular to the tube axis, and are unique to one-dimensional objects interacting with two-dimensional substrates.

Nanotube alignment on a graphite substrate is sensitive to the variation of the tube-substrate binding energy under shifts in registry between graphene layers. Thus, a careful choice of the interaction potential is required. A standard Lennard-Jones potential is valuable for averaged treatments of the overall binding [14] and for qualitative indications of registration-dependent effects. However, this potential underestimates the corrugation in the interlayer interaction. An improved interlayer potential that treats explicitly the short-ranged (e.g. orbital overlap) corrugation effects has been proposed previously [15]. This potential was trained on data for sliding between two flat and parallel graphene layers. Recent first-principles calculations suggest that this preliminary potential tends to overestimate the corrugation of nanotube/nanotube and graphite/nanotube sliding by a factor of roughly two. We have since refined the potential and reduced this discrepancy; details of the new potential are provided in a separate publication [16].

For simplicity, we consider first a rigid nanotube resting on a flat graphitic surface. The tube center of mass has three degrees of translational freedom. The tube can also spin about its axis. We assume that the tube axis lies parallel to the plane of the substrate, which eliminates one rotational degree of freedom. The remaining angular degree of freedom, namely the angle about an axis perpendicular to the substrate, is the main variable of interest. We hold this angle fixed at a succession of values (every 0.1 degrees) while carefully optimizing the

other parameters for each of these initial positions. For a fully incommensurate system, shifts of the center of mass parallel to the plane of the substrate do not change the energy; otherwise a careful minimization is required. To minimize finite-size fluctuations, the tubes are very long (about 300 nm). In all cases we treat the substrate as a single rigid graphene layer. Note that subtle long-ranged effects (e.g., due to scattering by the tube of graphene electrons in low energy states) also might affect the orientation dependence of the tube-substrate binding energy. Such effects, which are not treated in the short-ranged potential used here, might be suppressed by using an alternative substrate—e.g., hexagonal B-N.

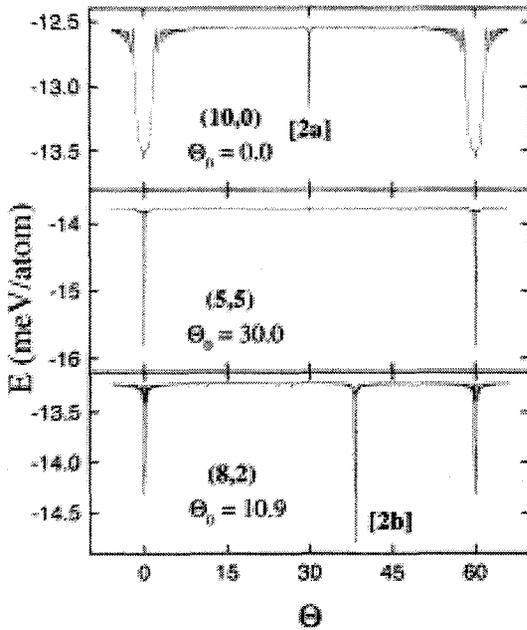


FIG. 1. The nanotube-graphene interaction energy, measured in meV per atom in the tube, as a function of angle about an axis perpendicular to the substrate. The zero angle is shifted to match the helical angle  $\theta_0$ . In this first calculation we assume matching bond lengths in the nanotube and graphene substrate. The distributions of interlayer registries for the minima marked “[2a]” and “[2b]” (at 30.0 and 38.2 degrees respectively) are shown in Fig. 2.

We begin with the case where all nanotube C-C bonds have the same length as in bulk graphite; this provides a helpful starting point for the later inclusion of more subtle effects. Fig. 1 shows the angular dependence of the tube-substrate interaction energy for three nanotubes with similar diameters but different helical angles. As expected, all tubes have a sharp minimum precisely at  $\theta_0$ , repeating every 60 degrees [13]. The gain in the binding

energy at the preferred orientation is substantial, about 8% of the total binding energy and tens of electron volts for tubes of a few hundred nanometers in length.

The curve between the principal minima is not entirely flat. Some of the features are known accidental commensurations for graphite [17]. For example, two graphitic layers become commensurate at 38.2 degrees ( $\cos^{-1}(11/14)$ ). However, the highly symmetric (10,0) and (5,5) tubes have additional minima at *incommensurate* angles, e.g. 30 degrees. These unexpected features can be explained by looking at the patterns in the distribution of local interlayer registries. If we take the coordinates of the atoms in the tube which lie above each unit cell of the substrate and translate these points back into a single substrate unit cell, we construct a convenient representation for the global distribution of local interlayer registries, as shown in Fig. 2. In commensurate systems, the points cluster into a small finite set whose energetics can be optimized through center of mass motion of the nanotube relative to the substrate or spinning about the tube axis. In normal incommensurate systems, the points smear out and cover the entire unit cell uniformly, yielding a smooth interaction. However, the finite transverse extent of the nanotube allows a third possibility, which is observed here: the points can spread uniformly, but *only over a discrete set of parallel lines* that slice through the substrate unit cell.

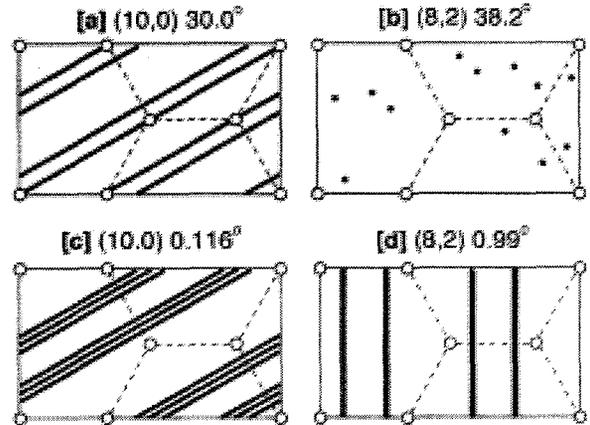


FIG. 2. Solid points and lines represent the distribution of nanotube atoms in the area of contact with the substrate, mapped back into a single substrate unit cell, which is depicted by open circles and dashed lines. (a) and (b) are for equal bond lengths in tube and substrate. In (c) and (d) the bonds on the tubes are extended by 0.35% along the axis and 0.45% perpendicular to it.

In this third case, even though the system is axially incommensurate, the energy can be lowered by spinning the tube about its axis and/or shifting the tube’s center of mass parallel to the substrate and perpendicular to the

tube axis. The effect is largest for the high-symmetry zigzag nanotubes with short axial unit cell, at angles  $\theta = 30.0, 41.4$  degrees ( $41.4 = \cos^{-1}(3/4)$ ). This case is not present in normal two-dimensional thin-film growth, since it is a nanoscale finite-size effect. The system is part-way between the commensurate and incommensurate states, so we term it a “pseudo-commensuration”. Note that this effect is purely geometric and does not depend on any special characteristics of the interlayer interaction. It would appear also in a Lennard-Jones treatment or for a hexagonal non-graphitic (or doped graphite) substrate.

The separation of the primary minima for the (10, 0) tube of Fig. 1 into a broad valley and a sharp downward central projection results from similar physics. The sharp minimum occurs as the set of projected registries condenses from lines into isolated points. The broader valley follows the extension of these lines across the unit cell and their subsequent smearing into a uniform and fully incommensurate coverage. The angular width  $\Delta\theta$  of the primary minima depends on the tube length as  $1/\sqrt{L}$ . For zig-zag tubes  $\Delta\theta \approx 1/\sqrt{N}$ , where  $N$  is the number of axial unit cells.

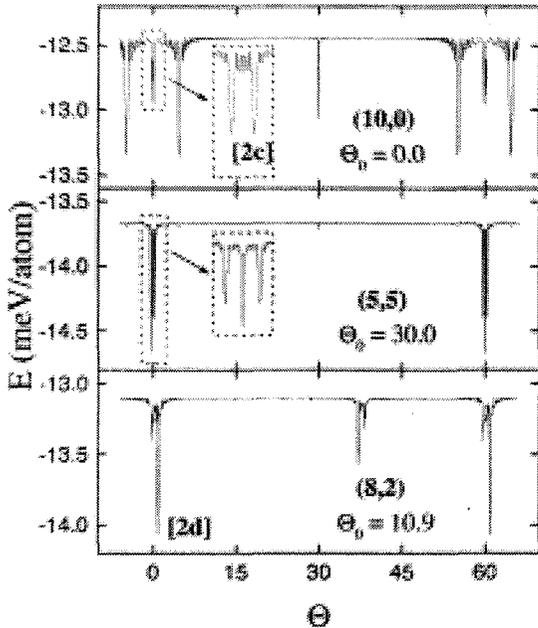


FIG. 3. Same as Fig. 1, but the C-C bonds in the nanotube are extended by 0.35% along the axis and 0.45% perpendicular to it, as described in the text. The samplings for c and d are shown in Figs. 2c,d.

Careful *ab initio* studies [18] show that the C-C bonds lengthen due to curvature effects when graphene is rolled

into a nanotube. For tubes of the diameter studied here, the mismatch is about 0.40%, meaning that even for the perfect angular alignment at  $\theta_0$ , registry is destroyed over about 40 nm (barring axial relaxation of the tube, to be discussed later). Do any substantial commensurate valleys survive this bond-length mismatch in long tubes? To answer this question, we treat next the case of mismatched bonds. Bonds parallel to the tube axis ( $a_{\parallel}$ ) are extended by 0.35%. Bonds perpendicular ( $a_{\perp}$ ) are extended by 0.45% [18]. The other bonds are extended according to a linear interpolation. Strikingly, rather strong valleys survive, as seen in Fig. 3. The primary peaks shrink by less than 20% (except for the armchair tube) compared to the ideal case of Fig. 1. Several new minima appear, none of which is a standard commensuration: for mismatched bonds, *essentially all preferred angles result from the new pseudo-commensurate sampling described above*. For example, in the (10, 0) tube minima are now at 0.0, 0.116, and 4.8 degrees. The second angle solves the equation  $\sqrt{3} = (a_{\parallel} \cos \theta - a_{\text{graphene}})/(a_{\parallel} \sin \theta)$ , which yields  $\theta = \sin^{-1}((a_{\parallel} - a_{\text{graphene}})/(\sqrt{3}a_{\parallel}))$  for small  $\theta$ 's. The 4.8 degree valley occurs when the projected parallel bond in the nanotube matches the substrate:  $\theta = \cos^{-1}(a_{\text{graphene}}/a_{\parallel})$ . For chiral tubes this happens when the angle  $\theta$  satisfies  $a_{\parallel} \cos(\theta + \theta_0) = a_{\text{graphene}} \cos(\theta_0)$ .

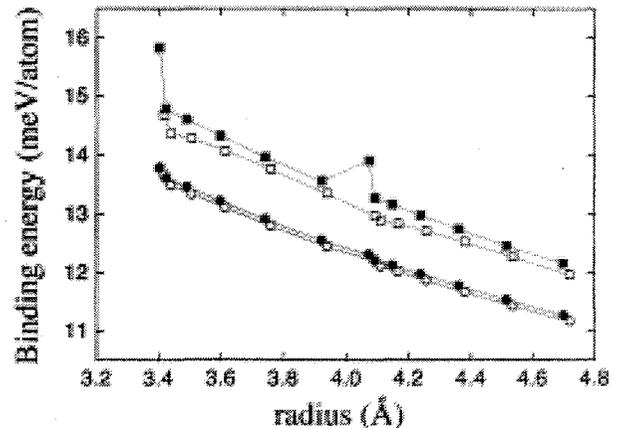


FIG. 4. Average (circles) and maximum (squares) binding energy as a function of nanotube radius for nanotubes of different wrapping indices (from left to right: (5, 5), (6, 4), (7, 3), (8, 2), (9, 1), (10, 0), (6, 6), (7, 5), (8, 4), (9, 3), (10, 2), (11, 1), (12, 0)). The solid points are for matching bond lengths ( $a_{\parallel} = a_{\text{graphene}}$ ). The hollow points are for extended bonds on the tube:  $a_{\parallel} = 1.0035 a_{\text{graphene}}$  and  $a_{\perp} = 1.0045 a_{\text{graphene}}$ .

Fig. 4 summarizes the typical (i.e. plateau) and maximal binding energies for several tubes. The substantial displacement between the maximal and typical binding curves, even in the realistic mismatched-bond-length case, suggests that an ensemble of tubes could be distinguished, or perhaps even separated, based on their

angle-dependent interactions with a substrate of hexagonal symmetry [19]. Any such separation would have to satisfy at least three requirements. First, the nanotube free energy within the ambient (e.g. a solution or suspension [20]) must be comparable to the average tube-substrate interaction to facilitate equilibration. Second, the tube sample must have a fairly narrow diameter distribution [8–11]. Third, a preferred orientation must be imposed on the nanotube population, for example by pre-aligning the tubes in an ambient fluid (e.g. through extensional fluid flow or external fields [21]) or patterning the substrate [22,23].

Although the C-C bond is extremely stiff, deformations due to the tube-substrate interaction are possible. Thus, we investigate the role of tube deformations using the Tersoff-Brenner potential [24] to permit relaxation of the tubes' internal coordinates. However, because these calculations are so computationally intensive, they are performed for only a subset of the systems described above. The attractive interaction between tube and substrate flattens the tube slightly to increase the contact area. However, even for a relatively large (10,10) tube, the tube-substrate binding energy increases by less than 10%, and the angular dependence of the binding energy shows no substantial changes. The tube also can relax along its axis, as in the Frenkel-Kontorowa model [25]. A sufficient axial compression could restore equal bond-lengths in tube and substrate. Compressing an isolated small-diameter nanotube from equilibrium to a length corresponding to the C-C bond length of flat graphene costs about 0.3 meV per atom [18], which is comparable to the difference in the tube-substrate interaction energy for matched and unmatched bonds (0.1 – 0.2 meV per atom). Since these energies are comparable, the nanotubes could deform along their axis and lock into commensurations with the substrate, even if the equilibrium bond length in an isolated tube is slightly extended. To study axial relaxation, we simulated a 10 nm long nanotube with free hydrogenated ends, on a graphene sheet. The nanotube typically does not escape the local minimum, meaning that (1) a slightly compressed bond-matched tube at the main commensurate angle remains compressed due to interactions with the substrate [26], and (2) a bond-mismatched (i.e. equilibrium length) tube at a pseudo-commensurate angle retains mismatched bonds. The energies of states (1) and (2) for the same tube are nearly indistinguishable, except for the armchair tubes, where the commensurate state is more favorable.

To summarize, we demonstrate a new type of registry-dependent interaction that is unique to a one-dimensional system on a two-dimensional substrate: certain tube/substrate orientations are preferred due to finite size effects, even though they are manifestly incommensurate. We also identify a possible mechanism to distinguish carbon nanotubes by helical angle, which could improve our ability to produce nanotubes with precisely

defined structure and properties.

VHC & AK acknowledge NSF DMR-0305035. JE & MSS acknowledge the MITRE Technology Program and discussions with L. Carlivati, P. Weiss and D. Srivastava.

- 
- [1] S. Iijima, *Nature* **354**, 56 (1991).
  - [2] R. H. Baughman, A. A. Zakhidov and W. A. de Heer, *Science* **297**, 787 (2002); J. Ouellette, *Indust. Phys.*, Dec. 2002-Jan. 2003, 18.
  - [3] N. Hamada, S. Sawada, and A. Oshiyama, *Phys. Rev. Lett.* **68**, 1579 (1992); J. W. Mintmire, B. I. Dunlap, and C. T. White, *Phys. Rev. Lett.* **68**, 631 (1992); R. Saito, M. Fujita, G. Dresselhaus and M. S. Dresselhaus, *Appl. Phys. Lett.* **60**, 2204 (1992).
  - [4] G. G. Samsonidze, G. G. Samsonidze and B. I. Yakobson, *Phys. Rev. Lett.* **88**, 065501 (2002); M. Buongiorno Nardelli, B. I. Yakobson and J. Bernholc, *Phys. Rev. B* **57**, R4277 (1998); B. I. Yakobson, *Appl. Phys. Lett.* **72**, 918 (1998); P. Zhang, P. E. Lammert and V. H. Crespi, *Phys. Rev. Lett.* **81**, 5346 (1998).
  - [5] M. S. Dresselhaus, G. Dresselhaus and P. C. Eklund, *Science of Fullerenes and Carbon Nanotubes* (Academic Press, San Diego, 1996).
  - [6] P. G. Collins, M. S. Arnold and P. Avouris, *Science* **292**, 706 (2001).
  - [7] R. Krupke, F. Hennrich, H. v. Lohneysen and M. M. Kappes, *Science* **301**, 344 (2003).
  - [8] S. Bandow et al., *Phys. Rev. Lett.* **80**, 3779 (1998).
  - [9] P. Nikolaev et al., *Chem. Phys. Lett.* **313**, 91 (1999).
  - [10] K. Hernadi et al., *Zeolites* **17**, 416-423 (1996).
  - [11] S. Farhat et al., *J. Chem. Phys.* **115**, 6752 (2001).
  - [12] J. Liu et al., *Science* **280**, 1253 (1998); M. R. Falvo et al., *Nature* **397**, 236 (1999); M. R. Falvo et al., *Phys. Rev. B* **62**, R10665 (2000); H. Yanagi, E. Sawada, A. Manivannan and L. A. Nagahara, *Appl. Phys. Lett.* **78**, 1355 (2001).
  - [13] A. Buldum and J. P. Lu, *Phys. Rev. Lett.* **83**, 5050 (1999).
  - [14] L. A. Girifalco, M. Hodak and R. S. Lee, *Phys. Rev. B* **62**, 13104 (2000).
  - [15] A. N. Kolmogorov and V. H. Crespi, *Phys. Rev. Lett.* **85**, 4727 (2000).
  - [16] A. N. Kolmogorov and V. H. Crespi, manuscript in preparation.
  - [17] H. Beyer, M. Muller and Th. Schimmel, *Appl. Phys. A* **68**, 163 (1999).
  - [18] D. Sanchez-Portal et al., *Phys. Rev. B* **59**, 12678 (1999).
  - [19] The  $(n, n)$  tubes have unexpectedly large binding energies for matching bond lengths. In a narrow highly curved  $(n, n)$  tube, a central axial row of atoms forming the line of contact with the substrate can be placed in the most energetically favorable position: above the hexagonal centers in the graphite substrate (as in AB stacked graphite). Neighboring rows of atoms, which are positioned in energetically less favorable positions directly above atoms in the substrate, curve away from the substrate due to tube curvature, so have less important interactions. Tubes of other helicities offer no such possibility. If the bonds on the  $(n, n)$  nanotube are mismatched to the substrate, then this effect disappears, since atoms on

the nanotube are uniformly spread along the substrate unit cell. Therefore, this effect is restricted to very short and narrow armchair nanotubes on graphitic substrates.

- [20] V. Georgakilas et al., *J. Am. Chem. Soc.* **124**, 760 (2002); M. Diehl et al., *Bull. Am. Phys. Soc.* **46**, 866 (2001).
- [21] Y. Huang, X. Duan, Q. Wei and C. M. Lieber, *Science* **291**, 630 (2001); B. H. Fishbine, *Full. Sci. and Tech.* **4**, 87 (1996).
- [22] M. H. Schleier-Smith, "A Proposed Bulk Process for the Separation of Single-Walled Carbon Nanotubes According to Their Chirality," Report No. MP 00W00000309, The MITRE Corporation, McLean, VA, November 2000.
- [23] M. H. Scheleier-Smith and J. C. Ellenbogen, U.S. Patent No. 0,000,000. Allowed Feb. 2003. Anticipated issue date Oct. 2003. "Method for the Bulk Separation of Single-Walled Tubular Fullerenes Based Upon Chirality."
- [24] D. W. Brenner et al., *J. Phys. Cond. Mat.* **14**, 783 (2002).
- [25] P. M. Chaikin, T. C. Lubensky, *Principles of condensed matter physics*, 601, Cambridge University Press, Cambridge 1995.
- [26] The (10,0) tube does extend slightly, since the commensuration turns into a pseudo-commensuration under axial extension for this special case.