Coating carbon nanotubes: Geometry of incommensurate long-range-ordered physisorbed monolayers

Antonio Šiber*

Institute of Physics, P.O. Box 304, 10001 Zagreb, Croatia
(Received 13 May 2003; published 15 July 2003)

The structures of a long-range-ordered physisorbed monolayer on a carbon nanotube are examined. Geometrical and energetical constraints determining the order of such monolayers are discussed. A number of symmetrically different, strongly bound adsorbate structures is found for Xe adsorbates, some of which differ very little in energy. The presented results suggest that the atomically uniform coating of carbon nanotubes is possible and offer a clear visualization of such coatings.

Carbon nanotubes have already found a number of interesting applications.[1] However, to truly assess their potential for various applications, a detailed description of the interaction of carbon nanotubes with the atoms and molecules of their surroundings is required. In this context, it has been suggested that coating the carbon nanotubes with atoms may improve their properties that are important for various uses (see, e.g., Refs. 2 and 3). The experimental demonstration of coating of carbon nanotubes with crystalline sheets of V_2O_5 layer-like structures was presented in Ref. 3. However, it is not clear yet how to create fine, ordered coatings of monoatomic thickness. The long-wavelength vibrational properties of such coatings have been examined in the literature (see, e.g., Ref. 4), but the coatings are not easily visualized since the confinement of atoms and molecules on a nanotube (cylindrical) surface imposes a specific ordering of such structures, as will be shown here.

In this report, we are interested in the geometry and binding energies of long-range ordered monoatomically thick coatings of carbon nanotubes. We consider capped nanotubes; thus, the monolayer coating is on the outer side of the nanotube (exohedral adsorption). The microscopic arrangement of the adsorbed layer of atoms depends on the details of both the adsorbate-adsorbate and adsorbate-substrate interactions. These interactions are not precisely known yet with the exception of physisorbed gases. A large amount of experimental and theoretical data exist for physisorption of gases on graphite surfaces,[5] which enables one to use this information and reconstruct the relevant potentials that can then be applied to the present case of interest.[7–10] Even with the information on potentials, it is still not trivial to find ordered adsorbate structures that minimize the free energy of the system. This is mainly because there are many different configurations with very similar energy. The adsorbate-substrate potential exhibits corrugation, and in the case of very large corrugation amplitudes the adsorbate overlayer will follow the periodicity of the nanotube, since the energy it loses due to the unfavorable positions of its neighbors is less than the one gained due to the fact that all the atoms sit in the minima of the substrate potential, i.e., the overlayer structure will be commensurate with the substrate. In the other extreme case in which the corrugation of the substrate is negligible, the adsorbate layer will order in such a way as to maximize the binding energy resulting from the interadsorbate interactions,

and the resulting structure will be incommensurate.[6] The corrugation of graphite is in between the two extremes, and a number of different phases of gases physisorbed on the graphite surface (commensurate and incommensurate) has been reported in the literature,[5] also depending on the substrate temperature. In what follows, I shall assume that the adsorbate structure is indeed incommensurate with the corrugation of the carbon nanotube. In this case, the adsorbate-nanotube potential can be treated as smooth, i.e., one can neglect its corrugation when calculating the total energy of the structure.

Assume for the moment that all of the adsorbate atoms are at the same distance from the nanotube axis, i.e. that their centers lie on a cylinder of radius R, $R = R_t + h$, where R_t is the nanotube radius and h is the height of the coating above the surface of the nanotube. It can be *a priori* expected (I shall not do so) that the adsorbate structure with minimum energy will locally have a nearly hexagonal order. It is nevertheless not completely obvious how to reconcile this local arrangement of atoms with the fact that *all* adsorbate sites on a cylinder surface must be equivalent.

We define two vectors ($\mathbf{a}_1$ and $\mathbf{a}_2$) on a cylinder surface connecting nearest neighboring adsorbate atoms along two inequivalent directions. Any of the two vectors can be specified by a polar angle spanned by the vector's starting and ending points, and by the projection of the vector on the cylinder axis (z axis):

$$\mathbf{a}_1 = (\alpha, a\alpha),$$
$$\mathbf{a}_2 = (\beta, b\beta). \tag{1}$$

The vectors are defined on a cylinder surface, i.e., each of them specifies one of the cylinder geodesics which are simple coil curves (see Fig. 1). The lengths of the vectors are not necessarily the same, and it is in principle possible that the nearest neighbor distances are not the same along the two geodesics.

In order to obtain a long range ordered adsorbate structure, all the adsorbate position vectors $\mathbf{r}_l$ should be linear combinations of the elementary vectors $\mathbf{a}_1$ and $\mathbf{a}_2$, i.e.,

$$\mathbf{r}_l \equiv \mathbf{r}_{i,j} = i\mathbf{a}_1 + j\mathbf{a}_2$$
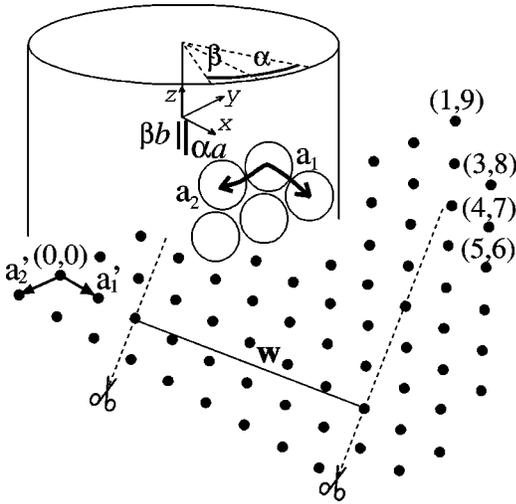$$= [R\cos(i\alpha + j\beta), R\sin(i\alpha + j\beta), ia\alpha + jb\beta], \tag{2}$$

FIG. 1. Nearly perfect hexagonal lattice of points. The way to turn this lattice into an adsorbate coating is illustrated by the dashed lines and "scissors" (cutting along the dashed lines and wrapping the **w** vector around the $z=0$ cross section of the nanotube). The basis vectors $\mathbf{a}_1'$ and $\mathbf{a}_2'$ used to specify any wrapping vector **w** are denoted. Several minimum energy structures obtained for (5,5) nanotubes are indicated. Note that although all these structures are indicated on the *same* hexagonal lattice, they in fact belong to *slightly different* nearly perfect hexagonal lattices as discussed in the text. The inset displays $\mathbf{a}_1$ and $\mathbf{a}_2$ vectors and their components.

where i and j are integers, and in the last line of the above equation $\mathbf{r}_{i,j}$ are given in Cartesian coordinates. There is an additional condition that must be satisfied by the parameters of the structure. Starting from one crossing point of two geodesics, the next crossing point should be reached by integer numbers (m,n) of primitive vector translations along both geodesics. This yields

$$m\alpha = n\beta + 2\pi,$$
$$ma\alpha = nb\beta. \tag{3}$$

The adsorbate structure is thus defined by $\alpha, \beta, a,$ and b which satisfy Eq. (3).

The total energy of the adsorbate structure can be written as a sum of all adsorbate-adsorbate interactions, v, and interaction of the adsorbates with the carbon nanotube, V (this neglects the energy of adsorbate zero-point motion). The energy per adsorbate atom is thus

$$E_b = \sum_{i=-\infty}^{\infty} \sum_{j=0}^{n-1} {}' v(\mathbf{r}_{i,j}-\mathbf{r}_{0,0}) + V(\mathbf{r}_{0,0}), \tag{4}$$

where $\mathbf{r}_{i,j}$ is given by Eq. (2), and the prime on the sum indicates that the term with $i=j=0$ is excluded.

We now look for the structure with minimum adsorbate energy, i.e., we minimize Eq. (4) with respect to its parameters. Explicitly, the minimization procedure consists of choosing the height of the overlayer h, α, and a parameters of the first geodesic, integer numbers m and n that determine β and b of the second geodesic [Eq. (3)], and calculating the energy of the resulting structure from Eq. (4). Since we mini-

mize the internal energy of the overlayer and not its free energy, our results are applicable at zero temperature only.

The indexing of the structures with (m,n) is not unique because the integers m and n depend on the two nearest-neighbor geodesics one chooses (e.g., instead of two geodesics defined by $\mathbf{a}_1$ and $\mathbf{a}_2$ one could have chosen the two with $-\mathbf{a}_1$ and $\mathbf{a}_2$, or $\mathbf{a}_1$ and $\mathbf{a}_1 \pm \mathbf{a}_2$, presuming that $\mathbf{a}_1 \pm \mathbf{a}_2$ still points to the nearest neighbor; see Fig. 1). However, the representation of adsorbate structures of interest in terms of planar adsorbate arrangements folded onto a cylinder surface is possible and allows for a unique indexing. All strongly bound structures of interest exhibit a quasihexagonal order of adsorbates, with all six nearest neighbor atoms nearly equally separated from the atom in the center of a hexagon. Nevertheless, these quasihexagons cannot in general be obtained by a mathematical wrapping of the *perfect* hexagonal planar lattice of minimal energy. This is a consequence of the fact that the sum of interadsorbate interactions is different when the adsorbates are positioned on the surface of a cylinder (Cartesian distances change), and that the whole structure must "fit" onto the cylinder. To specify the geometry of the adsorbate coating it is sufficient to characterize two points in the planar, nearly hexagonal structure obtained by unwrapping the coating (the cutting preceding the unwrapping is parallel to the z axis). The vector **w** connecting these two points can be thought of as being wrapped around the $z=0$ cross section of the cylinder. The whole planar structure is assumed to follow this "wrapping" procedure. This is quite similar to the usual way of indexing of carbon nanotubes.[1] The wrapping procedure is sketched in Fig. 1.

The vector **w** can also be expressed as

$$\mathbf{w} = m\mathbf{a}_1' - n\mathbf{a}_2', \tag{5}$$

where $\mathbf{a}_1'$ and $\mathbf{a}_2'$ are basis vectors of the planar, nearly hexagonal adsorbate structure which, when wrapped around the cylinder, produce the vectors $\mathbf{a}_1$ and $\mathbf{a}_2$ in Eq. (1), and the integers m and n correspond to those in Eq. (3). If one chooses $\mathbf{a}_1'$ and $\mathbf{a}_2'$ in the way sketched in Fig. 1 (angle between $\mathbf{a}_1'$ and $\mathbf{a}_2'$ greater than $\pi/2$), the indexing of coatings in terms of m and n [or wrapping vector in Eq. (5)] becomes unique and that is what we shall use to specify the symmetries of the coatings. Note that the minus sign in Eq. (5) is a convention: one can also choose the plus sign and redefine vectors $\mathbf{a}_1'$ and $\mathbf{a}_2'$, so that the angle between them is smaller than $\pi/2$. Alternatively, m and n numbers are those pertaining to $\mathbf{a}_1$ and $\mathbf{a}_2$ vectors chosen in such a way that the angle they span is maximum, while $\alpha a \beta b > 0$ [Eqs. (1) and (3)].

We now investigate the symmetries and binding energies of the adsorbate coatings as a function of the carbon nanotube radius. Adsorption of xenon on nanotube bundles has been experimentally studied (see Refs. 11 and 12) and molecular dynamics simulations of Xe adsorption on carbon nanotube have led the authors of Ref. 13 to conclude that the corrugation of the Xe-nanotube potential is not large enough to impose a commensurate Xe structure. That is why the Xe monolayer coatings are considered in the following, although the approach presented here can be easily extended to other adsorbates which physisorb on nanotubes.

TABLE I. Summary of the key characteristics of four lowest energy coatings with different symmetries for (5,5) and (10,10) single-walled carbon nanotubes. The wrapping vector (**w**), the height above the carbon nanotube surface (h), and the binding energy (E_b) are specified.

$R_t = 3.39$ Å; (5,5) nanotube				$R_t = 6.78$ Å; (10,10) nanotube			
Configuration	**w**; (m,n)	h[Å]	E_b [meV]	Configuration	**w**; (m,n)	h[Å]	E_b [meV]
0	(4,7)	3.710	−231.54	0	(4,12)	3.730	−242.23
1	(1,9)	3.705	−231.41	1	(1,14)	3.740	−242.10
2	(5,6)	3.700	−231.29	2	(5,11)	3.720	−241.88
3	(3,8)	3.740	−231.06	3	(3,13)	3.720	−241.72

The Xe-Xe (v) and Xe-nanotube (V) potentials are constructed as described in Ref. 7 (also see Refs. 9 and 14). These are not the most precise potentials, but are fairly simple and shall suffice to illustrate the most important points of this report.

Table I summarizes the results of calculations of binding energies per adsorbate atom for several lowest energy configurations of Xe coatings and for two different radii of a single wall carbon nanotube. The configurations are numbered as $0,1,2,\ldots$, and are ordered such that their energy increases with the increase of the configuration number. The radii chosen correspond to (5,5) and (10,10) carbon nanotubes. The symmetries of the coatings are denoted. The four lowest energy Xe structures on the (5,5) carbon nanotube are plotted in Fig. 2. The parameters for the lowest energy structure ($m=4$, $n=7$) on the (5,5) nanotube are $\alpha = 0.506$ rad, $\beta = -0.609$ rad, $a = -5.650$ Å/rad, and $b = 2.681$ Å/rad, while for the (4,12) coating on the (10,10) nanotube $\alpha = 0.302$ rad, $\beta = -0.423$ rad, $a = -10.87$ Å/rad, and $b = 2.583$ Å/rad.

One should bear in mind that it is possible to find a configuration of a Xe coating with the energy in between those specified in Table I. Such a structure can be realized by slightly straining the interadsorbate distances in the minimum energy configuration of a particular symmetry in such a way that the symmetry of the structure remains the same. For example, the minimum energy structure of a particular symmetry can be turned into a structure of the same symmetry but a smaller binding energy, by applying forces to the coating along the z direction to slightly squeeze (or stretch) it. The discrete energies quoted in Table I correspond to the
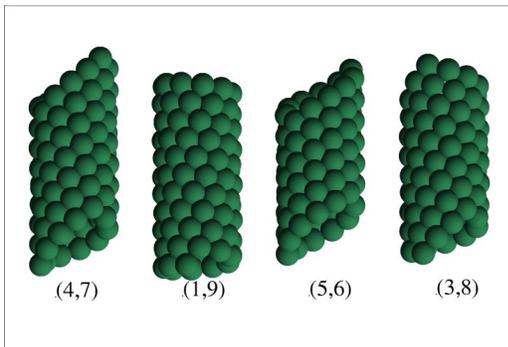

FIG. 2. Four lowest energy Xe structures on a (5,5) carbon nanotube. From left to right: (4,7), (1,9), (5,6), and (3,8) coatings.

lowest energy configurations of a coating with specified symmetry, and it is not possible to obtain lower energy by applying any set of *infinitesimal* changes to the adsorbate position vectors. Obviously, a large number of different symmetry coatings differing only a little in the binding energy is obtained. For example, for a (10,10) nanotube highly bound coatings are also those with wrapping indices (2,13), (6,10), (0,14), (8,9), (7,9), ... But coatings with different symmetries do not all find the minimum energy configuration at the same distance from the tube center (see Table I). This is due to the fact that it may be advantageous to the overlayer to move slightly away from the height at which it interacts with the nanotube most attractively, in order to "repack" itself in such a way to increase a part of the binding energy which is due to interadsorbate interactions. All the energies are in fact *doubly degenerate*, since for each choice of (α,β,a,b) there is a structure of exactly the same energy, but topologically different, with parameters ($\alpha,\beta,-a,-b$). This could be termed "helicity degeneracy." Furthermore, any rotation of the coating around the z axis does not change its energy.

Note also that *the adsorbate coatings do not in general show periodicity in the z direction*. This is due to the fact that the unwrapped two-dimensional hexagonal lattice is not perfect (see Fig. 1). Only when $m\alpha = 2f\pi$, where f is a rational number, and m and α from Eq. (3), is the adsorbate structure periodic in the z direction.

For multiwalled carbon nanotubes, the conclusions reached at here will not change significantly. In that case only the adsorbate-substrate potential changes, and the procedure described above applies equally well. Nevertheless, due to small energy differences between different configurations of the coatings, it is possible that the minimum energy configurations may exhibit different symmetries for single-walled nanotubes and multiwalled nanotubes with the same (external) radii. The presented approach can be also applied to the coatings which form *inside* the nanotubes. Essentially the only difference in this case is that h is negative. The packing of fullerene molecules in carbon nanotubes was considered in Ref. 15. Packing of hard spheres in cylinders was studied in Ref. 16. The authors of this reference emphasized the chirality aspect of the structures which is also obtained in this work. The lattices of hard spheres formed on cylindrical surfaces were studied in Ref. 17.

There is an additional degree of freedom available to the coating which was effectively "frozen" in the presented approach. That is, one could imagine a situation where the

adsorbate monolayer additionally relaxes in such a way that its height above the nanotube becomes positional dependent. This is similar to the phenomenon of the overlayer "buckling" encountered in some adsorbate/planar surface systems of for some clean surfaces (see, e.g., Ref. 18). The simplest form of "buckled" coating would be the one with the atomic centers positioned on an ellipse in the x-y plane (instead of a circle).

An interesting question which comes to mind, especially in view of such small energy differences among various configurations, is whether the inclusion of zero point motion energy would change the results presented in a qualitative way. The different structures are indeed expected to have unequal zero-point motion energies, since the potentials ex-

perienced by adsorbates differ in these configurations, at least slightly. This is probably a very small effect whose evaluation may require quite sophisticated techniques.

In conclusion, we have considered geometrical and energetical constraints and requirements associated with coating the nanotube with a monolayer of physisorbed atoms. We have theoretically predicted a number of symmetrically different coatings, some of which differ only a little in their binding energy. The results should be of importance for future experiments directed towards the functionalization of carbon nanotubes by such fine, monoatomically thick coatings.

---

*Electronic address: asiber@ifs.hr

[1] H. Dai, Surf. Sci. **500**, 218 (2002).

[2] P.M. Ajayan and T.W. Ebbesen, Rep. Prog. Phys. **60**, 1025 (1997).

[3] P.M. Ajayan, O. Stephan, Ph. Redlich, and C. Colliex, Nature (London) **564**, 375 (1995).

[4] A.M. Vidales, V.H. Crespi, and M.W. Cole, Phys. Rev. B **58**, R13 426 (1998).

[5] L. W. Bruch, M. W. Cole, and E. Zaremba, *Physical Adsorption: Forces and Phenomena* (Clarendon, Oxford, 1997).

[6] P. Bak, Rep. Prog. Phys. **45**, 587 (1982).

[7] G. Stan, M.J. Bojan, S. Curtarolo, S.M. Gatica, and M.W. Cole, Phys. Rev. B **62**, 2173 (2000).

[8] A. Šiber and H. Buljan, Phys. Rev. B **66**, 075415 (2002).

[9] A. Šiber, Phys. Rev. B **66**, 235414 (2002).

[10] A. Šiber, Phys. Rev. B **66**, 205406 (2002).

[11] S. Talapatra, A.Z. Zambano, S.E. Weber, and A.D. Migone, Phys. Rev. Lett. **85**, 138 (2000); A.J. Zambano, S. Talapatra, and A.D. Migone, Phys. Rev. B **64**, 075415 (2001).

[12] A. Kuznetsova, J.T. Yates, Jr., J. Liu, and R.E. Smalley, J. Chem. Phys. **112**, 9590 (2000).

[13] V.V. Simonyan, J.K. Johnson, A. Kuznetsova, and J.T. Yates, Jr., J. Chem. Phys. **114**, 4180 (2001).

[14] M.T. Cvitaš and A. Šiber, Phys. Rev. B **67**, 193401 (2003).

[15] M. Hodak and L.A. Girifalco, Phys. Rev. B **67**, 075419 (2003).

[16] G.T. Pickett, M. Gross, and H. Okuyama, Phys. Rev. Lett. **85**, 3652 (2000).

[17] R.O. Erickson, Science **181**, 705 (1973).

[18] A. Zangwill, *Physics at Surfaces* (Cambridge University Press, Cambridge, 1988).