



## Large-scale quantum mechanical simulations of carbon nanowires

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*(Received 28 February 2000)*

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The stability of quasi-one-dimensional structures of carbon is investigated using a generalized tight-binding molecular-dynamics scheme. Large-scale simulations are made possible by the parallel implementation of the diagonalization routines. Our results show that these structures can be stable provided that their geometries consist of a core of four-fold coordinated atoms, surrounded by a three-fold coordinated outer surface accommodating one of the most stable reconstructions of bulk diamond structure.

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**Key words:** nanotubes, molecular dynamics, clusters, eigenvalues.

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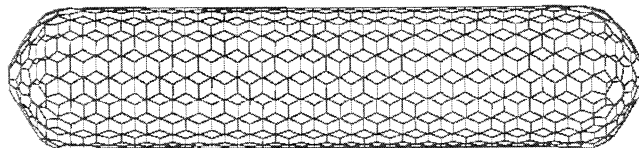
The potential applications of carbon nanotubes have aroused much speculation [1–5]. Single-wall carbon nanotubes (SWNT) are now abundantly being produced in experiments. While much excitement has been associated with carbon nanotubes, potential useful applications of other quasi-one-dimensional (QOD) solid forms of carbon cannot be overlooked. Recently, an alternative approach to the synthesis of nanoscale structures based on nanotubes has resulted in the production of nanorods (nanowires). These rods have been found to share the properties of the bulk materials (such as magnetism and superconductivity), suggesting that they might allow the investigation of the effects of confinement and reduced dimensionality on such solid-state properties [6]. Some of the nanorods exhibit unique morphologies, such as helical nanorods [6]. The precise structures of these nanorods are not known at present.

In this work we propose a novel, physically motivated approach supported by a quantum molecular dynamics method to the QOD structures of carbon. We base our approach on the premise that robust nontubular structures of carbon can be made stable by having a four-fold coordinated core surrounded by an outer surface of atoms with three-fold coordination. The models proposed for the QOD geometries for C can be broadly categorized into two distinct classes with various degrees of surface to bulk ratio of atoms. All the structures proposed have been fully optimized without any symmetry constraints using a quantum molecular dynamics method.

The theoretical method used in the present work is the quantum mechanical generalized tight-binding molecular dynamics (GTBMD) scheme of Menon and Subbaswamy [7] that allows for full relaxation of

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**Fig. 1.** The GTBMD relaxed (10,10) capsule. Parallel implementation of the GTBMD code was used in relaxing this 1000-atom cluster.

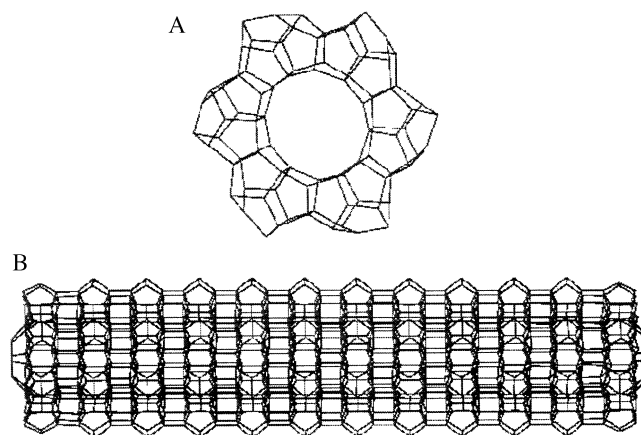
covalent systems with no symmetry constraints. This method has been found to be very reliable in obtaining very good agreement with experimental and local density approximation (LDA) results for the structural and vibrational properties of fullerenes and nanotubes [7]. For details of the formalism we refer the readers to Ref. [7] which also contains applications to the structural and vibrational properties of nanotubes. Briefly, in the GTBMD scheme a system is completely characterized by a parametrized Hamiltonian ( $\mathbf{H}$ ) and an overlap matrix ( $\mathbf{S}$ ). A generalized eigenvalue equation  $\mathbf{H}\psi = \varepsilon_n\mathbf{S}\psi$  is solved to determine the eigenvalues  $\varepsilon_n$  and eigenvectors  $\psi$  of the system. These are then used in the determination of the forces for performing molecular dynamics simulations. The solution of the eigenvalue problem is the computationally most demanding part of the GTBMD method. For a realistic simulations of any system, however, one needs to model the system with a large number of atoms, resulting in a large eigenvalue problem. It is not feasible to solve the associated generalized eigenvalue problem on typical workstations; a parallel solution is essential. It should be noted that both matrices  $\mathbf{H}$  and  $\mathbf{S}$  are real symmetric and sparse with sparsity increasing rapidly with the system size. Also, since we are interested mainly in total energies and forces, only half of the eigenvalues and eigenvectors need be evaluated.

The generalized eigenvalue computation is intrinsically expensive; for  $N \times N$  matrices, the storage requirements grow as  $N^2$  while the number of operations grow as  $N^3$ . Consider a 1061-atom simulation which yields a generalized eigenvalue problem of dimension 4244. On a high-performance workstation using eigenvalue codes from LAPACK [8] the computation time is well over an hour for a single timestep, making the overall simulation infeasible. The simulations reported here were made possible by using a cluster of workstations and dense parallel eigensolvers from ScaLAPACK [9]. These codes are MPI [10] based and are portable across a variety of parallel platforms. The codes use explicit block-cyclic distribution of the dense matrices and cache-efficient matrix operation kernels to reduce overall time. For well-conditioned matrices, the speed-ups are near ideal for small numbers of processors.

We first apply the parallel GTBMD formalism to relax a nanotube 'capsule' obtained by capping the ends of a (10,10) nanotube. The relaxed geometry is shown in Fig. 1 and contains 1000 atoms. Under optimal conditions each timestep of the molecular dynamics simulation took about 5.5 min.

We next consider the QOD structures of carbon. All geometries considered in this work were carefully relaxed to structures that are true local minima of the total energy. The vibrational frequencies were then computed for these relaxed structures within the GTBMD scheme [7] as a further check for stability. None of the structures proposed here had any imaginary frequencies, indicating them to be true local minima of the total energy. Henceforth in this work the term 'locally stable' would indicate the absence of any imaginary frequencies.

The building blocks for class 1 QOD structures are multiply connected 'superatom' clusters with  $D_{nh}$  symmetry with a small hollow region in the middle. Figure 2A shows a representative with  $D_{6h}$  symmetry. This superatom cluster contains 84 atoms and can be visualized as consisting of six circularly connected closed units of 14 atoms each with faces composed of pentagons and hexagons, with 60 of these atoms having three-fold coordination. The remaining atoms in the unit are all four-fold coordinated. All outer surface atoms participate in forming geometric configurations that resemble very closely the surface of bulk diamond. The bonding of the atoms at the top and bottom, along the symmetry axis, to their three neighbors resemble the unreconstructed (111) surface of diamond. The atoms on the surface farthest from the symmetry axis form



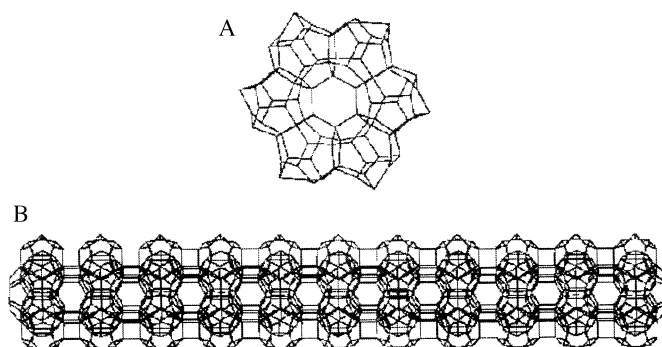
**Fig. 2.** A, The 'superatom' cluster containing 84 atoms ( $D_{6h}$  symmetry). Surface reconstruction results in the formation of symmetric tilted dimers. B, A section of QOD (class 1) wire obtained by stacking the superatom units on top of each other and performing GTBMD relaxation. The ends of the segment show (111) features.

dimers as a result of the  $2 \times 1$  reconstruction; the unreconstructed surface resembling the (100) surface of diamond. Note that the buckled dimers are all tilted in the same direction (symmetric dimer configuration). The dimer bond length is 1.59 Å. Molecular dynamics relaxations starting with an untilted configuration resulted in the formation of asymmetric tilted dimers. The symmetric tilted dimer configuration shown in Fig. 2A is found to be isoenergetic with the asymmetric case. As seen in the figure, the surface dimers are all aligned along the circumference.

The QOD structures are obtained by stacking these clusters along the symmetry axis. Figure 2B shows a large QOD cluster consisting of 1020 atoms obtained by stacking these units. The stacking results in four-fold coordination for all the (111) type atoms as they form bonds with similar atoms on neighboring unit cells. It is worth noting that (111) surfaces have the lowest surface energy among all other surfaces of diamond. The surface dimers, however, remain three-fold coordinated and do not form bonds with atoms in the neighboring unit cells. The wire-like geometry thus obtained is found to be locally stable. Other class 1 QOD structures of  $D_{nh}$  symmetries with  $n \neq 6$  can be constructed using the prescription give above.

The class 1 structures can also be used to derive another class of QOD structures with similar structural properties (four-fold coordinated atoms in the interior and three-fold on the outside). In one case (class 2), we consider stable structures with smaller surface-to-bulk ratios. The superatom unit for these classes of QOD structures, consisting of 90 atoms, is obtained from class 1 unit structure by adding a ring of six C atoms around the symmetry axis in the center (Fig. 3A). The GTBMD-relaxed QOD structure contains surface dimers each with a bond length of 1.52 Å and aligned along the circumference. The wire-like structures generated by stacking these clusters are also locally stable. Structure similar to this has also been independently reported by other groups, although no relaxation was performed [11].

In Table 1 we give a summary of relative binding energies. Also, in the same table, the values of the energy difference between the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) are given. As is evident from the binding energies in the table, the structure belonging to class 2 is more stable than that belonging to class 1. The relatively large difference in the HOMO-LUMO gaps between the two classes may be used to help distinguish the two structures experimentally through photo-emission measurements. Interestingly, similar wire structures for Si were also found to be stable in our earlier work [12]. The ordering of energies, however, between classes 1 and 2 were reversed, illustrating the critical differences in bonding in carbon and silicon.



**Fig. 3.** A, 'Superatom' cluster unit for QOD structures belonging to (class 2) B, and a section of QCD (class 2) wire obtained by stacking the superatom on top of each other and performing GTBMD relaxation.

Structure	Energy (eV/atom)	HOMO–LUMO gap (eV)
(10,10) capsule (Fig. 1)	0.00	0.00
Class 1 wire (Fig. 2)	1.08	1.30
Class 2 wire (Fig. 3)	0.62	1.61

The relatively large bond lengths for the three-fold coordinated atoms belonging to classes 1 and 3 may seem counter-intuitive; since in crystalline diamond the surface atoms tend to have shorter bond lengths when compared with the core atoms. A careful examination, however, reveals this 'anomalous' increase in the bond length for surface dimers to be due to the strain caused by the alignment of dimers along the circumference. Also, since the only surface reconstruction for these QOD structures are the  $2 \times 1$  type, we expect the surfaces to be at least as reactive as those of the bulk  $2 \times 1$  surface. The passivation of the surface dangling-bond orbitals through reconstruction is believed to lead to low reactivity.

The presence of large interstitial regions in all these nanostructures may make doping with group III or V elements relatively easy. This may prove to be an important advantage in device fabrication.

In summary, we have proposed novel QOD structures of carbon whose surfaces closely resemble one of the most stable reconstructions of the crystalline diamond with a core of bulk-like four-fold coordinated atoms.

*Acknowledgements*—The present work is supported by grants from NSF (OSR 99-07463, ACI-9721361, CDA-9529459 and MRSEC), DEPSCoR, the Semiconductor Research Corporation (SRC), and by the University of Kentucky Center for Computational Sciences.

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