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Carbon allotropes and strong nanotube bundles

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Abstract

We have used density functional pseudopotential calculations and molecular dynamics to predict new carbon structures of high stability. The new phases are strongly bound and involve the smallest radius nanotubes. It was found that it is possible to covalently link smallest/larger, smallest/smallest radius nanotubes together as well as larger nanotube/ C_{20} 1D-chains, resulting in extremely large interlinkage and consequent increase in the resistance to slippage. This procedure may enable the construction of extremely stiff nanotube bundles capable of making full use of the tensile properties of individual nanotubes, while enhancing the crystallinity of the material. Some of the carbon allotropes studied are the lowest energy non-diamond sp^3 hybridized structures ever found.

(Some figures in this article are in colour only in the electronic version)

A number of investigations have been carried out on nanotube ropes and solids of large radius nanotubes. It has been established that sp^2 bonded nanotubes do not covalently bind to each other unless there is a large applied pressure and then the resulting bonding is relatively weak [1]. The smallest radius nanotubes known to exist [2] are among the stiffest one-dimensional systems known [3, 4]; they are threefold coordinated and show characteristics of sp^3 hybridization. Hence, they may have the potential to aggregate new structures of remarkable stability. The investigation of dimers of (2, 2), (3, 0), (4, 0) and of other very small radius nanotubes and associated solid phases may yield solids of large stiffness. In addition, it is unknown how these tubes interact with each other and with larger radius ones since their graphitic sheets are dramatically curved. In this work we report the stability, bonding and electronic properties of the smallest nanotube assembled solids and dimers that form without applied pressure and are strongly covalently bound. We have calculated structures of connected larger radius/smallest radius nanotubes, forming solids and dimers. The structures of larger radius nanotubes/ C_{20} cluster 1D-chains, forming dimers and trimers, were also investigated and their properties examined. We have related them to those of other known carbon structures of high stability. The fabrication of these structures is technologically challenging. The smallest tubes have so far only been synthesized inside MWCNs or zeolites [2, 5, 6] but it is possible

that they can be extracted and isolated. The nanotube/ C_{20} 1D-chain aggregates are technically possible.

The calculations were done using density functional theory with a plane wave expansion and within the GGA approximation, using the BFGS algorithm and no symmetry constraints. The parameterization was by Perdew–Wang [7] and implemented in the computer code CASTEP [8]. Periodic boundary conditions were used and the pseudopotentials were of the ultrasoft type [9], with a kinetic energy cutoff of 310 eV, and included s and p projectors. Atomic relaxation was carried out until all forces were equal to or less than $0.05 \text{ eV } \text{Å}^{-1}$ for every atom and the total energy converged to less than $2 \times 10^{-5} \text{ eV}$. The k -point sampling, of the Monkhorst–Pack type [11], had a density of 0.06 Å^{-1} in every case. The Mulliken, overlap populations (B.O.) and partial density of states (PDOS) were calculated [10]. The binding energies are the atomization energies with respect to the isolated elements within the GGA, in the same conditions. The stabilization energies were evaluated with respect to corresponding monomers.

We have also carried out molecular dynamics (MD) calculations in the microcanonical (NVE) ensemble at 273 K external temperature for all the dimers and for the three least stable of the solids. The simulation time was 0.5 ps, which was considered enough, since the energies showed no significant drift in that time. The time step used was 0.001 ps and we have started from optimized geometries. The simulation used the Verlet integrator with velocity scaling. For two of the systems we have, in addition, used the NVT ensemble in order to confirm the stability of the 2D periodic structures. The internal temperature used was 273 K and the Nosé–Hoover thermostat was used. Convergence was obtained, with energy drifts naturally higher than in the microcanonical ensemble. The geometrical configuration evolution on the NVE ensemble was monitored, and the phase space sampled and used to investigate the metastability of the structures. The NVT ensemble calculations converged to a final configuration that was not significantly different from the starting geometry at zero temperature. All the inputs to the MD runs resulted from full geometry optimization.

The MD calculations cannot be regarded as unequivocal proof of high temperature stability, but constitute the best indication obtainable within this context that the structures are not highly metastable. The simulation temperature is a measure of the kinetic energy of the ions and introduces an artificial dynamics, but it does not clarify the possible pathways for the formation of such structures. It merely states that they are stable local minima.

Table 1 shows the binding energies for the nanotubes, dimers and solid phases resulting from their aggregation under zero applied pressure. The solids considered are composed of the same nanotube and of mixed types. The symmetries of the solids are also indicated, as well as the coordination fractions. It is shown that several types may combine to form high stability structures of increasing complexity. The stabilization energies are given later.

The first observation is that all structures had a binding energy larger than or of the same magnitude as the observed C_{20} cluster. Also, the fcc- C_{20} solid had smaller binding energy than any of the solids and some of the dimers. The MD calculations showed that the dimers were all stable at 273 K with negligible variations in energy.

Figure 1 shows several stable dimers. The type of coordination is shown and the dimers are connected by sp^3 type bonds. The (4, 0) dimer is stabilized by 0.073 eV/atom and the solids by 0.135 and 0.312 eV/atom (see figure 2). These energies are large in comparison with the typical 0.02 eV/atom for nanotube phases under pressure [1]. The (2, 2) structures' stabilization energies are 0.099 eV/atom for the dimer and 0.731 and 0.435 eV/atom for the solids. The highest stabilization energy obtained for (3, 0) structures was with 0.130 and 0.177 eV/atom for the dimers and 0.614 eV/atom for the solid. These values are up to 30 times higher than the stabilization energies of sp^2 nanotubes under pressure. In addition, the

Table 1. The binding energies (BE in eV/atom) for the isolated structures, dimers and solids are shown. The space group symmetry and coordination refer to the solids. ns stands for non-stable structure. In this case the nanotubes merge to form a lower energy, larger radius nanotube.

System	BE	Dimer BE	Solid BE	Symmetry	Solids Coord. sp ² /sp ³ (%)
Graphite	—	—	9.467	<i>P6₃/mmc</i>	100/0
Diamond	—	—	9.317	<i>Fd$\bar{3}m$</i>	0/100
C ₂₀	8.299	—	—	—	—
C ₂₀ 1D	8.427	—	—	—	—
fcc-C ₂₂	8.299	—	8.710	<i>Fm$\bar{3}$</i>	54.54/45.46
(4, 0)	8.693	8.766	8.828	<i>P4/mmm</i>	75/25
(4, 0)	8.693	ns	9.005	<i>I4/mcm</i>	0/100
(2, 2)	8.375	8.474	8.810	<i>I4/mmm(1)</i>	0/100
(2, 2)	8.375	ns	9.106	<i>I4/mmm(2)</i>	0/100
(3, 0)	8.275	8.405	—	—	100/0
(3, 0)	8.275	8.452	8.889	<i>Pmma</i>	0/100
(4, 4)	9.203	—	9.093	<i>P1</i>	50/50
(7, 0)	9.217	—	—	—	—
(4, 4)/(2, 2)	9.203/8.375	ns	9.090	<i>I4/mmm</i>	66.66/33.33
(4, 4)/(2, 2)	9.203/8.375	8.943	8.974	<i>I4/mcm</i>	66.66/33.33
(7, 0)/(4, 0)	9.217/8.693	9.046	—	—	—
(4, 4)/C ₂₀ 1D	9.203/8.299	8.919	—	—	—
(4, 4)/C ₂₀ 1D/(4, 4)	9.203/8.299/9.203	9.075	—	—	—

stabilization energy for the solid mixing two different radius nanotubes was 0.163 eV/atom for *I4/mmm* and 0.047 eV/atom for *I4/mcm*. The (4, 0) nanotubes are sp² coordinated structures and the (2, 2) and (3, 0) tubes are a mix of characters of sp² and sp³, due to their large curvature [4]. The smallest nanotube solid phases are sp³ hybridized, except for (4, 0) *P4/mmm* where the coordination mix is 50% sp²/50% sp³.

The diamond bond within our conditions for calculation is 1.532 Å (sp³) and graphite is 1.408 Å (sp²). We note that the (4, 0) *P4/mmm* phase has four different bond lengths: one at about 1.34 Å (sp²), corresponding to double bonding along the vertical of the nanotubes; one at about 1.51 Å (sp²), corresponding to the horizontal zig-zag bonds; one at about 1.54 Å (sp³), corresponding to the vertical of the inter-nanotube four-atom ring and the horizontal inter-nanotube bonding of 1.60 Å (sp³). This structure is an sp²/sp³ hybrid (50% threefold and 50% fourfold coordination) of high stability and is a conductor. The comparison with the isolated nanotube and dimer holds that the dimer has four distinct ranges of bond lengths and is an sp²/sp³ hybrid. The nanotube is purely sp².

Figure 2 shows the top view for the structures of the stable solids. The symmetries and the DOS are included.

The (4, 0) *I4/mcm* phase has a higher density of inter-nanotube bonding and is even more stable. There are three distinct bond lengths of 1.49 Å (sp²), corresponding to the intra-nanotube horizontal bonding, 1.54 Å (sp³) for the vertical intra-tube bonding and 1.56 Å (sp³) for the horizontal four-atom ring bonds. The solid is 100% sp³, bearing relation to the diamond structure. The band structure shows a large direct band gap of 3.18 eV. The gap is smaller than that of diamond, which is interpreted in terms of bond angle distortions that deviate from the perfect sp³ bonds, leading to the gap closing. This phase is highly stable.

The (2, 2) *I4/mmm(1)* phase is the least stable of the two. All the atoms are fourfold coordinated with a direct band gap of 0.70 eV. The bonding is entirely sp³ and there are three distinct bond lengths: centred at 1.50 Å, corresponding to the horizontal intra-tube bonds;

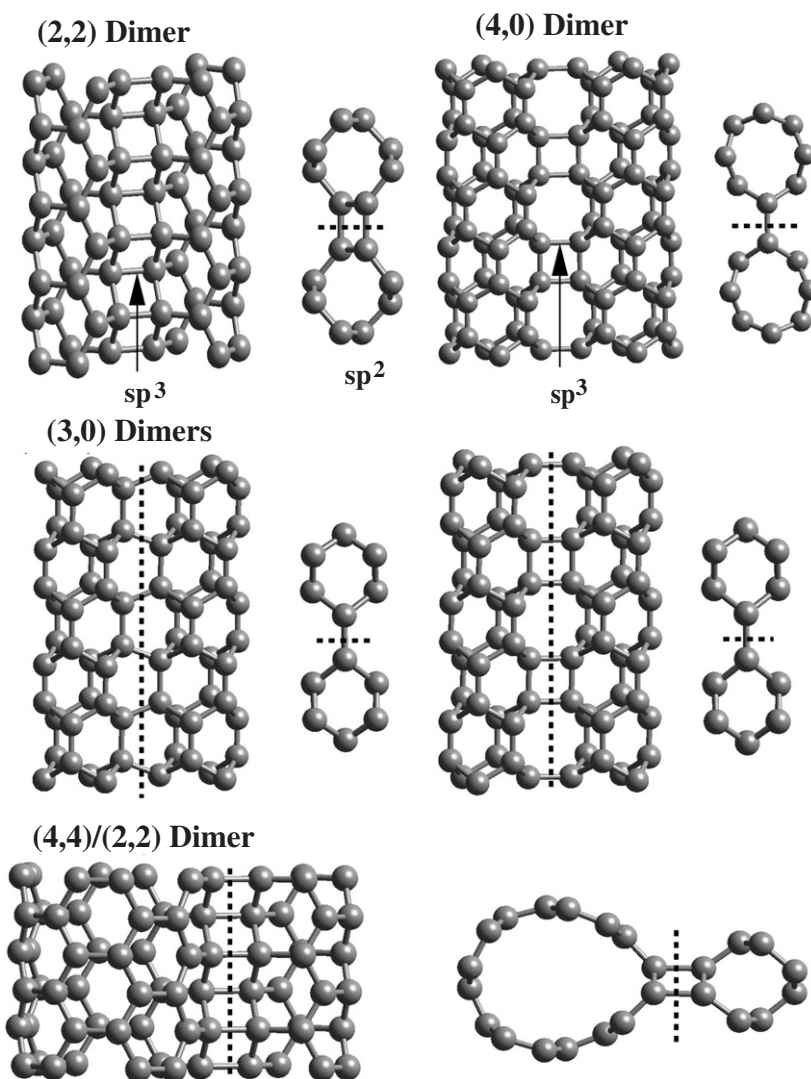


Figure 1. Side and top view of highly stable dimers. A large interlinkage of an sp^3 type and the remaining bonds sp^2 coordinated are common to these structures.

another at 1.53 Å for the intra-nanotube zig-zag; and at 1.57 Å for the inter-nanotube bonds. The (2, 2) $I4/mmm(2)$ phase is the most stable of the two and there are two bond density peaks at 1.50 and 1.56 Å, where the smaller corresponds to the inter-nanotube zig-zag bonding and the longest to horizontal four-atom rings. The solid is sp^3 coordinated with a band gap of 2.59 eV. Despite (1) being more stable than (2) the dimers of (1) are unstable and we conclude that (2) is more probable for assembly.

The (3, 0) $Pmma$ phase yields a stabilization energy of 0.614 eV/atom. This extremely large value is due to the high covalent bonding density. The nanotubes are connected side by side with each carbon atom bound to another nanotube. All the bridging bonds are sp^3 type and have a length of about 1.51–1.56 Å. The bond angles are significantly distorted with respect to the diamond structure. This is a wide band gap semiconductor with 3.82 eV gap.

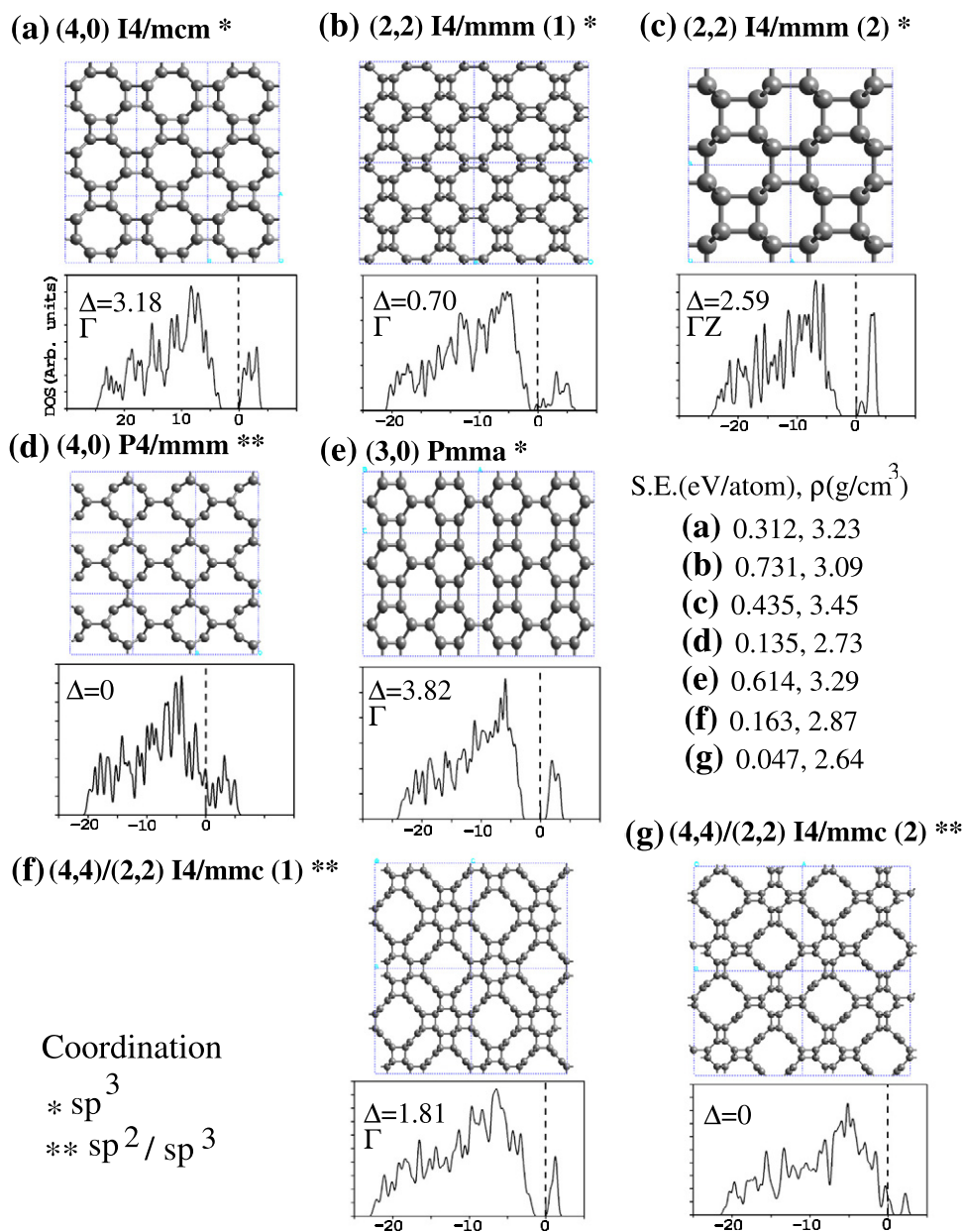


Figure 2. Top view of the solids and DOS for each one. The abscissa is in electronvolts and the zero of the chemical potential is shown. The band gap (Δ) is indicated in electronvolts, as well as the special symmetry points between the top of the valence band and the bottom of the conduction band. The stabilization energies are shown, followed by the density.

The dimers can bind in at least two different ways, one of which is more stable than the other by about 0.047 eV/atom. The bonding atoms have lengths of 1.51 Å in the most stable dimer and 1.55 Å in the other. Both have metallic properties and the least stable structure has a DOS peak at the Fermi level of dominant p type orbital character.

The (4, 4) simple cubic phase is not stable and has a negative stabilization energy of -0.123 eV/atom, indicating that nanotubes of this type do not bind and that it is impossible to form covalently bound bundles without applied pressure.

The mixed (4, 4)/(2, 2) nanotube phases illustrate the dense linkage of two different types of tubes. The (2, 2) and the (4, 4) nanotubes are bound in a structure that is a mix of sp^2 and sp^3 coordination. The atoms in the (2, 2) nanotube are sp^3 hybridized and some in the (4, 4) tube are sp^2 . The $I4/mmc(2)$ phase has a very small stabilization energy/atom, while the $I4/mmm$ has a stabilization energy of 0.163 eV/atom, which is a relevant value of about eight times the stabilization energy of larger radius nanotubes under pressure [1]. These phases suggest that the smallest radius nanotubes may be used, at least in some cases, to bind larger radius nanotubes with a high degree of strength and crystallinity. The resulting structures anticipate the possibility of bundling the smallest and large radius nanotubes, resulting in covalent bonding between them with a high sp^3 bridging density and considerable resistance to slippage. (4, 0) and (3, 0) tubes show the same potential for 'gluing' larger radius nanotubes, as well as most of the smallest nanotubes. This method has the advantage of not introducing defects in the nanotubes and hence does not degrade the tensile properties of large radius tubes to a large extent. The solid is a semiconductor. Other nanotube arrangements can show intrinsic metallicity and the material can be doped to display conductive characteristics.

To confirm this result we have carried out the calculation of a mixed dimer of a (4, 4)/(2, 2) nanotube (see figure 1) and found that the tubes can bind with a stabilization energy of 0.016 eV/atom with respect to the isolated nanotubes. The bridging atoms are sp^3 coordinated, with a bond length of 1.65 Å. The bridging density is 8.2 nm $^{-1}$ for the dimer and 37.8 nm $^{-1}$ for the solid. These values are extremely large compared to the 0.8 nm $^{-1}$ obtained for irradiated carbon bundles [12–14]. The Young's modulus and the shear modulus are expected to be correspondingly larger for these structures. Even more noticeably the (7, 0)/(4, 0) dimer (see figure 3) has a stabilization energy of 0.019 eV/atom and an average bridging bond length of 1.58 Å with a density of 4.7 nm $^{-1}$.

We have found that not all smallest radius nanotubes bind covalently. Some of these will, when brought together in some cases, form a larger radius nanotube. This is not impeditive of the strengthening of bundles by including the smallest radius tubes, as they will either form sp^3 bridges or increase the density of interstitial carbon atoms in between the nanotubes. They bind with maximal interlinkage if they are axially commensurate (either both armchair or zig-zag and proportional wrapping indices). If they are not it is still possible to obtain less dense interlinkage, where the large radius nanotubes are least modified by the bonding.

Alternatively, it is shown that the mix of nanotubes with other carbon clusters and polymerized chains will form covalently bound bundles. We have calculated a (4, 4)/C₂₀ chain dimer and a (4, 4)/C₂₀ chain/(4, 4) trimer (see figure 3) and found that they are both stable by 0.020 eV/atom and 0.053 eV/atom relative to the isolated structures. These values are predictive of stability, and both structures are metallic. The interlink density is 4.10 nm $^{-1}$ for the dimer and double for the trimer. The C₂₀ chain is stable with respect to the isolated I_h symmetry C₂₀ isomer by 0.128 eV/atom and it binds to armchair nanotubes. A 90° axial rotation of the C₂₀ chain enables linkage between zig-zag nanotubes. The average bond length for the nanotube/C₂₀ polymer interlink is 1.58 Å. The bridging bonds increase the bond length of the neighbouring armchair bond to 1.61 Å and the cluster C–C parallel bond to 1.57 Å. All other bonds remain nearly unaltered, and thus the tensile properties of the individual nanotubes are less likely to be dramatically deteriorated by the interaction with the polymer chain.

Figure 3 shows the structures of the nanotube/C₂₀ chain and nanotube/smallest nanotube systems, the density of states for the three mixed dimers and the corrugation curves for all the dimers considered in this study. The corrugation energy is defined as the variation of the

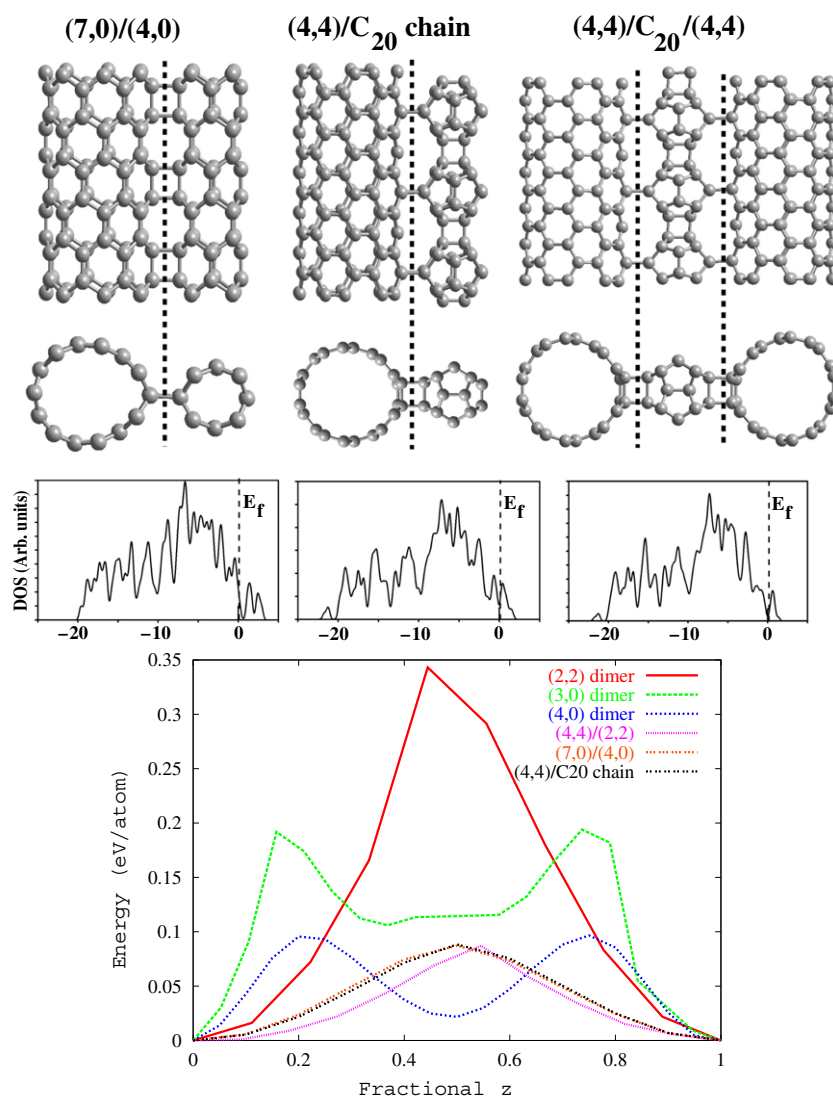


Figure 3. The DOS are in arbitrary units and the ordinates in eV. The corrugation curve shows large similarity between very different systems ((4, 4)/(2, 2), (7, 0)/(4, 0) and (4, 4)/C₂₀ chain).

total energy with respect to the sliding of the tubes through a repeating axial unit length, while maintaining the structure fixed. This quantity (the maximum of the curve) is related to the shear modulus and frictional coefficient. We note that the maximum corrugation values are up to 350 times larger than those for the interaction of a graphitic sheet with nanotubes [15], which are of the order of 1 meV. Since large nanotubes can be linked by n bridging elements the energy gain can be significantly increased. The smallest radius nanotube dimers (3, 0), (2, 2) and (4, 0) have much larger corrugation than the mixed dimers, which are nearly indistinguishable. The (3, 0) and (4, 0) dimers have two minima, corresponding to two different bonding combinations in the same unit cell. The typical corrugation for the mixed structures is 0.1 eV/atom (100 times that of nanotube–graphite).

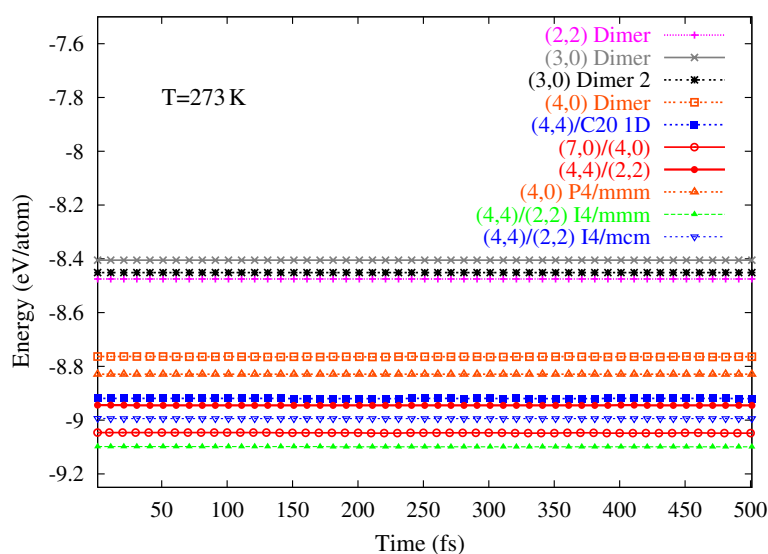


Figure 4. Molecular dynamics binding/cohesive energies as a function of time. The simulation time was 0.5 ps. No variations of binding/cohesive energy can be noted, confirming the non-artefactual character of the runs. For clarity only 100 points of each set are shown and 501 were calculated.

The results of the MD calculations are shown in figure 4. The variations in energy for the three least stable solids and all of the dimers were virtually zero and the atomic configurations did not change. The conclusion that the complex carbon structures are stable at high temperature leads to the suggestion that an infinite variety of low energy allotropes can be constructed by assembling smallest radius nanotubes among themselves and with larger radius ones. Even if the initial structures prove to be difficult or impossible to fabricate, at least some of the allotropes obtained in this way can be highly stable. Finally, the aggregation of hypothetical, small, low energy clusters and nanotubes is of interest in its own right as it can provide a way for the systematic generation of new crystal structures [16].

The NVT ensemble was also used, with the same conditions and Nosé–Hoover dynamics, but it turned out to be costly and more artefactual. In this case, for the same internal temperature, we have carried out 1 ps runs on two systems: the (4, 4)/(2, 2) and (3, 0) dimers. The energies were converged as of the start of the simulation and no structural transitions could be detected. A linear fit of the energies of 1000 points gave an horizontal line with $y_0 = -3734.7$ (eV) and $y_0 = -3721.7$ (eV), corresponding to binding energies of -8.908 (eV/atom) and -8.367 (eV/atom) respectively. These calculations reaffirm the reliability of the NVE ensemble in predicting the stability of the geometric configurations for the dimers. The NVT simulations, as implemented in CASTEP, are not well suited to the calculation of 3D periodic models.

The systems that were not investigated by MD were optimized first with the BFGS algorithm and then the atomic positions were randomly modified with small displacements of up to 0.5 Å. For all cases no lower energy structures were found and the optimized structures resulted in being the same as previously. This procedure has eliminated highly metastable states, but does not guarantee high temperature stability.

We have investigated dimers of the smallest possible nanotubes by geometry optimizations and MD. We have found that they can bind strongly without applied pressure and that the

resulting structures have the largest possible interlinkage with sp^3 type coordination. The dimers and solids were energetically very stable and should be observable at high temperatures (273 K at least). The smallest radius nanotubes can also bind to larger radius nanotubes, resulting in stable dimers and mixed nanotube solid phases with equal and different radius nanotubes. The consequences are dual. On the one hand there are phases of the smallest radius nanotubes that are sp^3 bonded and are related to the diamond structure. On the other hand, there exist stable mixed nanotube phases, allowing the construction of strongly bound nanotube bundles with large corrugation. This application can yield stronger nanotube based materials and constitute an important step towards the resolution of problems associated with slippage and superstrong nanoropes. It is proposed that large radius nanotubes should be mixed with the smallest radius ones in order to obtain densely bound carbon bundles with enhanced mechanical properties. This method is considered a technologically challenging alternative to the irradiation of nanotube bundles, with the advantage that the structure of individual, large nanotubes will not be significantly degraded. The multiplicity of stable carbon phases obtained by mixing nanotubes of smallest radius is infinite and anticipates the construction of solids of large stiffness. The results on the mixing of C_{20} chains/(4, 4) tubes shows that the structures are stable minima. They possess a large interlinkage and corrugation energies, providing another possible route to the improvement of the slippage properties of carbon nanotube bundles. Other clusters can bridge nanotubes and it is proposed that diamondoids, given their self-assembly and sp^3 bridging characteristics, deserve further investigation.

This work has pointed out the variety of stable phases and structures that can result from mixing smallest radius nanotubes, smallest with larger radius nanotubes, and larger radius nanotubes with small clusters. All these have potentially novel applications as high strength materials. Nevertheless, the carbon allotropes studied are among the lowest energy ones ever found. They are of interest in their own right, and the assembly that we have described can be interpreted as a systematic way for generating new carbon solids, even if the starting structures are not stable.

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