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Bundle and chirality influences on properties of carbon nanotubes studied with van der Waals density functional theory

Heiko Dumlich[*,1], **Michael Gegg**[1], **Frank Hennrich**[2], and **Stephanie Reich**[1]

[1] Fachbereich Physik, Freie Universität Berlin, Arnimallee 14, 14195 Berlin, Germany
[2] Institut für Nanotechnologie, Karlsruhe Institute of Technology, 76021 Karlsruhe, Germany

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[*] Corresponding author: e-mail heiko.dumlich@fu-berlin.de, Phone: +49-30-83856157, Fax: +49-30-83856081

We study the binding strength and intertube distance of carbon nanotube bundles in dependence of their structure (chirality) with van der Waals density functional theory. We try to understand the bundling and debundling process of nanotube bundles and test whether an influence of chirality exists. The distance between the nanotubes in the bundles vary only in a small range within 3.3 and 3.4 Å, without any chiral angle and diameter dependence. We find an increase of van der Waals energy per length with increasing diameter of the nanotubes $\left(E_{\mathrm{vdW}}^{\mathrm{length}} \propto d \text{ or } \sqrt{d}\right)$ for tubes with diameters between 5.6 and 27.3 Å, but no obvious correlation between the chirality of the tubes and the van der Waals energy per length. The van der Waals energy per atom is decreasing with increasing tube diameter $\left(E_{\mathrm{vdW}}^{\mathrm{atom}} \propto 1/d \text{ or } 1/\sqrt{d}\right)$.

1 Introduction Carbon nanotubes possess unique electronic and mechanical properties that depend to a large extend on their one dimensionality, but also on the exact arrangement of the carbon atoms that constitute their tubular structure [1, 2]. The arrangement of carbon atoms is called chirality and allows carbon nanotubes to be semiconducting, semi-metallic or metallic, as well as having modified mechanical properties in dependence of the nanotube chirality. In macroscopic amounts nanotubes are almost certainly found in bundles. Bundles develop, because nanotubes attract each other and cluster into bundles. Bundling changes the mechanical and electronic properties, as the one dimensionality character is reduced and the neighboring tubes interact through van der Waals interaction [3–8].

Isolated tubes are desired to study the extraordinary properties of nanotubes which are induced by their one dimensionality. Therefore the bundles need to be destroyed and tubes have to be isolated. This is achieved by the use of a combination of sonication or centrifugation and surfactants, e.g., sodium dodecyl sulfate (SDS) [9–12]. However the process of bundling and debundling is not well understood. Especially the influence of the chirality of the tubes on the binding strength is interesting, as this might help to explain the selectivity of certain surfactants or debundling methods for certain chiralities [13–16]. We study the binding strength in dependence of the chirality for inner tubes of nanotube bundles with a van der Waals density functional developed by Dion et al. [17], which was shown to be applicable to bundles of nanotubes [18].

In this paper we determine the intertube distance and van der Waals binding energy of monochiral carbon nanotube bundles as a function of chirality by van der Waals density functional theory. The intertube distances vary in a small range of 3.3–3.4 Å independently of chiral angle and diameter. The van der Waals energy per atom shows a $1/d$ or $1/\sqrt{d}$ dependence. For the diameters studied, the van der Waals energy per length shows a linear or $\sqrt{d}$ dependence on tube diameter.

2 Computational methods We performed density functional theory calculations with the *ab initio* package SIESTA [19–21]. To derive a decent bundle geometry we optimized the geometry of isolated tubes in the generalized gradient approximation parameterized by Perdew et al. [22], which is good in modeling covalent bonds within the nanotubes. First we optimized the lattice constant of isolated tubes by minimization of the total energy in dependence of the lattice constant. The geometry optimization was then performed within the conjugate gradient method to a maximal force tolerance of 0.04 eV/Å. The optimized coordinates of the isolated tubes were used to calculate the properties (binding strength and intertube distance) of the carbon nanotube bundles with the van der Waals density functional parameterized by Dion et al. [17]. We placed the relaxed tube in a hexagonal unit cell with periodic boundaries, see Fig. 1 for the example of a bundle of (14, 0)-tubes. The bundle has an infinite number of tubes (bulk-bundle). Our calculation is a good approximation for inner tubes (*I* in Fig. 1) of the bundle, as bundles have a trigonal structure where inner tubes *I* have six neighbors $(E_1, \ldots, E_6)$. External tubes E_i have less than six neighbors, e.g., three interacting neighbors (e.g., E_1 interacts with E_6, *I*, E_2) for the structure presented in Fig. 1. Triangle like interaction holes exist at the area where three tube surfaces meet (e.g., between E_1, E_2, and *I*). The inner tube was rotated in its unit cell for certain chiralities to include effects that arise from orientation. Therefore we did not perform a relaxation of the bundle structure resulting in remaining stress. The distortion caused by the bundling has little or no effect on the properties for tubes with diameters below 15 Å [8, 23].

The calculations used norm conserving non-local pseudopotentials [24]. We used a double-ζ (DZ) basis set to describe the valence electrons. Cutoff radii for the s and p orbital of the carbon atoms were $r_s = 5.949$ Bohr and $r_p = 7.450$ Bohr. The mesh cutoff for the real-space integration corresponded to about 350 Ry. We used a *k*-point sampling between $1 \times 1 \times 10$ and $1 \times 1 \times 14$ *k*-points in the Monkhorst–Pack scheme [25] to calculate the total energies; *z*-axis chosen as the tube-axis.

The difference between minimal total energy of the bundle and total energy of the isolated tube is regarded as total van der Waals energy. Dividing through the number of atoms of the unit cell yields the van der Waals energy per atom. Dividing the total van der Waals energy through the length of the unit cell yields the van der Waals energy per length. The intertube distance can be derived from the optimized *xy*-unit cell length by subtraction of the diameter of the tube. The optimized *xy*-unit cell length was derived by minimization of the total energy in dependence of *xy*-unit cell length. We derived the diameters of the tubes from the averaged values of the distances between the individual tube atoms to the center axis of the geometrically optimized tube.

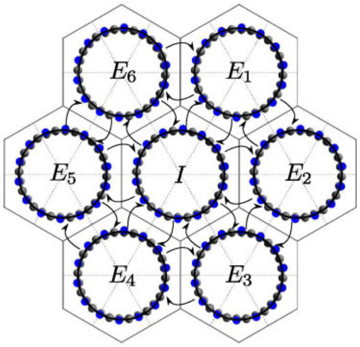

Figure 1 (online color at: www.pss-b.com) Sketch of a bundle of seven (14, 0)-tubes. The hexagon in the middle represents the unit cell for our bundle calculations. Lines connecting the middle points of the hexagons are added and every second atom is marked to better illustrate the symmetry of the system, which is trigonal. Triangle holes exist between three adjacent tubes (around the point of three adjacent hexagonal unit cells). External tubes E_i interact with three neighbors, inner tubes *I* interact with six neighbors.

3 Results and discussion

Table 1 presents an overview of the intertube distances and the van der Waals energies between the tubes of the bundle in dependence of their chirality and diameter; the values marked by an asterisk are taken from Dumlich and Reich [26] by averaging over all orientations of the tubes in the bundle. The orientation only affects chiralities with C_6-axis, e.g. (6, 6), details can be found in Ref. [26].

The intertube distance has no systematic dependence on chirality and diameter, which agrees with the major part of the literature [27]. The lack of chirality dependence results from the imperfect matching of the atomic structure of the neighboring tubes in the bundle. Each inner tube has six neighbors in a trigonal lattice. This leads to an averaged

Table 1 Binding energies and intertube distances for bundles of tubes of various chiralities and diameters.

(*n*, *m*)	*d* (Å)	*D* (Å)	$E_{\mathrm{vdW}}^{\mathrm{atom}}$ (meV)	$E_{\mathrm{vdW}}^{\mathrm{length}}$ (eV/Å)
(7, 0)	5.63	3.32	31.9	0.206
(8, 0)	6.41	3.31^*	31.2^*	0.231^*
(5, 5)	6.92	3.34^*	29.6^*	0.237^*
(9, 0)	7.19	3.26^*	31.8^*	0.264^*
(8, 2)	7.31	3.31^*	29.5^*	0.247^*
(7, 4)	7.68	3.29	28.7	0.253
(10, 0)	7.96	3.32	27.4	0.253
(6, 6)	8.27	3.26^*	29.0^*	0.279^*
(8, 4)	8.41	3.27	27.9	0.271
(11, 0)	8.75	3.34	25.9	0.263
(12, 0)	9.53	3.33^*	25.3^*	0.280^*
(7, 7)	9.62	3.29	25.1	0.282
(8, 6)	9.65	3.25	23.1	0.259
(8, 8)	10.98	3.35	22.4	0.288
(14, 0)	11.10	3.32^*	23.9^*	0.309^*
(9, 9)	12.34	3.38	20.3	0.294
(12, 6)	12.56	3.28^*	21.9^*	0.321^*
(10, 10)	13.70	3.29^*	22.4^*	0.360^*
(20, 0)	15.81	3.29	19.7	0.363
(12, 12)	16.42	3.28^*	20.5^*	0.394^*
(20, 20)	27.33	3.28	15.4	0.493

For chiralities marked with an asterisk the values were derived by averaging over values for various orientations of the tubes in the bundle as presented in Dumlich and Reich [26]. The diameters *d* are for the single tubes of the bundles, the intertube distance *D* is the nearest distance between the walls of two neighboring tubes of the bundle, $E_{\mathrm{vdW}}^{\mathrm{atom}}$ is the intertube binding energy per atom and $E_{\mathrm{vdW}}^{\mathrm{length}}$ is the intertube binding energy per length.

interaction between neighboring tubes, as arrangement of all surfaces between neighboring tubes is not geometrically possible. Considering real bundles at room temperature, we have to consider the effect of rotations, vibrations, twists, and defects which reduce effects of chirality.

We find intertube distances between 3.25 and 3.38 Å with a statistical average value of (3.30 ± 0.01) Å. Our results compare quite well to the intersheet distance for graphite of 3.35 Å (Ref. [29]) and also to intertube distances of 3.2–3.4 Å found previously [3, 6, 30, 31].

We find a $1/d$ or $1/\sqrt{d}$ dependence of the van der Waals energy per atom, see Fig. 2. The adjusted R^2-value, which is a measure of how good the model fits the data, for $1/d$ is $R^2_{1/d} = 0.929$ and for $1/\sqrt{d}$ it is $R^2_{1/\sqrt{d}} = 0.936$. The fitted functions for both models are $E^{\text{atom}}_{\text{vdW}}(d(\text{Å})) = 125.0/d + 12.0\,(\text{meV})$ and $E^{\text{atom}}_{\text{vdW}}(\sqrt{d(\text{Å})}) = 78.4/\sqrt{d} + 0.04\,(\text{meV})$. Both models describe the correlation between the van der Waals energy per atom $E^{\text{atom}}_{\text{vdW}}$ and d about equally well. Large tube diameters transform the bundle structure to a structure of two carbon layers, which are the walls of the neighboring tubes, followed by large empty spaces. This might lead to the idea to compare the binding energy to bilayer graphene, however, triangle holes increase in size and reduce the binding energy per atom. We get a rough estimate of $E^{\text{bundle}}_{\text{min}} = 8{-}13\,\text{meV/atom}$ for the minimal binding energy for which the bulk bundle can be stable, which we extracted from the fitted functions in combination with the maximal diameter of single walled carbon nanotubes of about 10 nm [28].

Our results show good agreement for the (8, 0)-bundle with $E^{\text{atom}}_{\text{vdW}} = 31.2\,\text{meV}$ compared to $E^{\text{atom}}_{\text{vdW}} = 30\,\text{meV}$ [18] and for armchair-bundles reported by Lu [3], see Fig. 2. Kleis et al. [18] used the same van der Waals density functional and the non-self-consistent (post-GGA) implementation [17] compared to the self-consistent approach [21] of our study, however, the results are in good agreement. The agreement between the two methods concurs to previous results that the effect of the self-consistency is low [32]. The binding energies per atom of carbon nanotube bundles are lower than in graphite; $E^{\text{atom}}_{\text{vdW}} = 39.5{-}45.7\,\text{meV}$ derived with the same parameters as for the bundles for the AA and AB stacking. Experimental values for the van der Waals energy per atom were derived from graphite with $\left(35^{+15}_{-10}\right)$ meV and more recently (52 ± 5) meV, which are comparable to our values for graphite [29, 33].

We find a linear or $\sqrt{d}$ dependence between diameter and the van der Waals energy per length, see Fig. 3. The adjusted R^2-value, for d is $R^2_d = 0.952$ and for $\sqrt{d}$ it is $R^2_{\sqrt{d}} = 0.959$. The fitted functions for both models are $E^{\text{length}}_{\text{vdW}}(d(\text{Å})) = 0.0131d + 0.1533\,(\text{eV/Å})$ and $E^{\text{length}}_{\text{vdW}}(\sqrt{d(\text{Å})}) = 0.0975\sqrt{d} - 0.0192\,(\text{eV/Å})$. Both models succeed to describe the diverging behavior for large values of d $\left(\lim_{d\to\infty} E^{\text{length}}_{\text{vdW}}(d) \to \infty\right)$ as increasing tube diameters lead to increasing tube circumferences with more atoms (linear increase [34])/larger areas participating in the binding between the tubes. However, the increasing triangle holes lower the binding energy per atom, which lowers the order of divergence.

Our result of $E^{\text{length}}_{\text{vdW}} = 0.231\,\text{eV/Å}$ shows good agreement for the (8, 0)-bundle compared to $E^{\text{length}}_{\text{vdW}} = 0.225\,\text{eV/Å}$ reported previously. [18] For the (10, 10)-bundle we derive a value of $E^{\text{length}}_{\text{vdW}} = 0.360\,\text{eV/Å}$, which lies between $E^{\text{length}}_{\text{vdW}} = 0.286\,\text{eV/Å}$ (Ref. [27]) and $E^{\text{length}}_{\text{vdW}} = 0.377\,\text{eV/Å}$ derived for a bulk-bundle of tubes [3].

In Ref. [27] the interaction between the tubes was modeled by a continuum model and Lennard–Jones potentials with Lennard–Jones constants derived from graphite. The electron density was continuously/uniformly distributed on the surfaces of cylindrical tubes to model a bundle of nanotubes with various chiralities and same diameter. A fit to their data lead to an energy function of

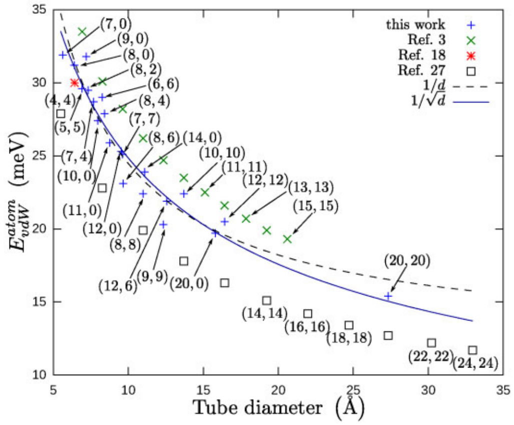

Figure 2 (online color at: www.pss-b.com) Calculated van der Waals energy per atom plotted over single tube diameter for various nanotube bundles. The calculated values are compared to literature values; for those that are available [3, 18, 27].

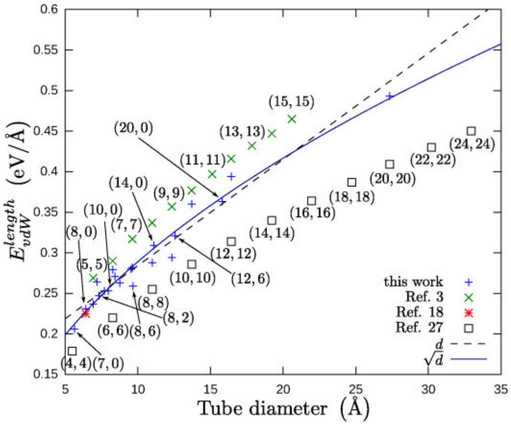

Figure 3 (online color at: www.pss-b.com) Van der Waals energy per length plotted in dependence of diameter for various nanotube bundles. The calculated values are compared to literature values; for those that are available [3, 18, 27].

$E_{\mathrm{vdw}}^{\mathrm{length}}(\sqrt{d(\text{Å})}) = -0.0803\sqrt{d} + 9.39 \times 10^{-3}(\text{eV/Å})$. [27] In Ref. [3] the van der Waals interaction was modeled by Lennard–Jones pair potentials with parameters derived from a measurement on single crystal graphite. Each atom was assumed to be the center of a spherically symmetric electron distribution. The structure of the nanotubes was obtained by conformal mapping of a graphite strip onto a cylindrical surface. The total intertube interaction was minimized in dependence of the intertube distance to obtain a fit of $E_{\mathrm{vdW}}^{\mathrm{atom}}(\sqrt{d(\text{Å})}) = 89.8/\sqrt{d}(\text{meV})$ for the van der Waals binding energy per atom [3]. Both models, continuum model and discrete atom–atom model, contain rough assumptions, in opposing directions [3, 27]. Our van der Waals density functional calculation should lead to results which are closer to reality as non-uniformly distributed electron densities are used and the discrete atomic structure is considered. This agrees with the result that our values are between the values of the discrete and continuum model.

An experimentally based value for the binding energy between two double walled carbon nanotubes of 4 nm diameter was derived with $E_{\mathrm{vdW}}^{\mathrm{length}} = 0.225\,\text{eV/Å}$ [35], which is comparable to our values for the van der Waals energy per length that lie between 0.206 and 0.493 eV/Å.

4 Conclusion In summary we presented intertube distances and van der Waals energies of various chiralities for inner carbon nanotubes of bundles. The intertube distances and binding strengths between the tubes are independent of chiral angle. We find a diameter dependence for the van der Waals energy, meaning the curvature of the carbon nanotubes is the most important factor for the intertube binding strengths. The intertube distance does not depend on the diameter.

In a future work it would be interesting to study the properties of an external tube, which interacts with only three or less neighbors and has a lower influence from its neighbors than an inner tube. External tubes are expected to show chirality dependence on its properties, e.g., on binding strength, as structure was found to have an influence, e.g., for monochiral C_6-axis tube bundles.

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