# Lennard-Jones Parameters for Small Diameter Carbon Nanotubes and Water for Molecular Mechanics Simulations from van der Waals Density Functional Calculations

M. Kaukonen,*[a] A. Gulans,[a] P. Havu,[a] and E. Kauppinen[a]

Lennard-Jones (LJ) parameters are derived for classical nonpolarizable force fields for carbon nanotubes (CNTs) and for CNT–water interaction from van der Waals (vdW) enhanced density functional calculations. The new LJ parameters for carbon–carbon interactions are of the same order as those previously used in the literature but differ significantly for CNT–water interactions. This may partially originate from the fact that in addition to pure vdW interactions the polarization and other quantum mechanics effects are embedded into the LJ-potential. © 2012 Wiley Periodicals, Inc.

DOI: 10.1002/jcc.22884

## Introduction

Carbon nanotube (CNT) is a novel material with exceptionally high thermal conductivity and mechanical strength. Depending on the chirality, CNTs exhibit different electrical properties. These attributes make the material suitable for a wide range of applications including flexible electron conductors and semiconducting devices, sensors, hardening of materials like cement, polymer films,[1–3] fuel storage, and solar cells.[4–6] In biological applications, CNTs can work as ion pores across cell membranes, as systems for drug delivery or as tools for targeted cell death.[7,8]

Design of such devices requires a substantial research, which also includes atom scale modeling. Quantum mechanical (QM) simulations have proven useful for various problems, where single CNTs are considered. However, most of the applications mentioned above involve large number of bundles of CNTs, where the van der Waals (vdW) interactions play an important role. The system size becomes so large that only empirical potentials are computationally affordable. The major difficulty is how to obtain accurate parameters for this types of forces as experiments suitable for their fitting are rarely available and the reliability of standard density functional theory (DFT) of weak noncovalent interactions are questionable. For that reason, the Lennard-Jones (LJ) parameters for CNT have been mainly obtained by fitting to experimental data available for either graphite or amino acids.[9–11]

In this article, we parametrize the noncovalent interactions using recent improvements in DFT, namely the vdW density functional (vdW-DF).[12,13] Its usefulness for noncovalent interactions has been shown in a number of studies summarized in Ref. [14]. The vdW-DF approach is computationally much cheaper than *ab initio* quantum chemistry methods such as MP2 and CCSD(T), which have been mainly applied to small model systems.[15,16] There are, however, other cheap alternatives to introduce the noncovalent interactions in the DFT description. However, these are essentially empirical approaches.[17–21] The variant we use here, vdW-DF, allows one to model noncovalent interactions at high accuracy without any empirical parameters. Especially, in the case of the CNT–molecule interactions, it has been shown that the physical picture a process depends on the details of LJ-parameters used in the simulation, as was demonstrated by Hummer et al.[22] with water diffusion through CNTs.[22] Here, parameters for the interaction between (i) two parallel nanotubes and (ii) nanotube and water molecule are derived.

This article is structured as follows: in the methods section, we start by describing the vdW-DF framework and proceed by outlining the fitting and testing procedures. Finally, we conclude by giving recommendations how to apply the obtained parameters in classical molecular mechanics (MM) or in mixed QM/MM simulations.

## Methods

### vdW-DF calculations

To perform vdW-DF calculations, we use modified versions of electronic structure codes SIESTA and VASP.[23,24] The SIESTA code is only used for the parameter fitting for the interaction between two parallel CNTs (Section LJ parameters for two rigid and parallel CNTs). The CNT–water calculations and all testing is performed out by the VASP code.

In the vdW-DF method, the exchange-correlation energy in this approach is defined as follows:

$$E_{xc}[n] = E_x^{revPBE}[n] + E_c^{LDA}[n] + E_c^{nl}[n], \qquad (1)$$

[a] M. Kaukonen, A. Gulans, P. Havu, E. Kauppinen
Department of Applied Physics, Aalto University,
School of Science and Technology, P.O. Box 11100,
FI-00076 AALTO, Finland
E-mail: markus.kaukonen@iki.fi

where the $E_x^{revPBE}[n]$ and $E_c^{LDA}$ describe the semilocal exchange and local correlation, respectively. The vdW interaction is described by nonlocal functional $E_c^{nl}[n]$, which is defined as

$$E_c^{nl}[n] = \frac{1}{2} \int n(\mathbf{r})\phi(\mathbf{r},\mathbf{r}')n(\mathbf{r}')d\mathbf{r}d\mathbf{r}', \tag{2}$$

where $\phi(\mathbf{r},\mathbf{r}')$ is the kernel function derived from the adiabatic-connection fluctuation-dissipation theorem using the plasmon-pole approximation to the dielectric function to make the approach tractable[25] and $n(\mathbf{r})$ is the electron density.

The SIESTA code is based on the linear combination of atomic orbitals. In the present calculations, the double-$\zeta$ with polarization split valence basis set with energy shift of 50 meV is utilized. A high mesh cut-off of 250 Ry is used to minimize the effect of the computational grid on the results. The convergence of these parameters has been discussed in Refs. [26, 27]. The localized basis sets used by the SIESTA code help to significantly reduce the computational effort in the calculations. However, this comes at the price that the basis set superposition error is introduced. We estimate it using the counterpoise correction.[28, 29]

In the VASP calculations, plane waves with an energy cutoff of 325 eV are used to describe the pseudo-valence electron wave functions. The core electrons are described using the projector augmented-wave method.[30]

Unless stated otherwise, in all calculations structures are optimized until the maximum force on an atom is less than 0.01 eV/Å. The Brillouin zone is sampled using at least 10 evenly spaced k-points along the CNT axis direction. Unless otherwise stated, one periodic cell along the tube axis is used in the vdW-DF calculations. The periodic boundary conditions in all dimensions are used. The periodic images of CNTs are separated by vacuum gaps of ∼10 Å. Our tests show that the CNT–CNT interaction becomes negligible at this separation.

## Classical force field and classical simulations

For the fitting and testing of the LJ parameters, we use the GROMACS simulation package.[31] A cutoff of 10 Å for noncovalent interactions is applied. Periodic boundary conditions are used in the same fashion as in the vdW-DF calculations described above. The LJ parameters are derived for the optimized potentials for liquid simulations for all atoms (OPLS/AA) force field, but they can be easily converted to other force fields.[32–34]

In the OPLS/AA simulations, total energy for distant pairs of atoms $i$ and $j$ is calculated as

$$E^{LJ}(r) = \sum_{i<j} 4\varepsilon_{ij}\left(\frac{\sigma_{ij}^{12}}{r_{ij}^{12}} - \frac{\sigma_{ij}^6}{r_{ij}^6}\right), \tag{3}$$

where $r_{ij}$ is the distance between the $i$-th and $j$-th atoms. This interaction is valid for atoms not connected by bonds or for atoms separated by more than three bonds. For atoms separated by three bonds, this interaction is scaled by a factor of 0.5. The interactions between closely bonded atoms are described by the bonded terms of the MM-potential (bond, angle, and dihedral terms) with no LJ-interaction. The parameters $\sigma_{ij}$ and $\varepsilon_{ij}$ stand

for the equilibrium distance for the pair and the corresponding interaction energy, respectively. Similarly, Coulomb interactions are calculated between atom pairs. However, in this study, the Coulomb interactions are zero due to the zero partial charges at atoms of CNTs. For a heteronuclear pair of atoms, the LJ parameters are calculated as the geometric average

$$\sigma_{ij} = \sqrt{\sigma_{ii}\sigma_{jj}}, \varepsilon_{ij} = \sqrt{\varepsilon_{ii}\varepsilon_{jj}}. \tag{4}$$

In OPLS/AA force field calculations, the energy of a stretched covalent bond is expressed as

$$E^b(r) = \sum_{i<j} \frac{1}{2}k_{ij}^b(r_{ij} - b_{ij})^2, \tag{5}$$

where $k_{ij}^b$ is the force constant for the bond stretching and $b_{ij}$ is the lowest energy atom–atom distance.

For bond angle energetics, we use

$$E^a(\theta_{ijk}) = \sum_{ijk} \frac{1}{2}k_{ijk}^a\left(\theta_{ijk} - \theta_{ijk}^0\right)^2, \tag{6}$$

where $k_{ijk}^a$ is the angle force constant and $\theta_{ijk}^0$ is the equilibrium angle. To keep the cross sections of CNTs nearly circular, we apply proper dihedral potentials

$$E^d(\theta_{ijkl}) = \sum_{ijkl} k^d\left(1 + \cos\left(n\theta_{ijkl} - \theta_{ijkl}^0\right)\right). \tag{7}$$

Here, $k^d$ is the dihedral force constant and $\theta_{ijkl}^0$ is the equilibration dihedral angle. The periodicity of the proper dihedral function is given by the integer $n$.

## LJ parameters for two rigid and parallel CNTs

For each pair of CNTs: $2\times\{(4,4), (5,5), (6,6), (7,7), (8,8), (9,9), (6,0), (8,0), (10,0), (12,0),$ or $(14,0)\}$, the following procedure was carried out. First, a set of single CNTs with different bond lengths were generated using program TubeASP.[35] Second, the equilibrium bond length for each single CNT was obtained by a third-order polynomial fit of the vdW-DF total energy with respect to the bond length using the atomic simulation environment (ASE)-package.[36] Finally, the positions of atoms in each single CNT were relaxed by vdW-DF.

Once the geometry of a single nanotube was established, the wall-to-wall distances ($r$ in the inset of Fig. 1) of two CNTs were varied from 2.6 to 8.5 Å with no further geometry relaxations (the rotational degrees of freedom of the CNTs were not optimized).

The total energy $E_{AB}$ is used to calculate the interaction energy $E_{int}(r)$ of CNTs A and B, which is defined as

$$E_{int}(r) = E_{AB}(r) - E_A - E_B, \tag{8}$$

where $E_A$ and $E_B$ are the total energies of the individual CNTs. This interaction energy contains only the noncovalent contributions, as the deformations of the CNTs are not allowed and the intratube interactions are canceled out.
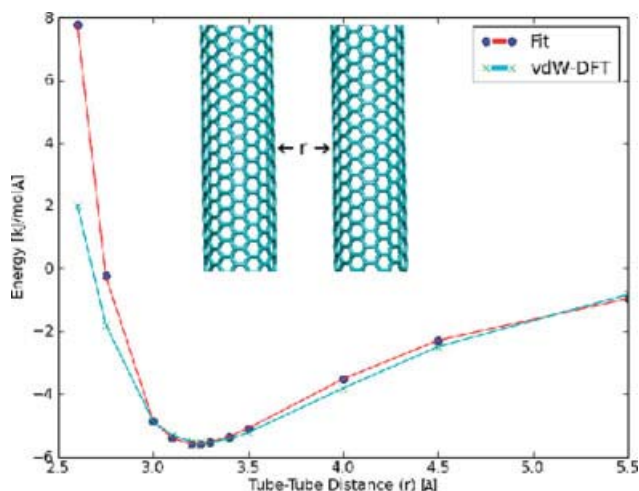
**Figure 1.** An example for the fitting of the LJ adhesion energy with respect to vdW-DF energy. There are two rigid parallel (9,9) CNTs in the figure. The LJ parameters of the classical force field are varied using near minimum weighted least squares fit. The fitting clearly fails at the small intertube distance.

The interaction energy of a distant pair of atoms in the MM force field calculations is obtained with trial LJ-parameters $(\sigma, \varepsilon)$ for the same geometries as in the SIESTA vdW-DF calculations. In these classical calculations, each of the two CNTs consists of 16 unit cells along the tube axis. The two other dimension of the unit cell are the same as in the vdW-DF simulations. The LJ parameters are obtained by a minimization of the weighted mean square deviation of the LJ interaction energies with respect to the one obtained with vdW-DF using Fmin algorithm of Scientific Python.[37] The calculations are performed for intertube distances 2.6–8.5 Å with a weight factor of 100 near the equilibrium distance (3.0–3.5 Å) and one elsewhere. As an example, the fit for a pair of (9,9) CNTs is shown in Figure 1. In the figure, it can be observed that the LJ potential fitted in the form of eq. (3) deviates from the reference vdW-DF result at short distances. This is a feature of the simple LJ potential. More accurate description would involve more elaborate potentials such as Buckingham potential or potentials including three-body terms.[38]

### LJ parameters for CNT–water interaction

A similar fitting procedure as for two parallel CNTs described above was carried out for a single water molecule outside a single CNT. Initially, a water molecule was positioned with a CNT-wall to oxygen atom of water distance $r = 3.0$ Å (Fig. 2). Thereafter,
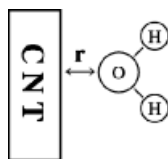


**Figure 2.** Schematics of the geometries used for deriving the LJ parameters for the CNT–water interaction. The water geometry is optimized first by minimizing the positions of its hydrogen atoms. In the subsequent calculations with fixed geometries, the water–CNT distance ($r$) is varied (2.6–8.5 Å).

the two hydrogen atoms of water were allowed to relax to optimize its rotational degree of freedom. Subsequently, the water–CNT distances were varied without further geometry relaxation using the same distances as with parallel nanotube systems described earlier. This fitting was done for the (6,6) and (8,0) CNTs. For the (6,6) and (8,0) CNTs there were five and three unit cells in the vdW-DF calculations, respectively, along the tube axis to prevent water interacting with its periodic images.

### Bonded terms

It is important to include reasonable energy parameters also for the bonded terms of the classical force field to describe systems with CNTs. Even if one is interested mainly in the intertube and tube–molecule interactions, the intratube bonded terms are important, because the deformation of the CNTs depend on the interplay between the bonded terms and the LJ interactions of the classical force field.

The bonded terms in the classical MM energy (bond, angle, and proper dihedral) were calculated based on QM Hessian using the approach suggested by Seminario.[39] In these calculations, the geometries of nonperiodic hydrogen terminated CNTs were optimized (an example of a relaxed structure is shown in Fig. 3) and the Hessians were evaluated by the computational chemistry program Turbomole.[40] Exchange-correlation functional was used,[41,42] with the SV(P) basis set and resolution of the identity (RI)-approximation to reduce the number of integrals to be evaluated.[43,44] The bonded parameters were obtained as averages over atoms in the middle along the tube axis of the CNT. The bonded parameters are shown in Table 1 and their forms in eqs. (5)–(7).

It can be noted that the zigzag CNTs have the order of 10% stronger force constants compared with the armchair ones. This is agreement with results by Sánchez-Portal et al.[45] who found that zigzag tubes have a higher Young's modulus.[45]
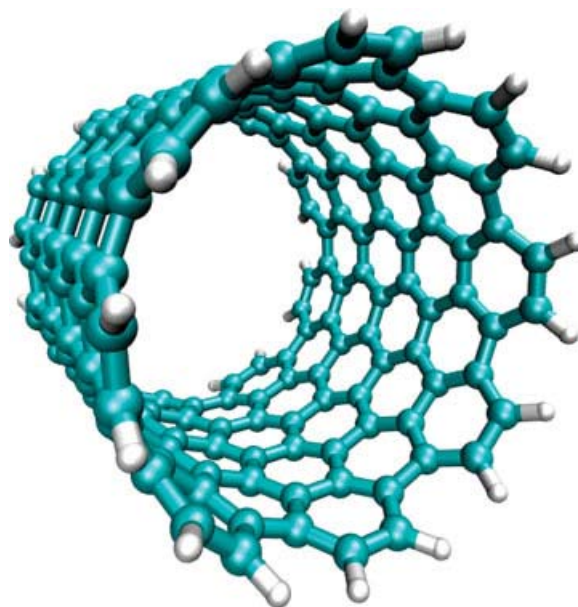


**Figure 3.** A hydrogen terminated (8,8) CNT. The bonded terms for the classical force field were derived using H-terminated CNTs with optimized geometries.

**Table 1.** The fitted parameters for bonded interactions in conducting and semiconducting CNTs with tube diameters less than ~1.2 nm are given.

| Tube | $b_0$[nm]/ $k_b$[kJ mol$^{-1}$nm$^{-2}$] | $\theta$[deg]/ $k_\theta$[kJ mol$^{-1}$rad$^{-2}$] | Multiplicity/ $k_\phi$ [kJ mol$^{-1}$] |
|---|---|---|---|
| (4,4) | 0.1441 / 228,145 | 118.5 / 1023 | 180; 2 / 38.7 |
| (5,5) | 0.1437 / 237,917 | 119.0 / 1048 | 180; 2 / 38.1 |
| (6,6) | 0.1434 / 244,955 | 119.3 / 1055 | 180; 2 / 37.6 |
| (7,7) | 0.1433 / 247,233 | 119.5 / 1068 | 180; 2 / 38.7 |
| (8,8) | 0.1432 / 248,653 | 119.7 / 1071 | 180; 2 / 40.4 |
| (9,9) | 0.1431 / 251,618 | 119.8 / 1047 | 180; 2 / 44.7 |
| (6,0) | 0.1425 / 253,244 | 119.9 / 998.7 | 180; 2 / 36.4 |
| (8,0) | 0.1435 / 262,984 | 118.1 / 1250 | 180; 2 / 51.9 |
| (10,0) | 0.1434 / 270,723 | 118.8 / 1313 | 180; 2 / 53.3 |
| (12,0) | 0.1432 / 281,015 | 119.2 / 1371 | 180; 2 / 54.4 |
| (14,0) | 0.1430 / 284,990 | 119.4 / 1386 | 180; 2 / 54.1 |

The bonding parameters $b_0$ and $k_b$ stand for equilibrium bond length and the bond force constant. Parameters $\theta$ and $k_\theta$ are the minimum energy angle and the angle force constant. The proper dihedral angle is set to 180° with multiplicity of two. The calculated dihedral force constants $k_\phi$ are shown in the last column.

All the bonded force constants get stronger with the increasing CNT diameter. This is natural because larger diameter means less curvature and less deviation from the ideal $sp^2$ bonding. The C—C bond force constants are on the weaker side of the spectrum of OPLS/AA C—C bond family and the angle ones at the stronger end of the parameter space of carbon species.

## Results

### New LJ parameters for carbon nanotubes

In general, the new LJ parameters for CNTs are close to the literature values. For instance, values for $\sigma_{CC} = 0.34$–0.36 nm (C$\cdots$C distance at the energy minimum) and $\varepsilon_{CC} = 0.29$–0.36 kJ/mol (the depth of the energy minimum) have been applied for CNTs.[11,22,46] The fitted LJ parameters for classical force field [eq. (3)] are shown in Table 2. The LJ parameters are independent

on the nanotube diameter and whether the CNT is metallic or semiconducting. This is in agreement with earlier computational results stating that the polarization perpendicular to the tube axis is independent whether the tube is metallic or semiconducting.[47,48] However, it was also found earlier that the perpendicular polarizability depends on the second power of the tube radius.[47,48] We can partially explain our result of nearly constant $\varepsilon_{CC}$ by noting that the number of interacting carbon pairs increases as second power of tube radius. The average values found here are: $\sigma_{CC} = 0.3534$ (C–C minimum energy distance), $\varepsilon_{CC} = 0.2906$ kJ/mol (minimum energy for a C–C pair) (Table 2). These values are used in the subsequent testing. The choice of average values is further motivated by the fact that using the individual values of the LJ-parameters (Table 2) instead of the average ones did not improve the results with respect to vdW-DF values.

### New LJ parameters for CNT–water interaction

The calculated energy parameter $\varepsilon$ for the oxygen atom in water for the CNT–water interactions are order of magnitude larger when compared to the standard OPLS/AA values (standard $\varepsilon_{OO} = 0.65$ kJ/mol, novel $\varepsilon_{OO} = 1.7$–8.9 kJ/mol). The position of the energy minimum for water oxygen gets shorter by 0.5–0.6 Å (standard $\sigma_{OO} = 3.17$ Å, novel $\sigma_{OO} = 2.6$–2.7 Å). Conversely, even a stronger binding of water (24 kJ/mol) on graphene is calculated by Feller and Jordan.[16] More indirectly, Birkett and Do also found that potential wells are too shallow when describing carbon black–water interactions with standard LJ-parameters (Ref. [49] and references therein). Our suggested values for LJ parameters for LJ-interaction between CNT and water are shown in Table 3, the combination rules for LJ parameters between different atom types are given in eq. (4).

In addition, nonzero LJ parameters for hydrogen in water interacting with CNTs are derived. The nonzero LJ-parameters are desirable, for example, in free energy calculations, where interactions are switched gradually off. In many cases, there is

**Table 2.** The calculated new LJ parameters for CNTs.

| Atom type | $\sigma_{CC}$ [nm] | $\varepsilon_{CC}$ [kJ/mol] |
|---|---|---|
| Std C | 0.3400 | 0.3612 |
| C in (4,4) | 0.3467 | 0.3312 |
| C in (5,5) | 0.3534 | 0.2929 |
| C in (6,6) | 0.3566 | 0.2913 |
| C in (7,7) | 0.3517 | 0.2893 |
| C in (8,8) | 0.3478 | 0.3025 |
| C in (9,9) | 0.3520 | 0.2838 |
| Armchair (avg.) | 0.3514 | 0.2985 |
| C in (6,0) | 0.3511 | 0.2980 |
| C in (8,0) | 0.3578 | 0.2647 |
| C in (10,0) | 0.3585 | 0.2576 |
| C in (12,0) | 0.3555 | 0.3167 |
| C in (14,0) | 0.3564 | 0.2683 |
| Zigzag (avg.) | 0.3559 | 0.2811 |
| Total (avg.) | 0.3534 | 0.2906 |

For comparison, also the parameters commonly used in the literature are given (Std C).[11]

**Table 3.** The calculated new LJ parameters for water interacting with armchair and zigzag CNTs (ArmCNT and ZigCNT in the table).

| System | $\sigma_{CO}$ [nm] | $\sigma_{CH}$ [nm] | $\varepsilon_{CO}$ [kJ/mol] | $\varepsilon_{CH}$ [kJ/mol] |
|---|---|---|---|---|
| StdCNT-H$_2$O | 0.3281 | 0 | 0.4845 | 0 |
| ArmCNT-H$_2$O | 0.3046 | 0 | 1.6072 | 0 |
| ZigCNT-H$_2$O | 0.3122 | 0 | 1.4454 | 0 |
| ArmCNT-H$_2$O(HW) | 0.3066 | 0.1933 | 1.4816 | 0.6257 |
| ZigCNT-H$_2$O(HW) | 0.3173 | 0.3067 | 0.6975 | 0.3981 |

For comparison, parameters resulting from standard OPLS/AA parameters for CNT: $\sigma_{CC} = 0.340$ nm, $\varepsilon_{CC} = 0.361$ kJ/mol and for water: $\sigma_{OO} = 0.317$ nm, $\varepsilon_{OO} = 0.650$, $\sigma_{HH} = 0.0$, $\varepsilon_{HH} = 0.0$ are shown at the first row (the standard OPLS/AA LJ parameters for water hydrogen are zero). The next two rows in the upper part of the table give LJ parameters for water interacting with armchair CNT and zigzag CNTs assuming zero LJ parameters for the water hydrogen. In the lower part of the table the LJ parameters for water interacting with either armchair or zigzag CNTs are given assuming nonzero LJ parameters for the water hydrogen. Water with LJ interacting hydrogens is indicated as H$_2$O(HW).

a risk for unphysical overlap of atom nuclei due to Coulomb attraction in case of zero LJ-interaction.

With the nonzero LJ parameters for hydrogen one gets for hydrogen either a short minimum energy distance and a deep potential well ($\sigma_{HH}$ = 1.1 Å, $\varepsilon_{HH}$ = 1.3 kJ/mol, second last row in Table 3) or alternatively a large minimum energy distance and a shallow well ($\sigma_{HH}$ = 2.7 Å, $\varepsilon_{HH}$ = 0.5 kJ/mol, the last row in Table 3). In the following section, we will test these alternatives.

As pointed out by Hummer et al.[22] small changes in the LJ-parameters can have drastic effect on the dynamics of the CNT–water system. Interestingly, they lowered the CNT–water interaction strength by at least a factor of two and found out the the filling of (6,6) CNTs with water became more pulse-like in time. Our results would indicate that the CNT–water interaction should be a factor two stronger compared to the interaction using standard parameters. This would imply that the pulse like filling of CNTs should be less likely. In addition, recent experimental findings by Cambré et al.[50] show that water is able to penetrate to smaller CNTs than predicted by earlier simulations.[50] This also points out that the water–CNT interaction may be stronger than believed.

## Tests

All the testing was carried out by comparing vdW-DF enhanced VASP 5.2 results with classical GROMACS data with the newly derived data with novel LJ and bonded parameters (in the figure, OLD-OPLS/AA and NEW-OPLS/AA, respectively). In the comparisons all-atom relaxed energy minimized geometries were used.

### Two parallel CNTs

In this test we compare the adhesion energy of two parallel infinitely long CNTs calculated by vdW-DF and by classical force field using the newly derived LJ-parameters and with literature value ones. In the testing two parallel CNTs are fully geometry optimized. The energy of this geometry is compared to the energy of two isolated CNTs to obtain the adhesion energy.

From Figure 4, one can see that the agreement between the classical force field and vdW-DF values is acceptable and there is a small improvement when moving from the literature LJ-parameters to the newly derived ones [the mean absolute error drops (MAE) from 0.50 to 0.26 kJ/mol for the armchair CNTs and from 0.50 to 0.25 kJ/mol for the zigzag ones].

In addition, it is found that setting the dihedral force constants to zero lead to a bigger deviation from the vdW-DF values. This observation demonstrates the importance of the interplay between the bonded and nonbonded interactions. Here, the discrepancy is due to the fact that when the dihedral forces are zero the tubes can deform more making more contact area and thus enhancing the the intertube vdW-bonding.

### Double-wall nanotubes

Adhesion energies for hypothetical double-wall CNT test systems are given in Table 4. These systems are at their relaxed energy minimum geometries (relaxed either by the classical force field or by vdW-DF).

Keeping in mind that the number of considered test cases is small, the data shown in Table 4 indicates that using the parameters introduced in this article are in better overall agreement with the reference vdW-DF data.
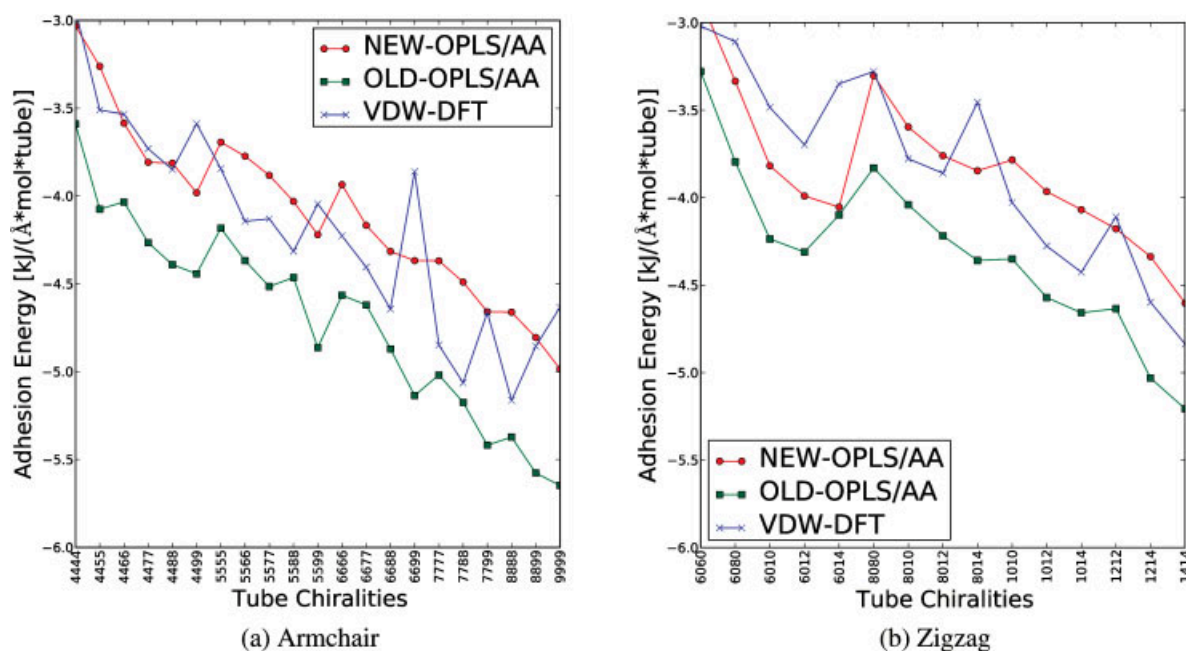


**Figure 4.** Fitting of the classical adhesion energies with respect to vdW-DF ones for (a) armchair (metallic) and (b) zigzag (mainly semiconducting) tubes. A set of two infinitely long parallel CNTs is used. The indexes on the x-axis refer to the chirality indexes of the two parallel tubes; for instance, "8012" stands for two parallel zigzag CNTs with chiralities (8,0) and (12,0).

**Table 4.** Adhesion energy in kJ/(mol × Å) of double-wall CNT systems.

| Geometry | Std C | New C | vdW-DF |
|---|---|---|---|
| (4,4)@(8,8) | +19.4 | +54.7 | +29.2 |
| (4,4)@(9,9) | −57.9 | −49.1 | −26.1 |
| (5,5)@(9,9) | +10.4 | +46.9 | +51.0 |
| (6,0)@(14,0) | −45.4 | −30.5 | −21.3 |
| MAE | 26.6 | 15.5 | — |

It is calculated by the classical OPLS/AA force field and by the vdW-DF (the last column). "Std C" stands for standard carbon parameters (Table 2). 'New C' column contains the adhesion energies calculated by the new LJ parameters derived in this article. MAE are shown at the last row.

### CNT–water interaction

The adhesion energies of an encapsulated single water molecule to various CNTs are shown in Table 5. With standard LJ-parameters the adhesion energies are clearly underestimated (the second column, StdCNT-H$_2$O) compared to the vdW-DF adhesion energies (the last column). All the new LJ parameters clearly improve the classical description as can be seen from the MAE (the last row). Best agreement is found using parameters derived from semiconducting tube—water fitting with nonzero hydrogen LJ parameters with mean absolute error less than 3 kJ/mol (ZigCNT-H$_2$(HW), the second last column).

**Table 5.** Adhesion energies of water inside armchair and zigzag CNTs calculated OPLS/AA classical force field with different LJ parameters and with vdW-DF (the last column); in [kJ/mol].

| Tube | StdCNT–H$_2$O | ArmCNT–H$_2$O | ArmCNT–H$_2$O(HW) | ZigCNT–H$_2$O | ZigCNT–H$_2$O(HW) | vdW-DF |
|---|---|---|---|---|---|---|
| (5,5) | −9.5 | −66.6 | −69.1 | −64.9 | −63.2 | −56.9 |
| (6,6) | −19.6 | −41.4 | −42.5 | −42.5 | −45.6 | −47.5 |
| (7,7) | −11.4 | −24.1 | −24.6 | −24.9 | −27.5 | −28.6 |
| (8,0) | −9.5 | −69.5 | −70.7 | −62.4 | −50.8 | −46.2 |
| (10,0) | −19.6 | −47.6 | −48.9 | −48.5 | −50.5 | −51.3 |
| (12,0) | −11.4 | −25.4 | −26.0 | −26.4 | −29.0 | −29.4 |
| MAE | 28.3 | 8.6 | 8.6 | 6.5 | 2.5 | — |

Other symbols in the table: "ArmCNT" armchair CNT, "ZigCNT" zigzag CNT. "H$_2$O": water with zero LJ energy parameter for hydrogens. "H$_2$O(HW)": water with nonzero LJ energy parameter for hydrogens. The values of the parameters ($\varepsilon, \sigma$) used in the testing are the same as given in Table 3, thus for instance, parameter set "ZigCNT-H$_2$O(HW)" stands for $\sigma_{CO} = 0.3173$ nm, $\sigma_{CH} = 0.3067$ nm, $\varepsilon_{CO} = 0.6975$, $\varepsilon_{CH} = 0.3981$.

Interestingly, according to our calculations the interaction energy of water and CNT has an minimum at an intermediate tube radius, around 6–7 Å. This is a consequence of balance between adding more carbon–water vdW-interacting-pairs and Pauli repulsion. However, in experiments water appears within CNTs not as a monomer, but rather as a hydrogen-bonded network of molecules. Then, at larger radii of CNTs, only the outermost water molecules have a strong interaction with the CNT (rest resembling bulk water) and the strength of the CNT–water interaction is likely to saturate.

One must bear in mind that our results are strictly valid only for CNT–water monomer interaction. Comparing calculated and experimentally observed properties of water droplets on graphene, Weder et al. concluded that values of $\sigma_{CO} = 0.319$ nm and $\varepsilon_{CO} = 0.392$ kJ/mol or $\varepsilon_{CO} = 0.564$ kJ/mol gave best agreement with two sets of experimental data. Thus, it is likely that the $\varepsilon_{CO}$ for CNT–water interaction decreases as the function of increasing number of water molecules when a simple nonpolarizable force field is used.[51]

## Conclusions

We have derived LJ force field parameters for parallel small diameter metallic and semiconducting CNTs. The fitting was done with respect to rigorous vdW-DF implemented in VASP and SIESTA codes. Similarly, the important CNT–water parameters were fitted.

The new recommended values for LJ parameters for CNTs of all chiralities when simulating a few parallel nanotubes are $\sigma_{CC} = 0.3534$ nm, $\varepsilon_{CC} = 0.2906$ kJ/mol. It has been found earlier that the vdW-interaction of two parallel CNTs is additive, so these parameters can also be applied for bundles of CNTs (for discussion see Ref. [12]). We find no significant difference in the LJ parameters between armchair and zigzag tubes.

Importantly, the vdW-DF fitting results in water–CNT interactions which are much stronger compared to earlier literature values. The recommended water oxygen LJ parameter in CNT–water interactions are: $\sigma_{CO} = 0.3122$ nm, $\varepsilon_{CO} = 1.4454$ kJ/mol in case of keeping LJ parameters of hydrogens of water zero. In case of non-zero water hydrogen parameters, we suggest $\sigma_{OO} = 0.3172$ nm, $\varepsilon_{CO} = 0.6975$ kJ/mol, $\sigma_{CH} = 0.3067$ nm, and $\varepsilon_{CH} = 0.3981$ kJ/mol. This implies that one must use different LJ parameters for water in water–water and water–CNT interactions at least when using nonpolarizable force fields.

Finally, one has to keep in mind that the recommended values for the LJ-parameters for CNT–water interaction are valid only for CNT–water monomer interaction. It is very likely that the strength of the CNT–water interaction decreases when the number of water molecules increase in this nonpolarizable force field description. Therefore, we hope to proceed in the direction guided by Söderhjelm and Ryde.[52] That is, combining the individual atomic polarizabilities which depend on the atom and residue with a similar description for the vdW interaction: each atom in a given residue would have its own vdW-parameters. Or possibly the atomic residue-wise polarizabilities would be sufficient and one could use a single ($\sigma, \varepsilon$)-pair of vdW-parameters for each element.

[1] P. Harris, *Carbon. Nanotube. Sci.* **2009**.

[2] R. Baughman, A. Zakhidov, W. De Heer, *Science* **2002**, *297*, 787.

[3] M. Burghard, *Surf. Sci. Rep.* **2005**, *58*, 1.

[4] C. Liu, Y. Fan, M. Liu, H. Cong, H. Cheng, M. Dresselhaus, *Science* **1999**, *286*, 1127.

[5] K. Gong, F. Du, Z. Xia, M. Durstock, L. Dai, *Science* **2009**, *323*, 760.

[6] P. Kamat, *Nano. Today* **2006**, *1*, 20.

[7] Y. Maniwa, K. Matsuda, H. Kyakuno, S. Ogasawara, T. Hibi, H. Kadowaki, S. Suzuki, Y. Achiba, H. Kataura, *Nat. Mater.* **2007**, *6*, 135.

[8] N. Kam, M. O'Connell, J. Wisdom, H. Dai, *Proc. Natl. Acad. Sci. USA* **2005**, *102*, 11600.

[9] K. Koga, G. Gao, H. Tanaka, X. Zeng, *Nature* **2001**, *412*, 802.

[10] A. Striolo, A. Chialvo, K. Gubbins, P. Cummings, *J. Chem. Phys.* **2005**, *122*, 234712.

[11] Y. Tu, P. Xiu, R. Wan, J. Hu, R. Zhou, H. Fang, *Proc. Nat. Acad. Sci.* **2009**, *106*, 18120.

[12] J. Kleis, E. Schröder, P. Hyldgaard, *Phys. Rev. B* **2008**, *77*, 205422.

[13] A. Gulans, M. Puska, R. Nieminen, *Phys. Rev. B* **2009**, *79*, 201105.

[14] J. Klimeš, D. Bowler, A. Michaelides, *Phys. Rev. B* **2011**, *83*, 195131.

[15] G. Lithoxoos, J. Samios, Y. Carissan, *J. Phys. Chem. C* **2008**, *112*, 16725.

[16] D. Feller, K. D. Jordan, *J. Phys. Chem. A* **2000**, *104*, 9971.

[17] M. Elstner, P. Hobza, T. Frauenheim, S. Suhai, E. Kaxiras, *J. Chem. Phys.* **2001**, *114*, 5149.

[18] U. Zimmerli, M. Parrinello, P. Koumoutsakos, *J. Chem. Phys.* **2004**, *120*, 2693.

[19] S. Grimme, *J. Comput. Chem.* **2004**, *25*, 1463.

[20] P. Jurečka, J. Černÿ, P. Hobza, D. Salahub, *J. Comput. Chem.* **2007**, *28*, 555.

[21] A. Tkatchenko, M. Scheffler, *Phys. Rev. Lett.* **2009**, *102*, 073005.

[22] G. Hummer, J. Rasaiah, J. Noworyta, *Nature* **2001**, *414*, 188.

[23] J. Soler, E. Artacho, J. Gale, A. García, J. Junquera, P. Ordejón, D. Sánchez-Portal, *J. Phys.: Condens. Matter.* **2002**, *14*, 2745.

[24] G. Kresse, J. Furthmuller, *Comput. Mater. Sci.* **1996**, *6*, 15.

[25] M. Dion, H. Rydberg, E. Schröder, D. Langreth, B. Lundqvist, *Phys. Rev. Lett.* **2004**, *92*, 246401.

[26] E. Artacho, D. Sánchez-Portal, P. Ordejón, A. García, J. M. Soler, *Phys. Status Solidi. B* **1999**, *215*, 809.

[27] J. Soler, E. Artacho, J. Gale, A. García, J. Junquera, P. Ordejón, D. Sánchez-Portal, *J. Phys.: Condens. Matter.* **2002**, *14*, 2745.

[28] F. A. Bulat, L. Couchman, W. Yang, *Nano. Lett.* **2009**, *9*, 1759.

[29] S. F. Boys, F. Bernardi, *Mol. Phys.* **1970**, *19*, 553.

[30] G. Kresse, D. Joubert, *Phys. Rev. B* **1999**, *59*, 1758.

[31] D. Van Der Spoel, E. Lindahl, B. Hess, G. Groenhof, A. Mark, H. Berendsen, *J. Comput. Chem.* **2005**, *26*, 1701.

[32] W. Jorgensen, D. Maxwell, J. Tirado-Rives, *J. Am. Chem. Soc.* **1996**, *118*, 11225.

[33] G. Kaminski, R. Friesner, J. Tirado-Rives, W. Jorgensen, *J. Phys. Chem. B* **2001**, *105*, 6474.

[34] C. Oostenbrink, A. Villa, A. Mark, W. Van Gunsteren, *J. Comput. Chem.* **2004**, *25*, 1656.

[35] R. Veiga, D. Tomanek, Available at http://k.1asphost.com/tubeasp/tubeasp.asp, 2009. Accessed on December 4, 2011.

[36] Available at https://wiki.fysik.dtu.dk/ase/. Accessed on December 4, 2011.

[37] Available at http://www.scipy.org, 2010. Accessed on December 4, 2011.

[38] P. Atkins, J. de Paula, R. Friedman, In Quanta, Matter and Charge, Vol. 1; Oxford University Press: Oxford, UK, 2009, pp. 233–238.

[39] J. Seminario, *Int. J. Quantum Chem.* **1996**, *60*, 1271.

[40] R. Ahlrichs, M. Bär, M. Häser, H. Horn, C. Kölmel, *Chem. Phys. Lett.* **1989**, *162*, 165.

[41] A. Becke, *Phys. Rev. A* **1988**, *38*, 3098.

[42] J. Perdew, *Phys. Rev. B* **1986**, *33*, 8822.

[43] A. Schafer, H. Horn, R. Ahlrichs, *J. Chem. Phys.* **1992**, *97*, 2571.

[44] K. Eichkorn, O. Treutler, H. Öhm, M. Häser, R. Ahlrichs, *Chem. Phys. Lett.* **1995**, *240*, 283.

[45] D. Sánchez-Portal, E. Artacho, J. M. Soler, A. Rubio, P. Ordejón, *Phys. Rev. B* **1999**, *59*, 12678.

[46] S. Joseph, N. R. Aluru, *Phys. Rev. Lett.* **2008**, *101*, 064502.

[47] L. X. Benedict, S. G. Louie, M. L. Cohen, *Phys. Rev. B* **1995**, *52*, 8541.

[48] B. Kozinsky, N. Marzari, *Phys. Rev. Lett.* **2006**, *96*, 166801.

[49] S. Fratiloiu, S. M. Fonseca, F. C. Grozema, H. D. Burrows, M. L. Costa, A. Charas, J. Morgado, L. D. A. Siebbeles, *J. Phys. Chem. C* **2007**, *111*, 5812.

[50] S. Cambré, B. Schoeters, S. Luyckx, E. Goovaerts, W. Wenseleers, *Phys. Rev. Lett.* **2010**, *104*, 207401.

[51] T. Werder, J. Walther, R. Jaffe, T. Halicioglu, P. Koumoutsakos, *J. Phys. Chem. B* **2003**, *107*, 1345.

[52] P. Söderhjelm, U. Ryde, *J. Comput. Chem.* **2009**, *30*, 750.