MC 3.1.8 Theoretische Chemie/ Quantenchemie
Computerübungen im Wintersemester 2019/2020

Übung 9: Elastic Modulus of Carbon Nanotubes

1 Introduction

Carbon nanotubes are a special modification of carbon, forming long tubes with extraordinary mechanical and electronic properties. There are interesting applications of the special properties of carbon nanotubes, including persistent information storage technologies with high data densities and short response times, field-effect transistors, mixing with ordinary polymere materials such as polyethene to increase their mechanical stability or their use in scanning tunneling microscopy as well defined, conductive tip of the microscope.

The extreme tensile strength of carbon nanotubes has led to ideas of more futuristic applications; their use for space elevators, overcoming the need to launch rocket based spaceships, avoiding to fight the deep gravitational well of earth with tons of fuel (see Phase II study of the NASA (hyperlink), and [6]). The difficulty is of course the enormous length and tensile strength a material for such an extended rope needs to have, in order to not collapse under its own weight. While carbon nanotubes could provide the necessary tensile strength in theory, this is only true for perfect carbon nanotubes without defects in their structure, but manufacturing those is not yet possible in the necessary quantities.

In this tutorial, we will estimate the Young's modulus E

$$E = \frac{\sigma}{\epsilon}, \tag{1}$$

and the ultimate tensile strength for a perfect carbon nanotube and a nanotube with two Stone-Wales-Thrower defects. In this case σ is the stress, meaning the uniaxial force per surface unit, and $\epsilon = \frac{\Delta l}{l_0}$ is the proportional deformation.

2 Computational Details

2.1 Geometry Optimization

Two structures of (5,5) carbon nanotubes, which are capped with C_{60} fullerene fragments to saturate them properly, are provided. They can be drawn using *Avogadro*'s carbon nanotube builder [1] and some manual adjustements for capping with the fullerene and for adding the defects. Optimize their structures using *CP2K* [3] with the TPSS functional [4] and double ζ molopt basis sets [5] in a non periodic unit cell.

Listing 1: *CP2K* input file for geometry optimization of carbon nanotubes in a non periodic box with TPSS

```
&global
project CNT
run_type geo_opt
print_level medium
&end global

&force_eval
method quickstep

&dft
basis_set_file_name BASIS_MOLOPT
potential_file_name GTH_POTENTIALS

&mgrid
cutoff 300
ngrids 5
&end mgrid

&qs
eps_default 1.0e-12
extrapolation aspc
extrapolation_order 5
&end qs

&scf
scf_guess atomic
max_scf 20
eps_scf 1.0e-6
max_diis 15
&outer_scf
max_scf 20
eps_scf 1.0e-6
&end outer_scf
&ot
preconditioner full_all
energy_gap 0.001
algorithm irac
minimizer diis
n_history_vec 20
&end ot
&end scf

&xc
&xc_functional tpss
&end xc_functional
&xc_grid
xc_deriv nn10_smooth
xc_smooth_rho nn10
&end xc_grid
&vdw_potential
dispersion_functional pair_potential
&pair_potential
type dftd3(bj)
parameter_file_name dftd3.dat
d3bj_scaling 1.000 0.4535 1.9435 4.4752
```

```
&end pair_potential
&end vdw_potential
&end xc

&poisson
periodic none
poisson_solver multipole
&end poisson
&end dft

&subsys
&cell
abc 15.0 15.0 50.0
periodic none
&end cell
&topology
coord_file_name CNT_5-5-DC.pdb
coord_file_format pdb
conn_file_format off
&center_coordinates .true.
&end center_coordinates
&end topology

&kind C
element C
basis_set dzvp-molopt-sr-gth
potential gth-pbe
&end kind
&end subsys
&end force_eval

&motion
&print
&restart_history on
&each
geo_opt 0
&end each
&end restart_history
&trajectory on
format xyz
&each
geo_opt 1
&end
&end trajectory
&end print
&geo_opt
optimizer bfgs
max_iter 5000
&end geo_opt
&end motion
```

Questions

- Visualize the structures and highlight the Stone-Wales-Thrower defects in the carbon nanotube. Explain Stone-Wales-Thrower defects.

- Explain chirality in carbon nanotubes. How does it influence their properties?

2.2 Molecular Dynamics

Use the optimized structures as initial configuration for ab initio molecular dynamics. We will propagate for only 5000 steps with timesteps of 1 fs. To simulate forces acting on the longitudinal axis of the carbon nanotube, we apply constraints to the length of the tube. Therefore, we define a collective variable to be constrained. We use two rings of carbon atoms of same longitudinal position in the tube, whose geometrical mid points (the centre of the ring) will be used to calculate and constrain the length of the tube (sections `&subsys&colvar` and `&constraint&collective`. Furthermore, we apply a restraint by using a weak external potential acting only on the the x and y coordinates of carbon atoms at the tips of the tube (section `&external_potential`).

Listing 2: *CP2K* input file for metadynamics with growing distance between two planes as a constraint.

```
&global
project CNT
run_type md
print_level low
&end global

&ext_restart
restart_file_name CNT-1.restart
&end ext_restart

&force_eval
method quickstep

&dft
basis_set_file_name BASIS_MOLOPT
potential_file_name GTH_POTENTIALS

&mgrid
cutoff 250
ngrids 5
&end mgrid

&qs
eps_default 1.0e-12
extrapolation aspc
extrapolation_order 5
&end qs

&scf
scf_guess atomic
max_scf 20
eps_scf 1.0e-6
max_diis 15
&outer_scf
max_scf 20
eps_scf 1.0e-6
```

```
&end outer_scf
&ot
preconditioner full_all
energy_gap 0.001
algorithm irac
minimizer diis
n_history_vec 20
&end ot
&end scf

&xc
&xc_functional tpss
&end xc_functional
&xc_grid
xc_deriv nn10_smooth
xc_smooth_rho nn10
&end xc_grid
&vdw_potential
dispersion_functional pair_potential
&pair_potential
type dftd3(bj)
parameter_file_name dftd3.dat
d3bj_scaling 1.000 0.4535 1.9435 4.4752
&end pair_potential
&end vdw_potential
&end xc

&poisson
periodic none
poisson_solver multipole
&end poisson
&end dft

&subsys
&cell
abc 15.0 15.0 50.0
periodic none
&end cell
&topology
coord_file_name CNT_OPT.xyz
coord_file_format xyz
conn_file_format off
&center_coordinates .true.
&end center_coordinates
&end topology

&kind C
element C
basis_set dzvp-molopt-sr-gth
potential gth-pbe
&end kind

# The length of the tube defined by the mid points of
# carbon rings at the beginning and end of the tube
&colvar # 1
&distance
# The first point for distance measurement is the
```

```
# geometric center of the following atoms
&point
atoms 265 255 257 268 244 254 276 275 251 242
type geo_center
&end point
# And the second point for distance measurement is
# the geometic center of the other following atoms
&point
atoms 209 201 227 219 220 230 203 212 233 231
&end point
points 1 2
# Only evaluate distance along z axis, we dont want
# shear forces
axis z
&end distance
&end colvar

# Print informations about pairwise distances in the
# two rings
&print
&structure_data
&each
md 1
&end each
distance 203 276
distance 212 275
distance 233 251
distance 231 242
distance 209 265
distance 201 255
distance 227 257
distance 219 268
distance 220 244
distance 230 254
filename =CNT-LayerDistance.dat
&end structure_data
&end print
&end subsys

# Restraint the position of the ends of the tube with
# a small harmonic potential
&external_potential
atoms_list 222 262
function A*(X-R0)^2
parameters A                    R0
units      kjmol*angstrom^-2  angstrom
values     50.0                 7.0
&end external_potential
&external_potential
atoms_list 222 262
function A*(Y-R0)^2
parameters A                    R0
units      kjmol*angstrom^-2  angstrom
values     50.0                 7.0
&end external_potential
&end force_eval
```

```
&motion
&print
&restart_history on
&each
geo_opt 0
&end each
&end restart_history
&trajectory on
format xyz
&each
geo_opt 1
&end
&end trajectory
&end print
&md
ensemble nvt
steps 10
timestep 1.0
temperature 350
&thermostat
type nose
&nose
timecon 50
&end nose
&end thermostat
&end md

# Force the tube to elongate by letting the plane-plane
# distance grow with 0.002 angstrom per femto second
&constraint
&collective
colvar 1
target [angstrom] 27.147
target_growth [angstrom*fs^-1] 0.0020
target_limit [angstrom] 35.0
intermolecular .true.
&end collective

&constraint_info
&each
md 1
&end each
filename =CNT-Constraints.log
&end constraint_info

&lagrange_multipliers
&each
md 1
&end each
filename =CNT-LAGRANGE.dat
&end lagrange_multipliers
shake_tolerance 1.0e-3
&end constraint
&end motion
```

Questions

- Visualize the constraints and restraints in the molecular structure, for example by highlighting the atoms used to define the restraints.
- Visualize and describe the process of rupturing of the nanotube and what happens after the tubes have ruptured. Highlight the defects during the visualization of the tube with the 2 Stone-Wales-Throwner defects and describe how they behave. Use *VMD* [2] to highlight open valencies when the tube ruptures. Describe the differences between the non defective and the defective tube.
- Calculate Young's modulus and the ultimate tensile strength for both carbon nanotubes, compare them with each other and other common materials as well as literature values for carbonaceous materials and explain your observations.

Literatur

[1] Marcus D Hanwell u. a. "Avogadro: an advanced semantic chemical editor, visualization, and analysis platform". In: *Journal of Cheminformatics* 4.1 (01/2012), S. 17. DOI: 10.1186/1758-2946-4-17.

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[4] Jianmin Tao u. a. "Climbing the density functional ladder: nonempirical meta-generalized gradient approximation designed for molecules and solids." In: *Physical review letters* 91.14 (10/2003), S. 146401. DOI: 10.1103/PhysRevLett.91.146401.

[5] Joost VandeVondele und Jürg Hutter. "Gaussian basis sets for accurate calculations on molecular systems in gas and condensed phases." In: *The Journal of chemical physics* 127.11 (09/2007), S. 114105. DOI: 10.1063/1.2770708.

[6] Liyan Zhu, Jinlan Wang und Feng Ding. "The Great Reduction of a Carbon Nanotube's Mechanical Performance by a Few Topological Defects." In: *ACS nano* 10.6 (06/2016), S. 6410–5. DOI: 10.1021/acsnano.6b03231.