# Molecular Dynamics Simulations of Poly C ss-DNA Adsorbing to a Single-Walled Carbon Nanotubes

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## Abstract

Carbon nanotubes (CNT) and single stranded (ss-DNA) hybrids have been recently used to construct nanoscale chemical sensors. In this work, we performed molecular dynamics simulations using the GROMACS MD package. We constructed a straight Poly C ss-DNA that is not available in *nucleic.x,* positioned it along the surface of a nanotube, hydrated the system and neutralized the charge with Na ions. After running simulations for systems with 10, 19 and 25 bases each we found evidence that not many rings remain separated from the CNT for Poly-C's with 25 bases or less. Also, the maximal separation stabilize at different distances for different lengths Finally, the 10-bases case shows that all the cytosine rings of the Poly-C remain adsorbed directly onto the CNT.

## 1. Introduction

Carbon nanotubes (CNT) and ss-DNA are both interesting and important systems in nanoscience that are completely compatible with one another. This compatibility enables the construction of ss-DNA-CNT hybrid devices that also have interesting properties. For example, ss-DNA-CNT hybrids have been recently used to construct nanoscale chemical sensors[1]. ss-DNA has also been used to separate and sort CNTs based metallicity[2].

It is understood that ss-DNA attaches readily to the CNT by the $\Pi$-$\Pi$ stacking interaction. However, these has not yet been a detailed study to determine the specific conformation of ss-DNA about a CNT. Here, we present the results of several MD simulations of Poly C ss-DNA adsorbing to a CNT. We also provide a detailed description of the procedure for setting up and running these simulations.

## 2. Background

### 2.1. carbon nanotubes

CNT were discovered in 1991. They are cylindrical sheets of carbon. CNT have diameters of ~1nm and lengths up to a few centimeters[2]. They are unique for their size and special properties. CNT have electronic and structural properties that vary depending on the diameter, chirality and length. Nanotubes can form both single-wall (SWNT) and multiple-wall (MWNT)[3] structures. They have many interesting properties such as high mechanical strength (nanotubes can have tensile strengths 60 times

larger than steel) and electronic stability (nanotubes can accomodate current densities 1000 times higher than copper and silver). These features make them possible candidates for practical applications. The figure 1 shows an example of the different forms of CNTs.
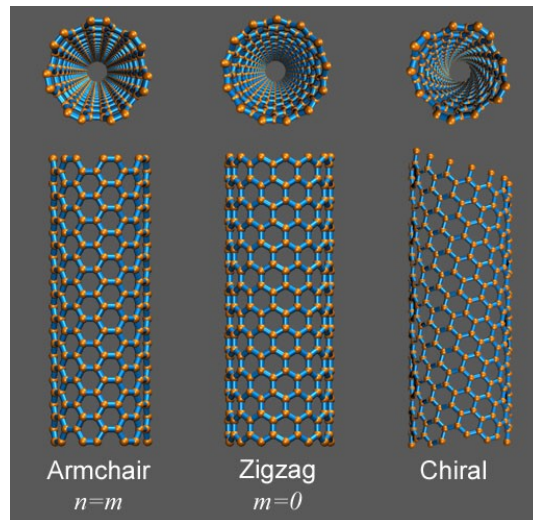


Figure 1. Different forms of CNTs[2].

## 2.2. **single stranded DNA**

Single stranded DNA (ss-DNA) is a DNA molecule consisting of only one chain of alternating sugars and phosphates[4]. They can assume different structures depending on the solvent and ionic environment. Figure 2 depicts the A structure and Figure 3 depicts the B structure.
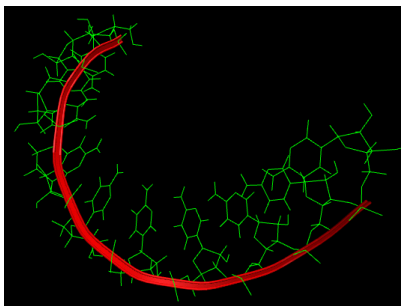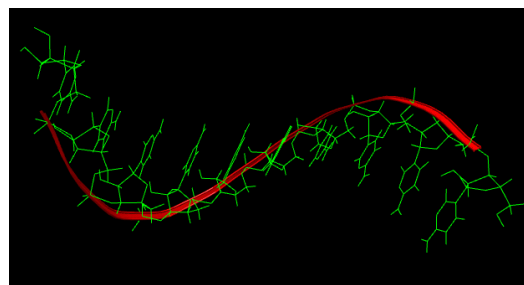


Figure 2. A form of a ss-DNA



Figure 3. B form of ss-DNA

### 2.2.1. *ss-DNA of Poly C*

For this work, we use ss-DNA composed of a repeating sequence of cytosines (Poly C ss-DNA).

### 2.2.2. *backbone torsion angles*

The backbone torsion angles are the dihedral angles formed between atoms residing on the DNA sugar-phosphate backbone. Figure 4 depicts one particular backbone torsion angle formed between the O3*, P, O5* and C5* atoms.
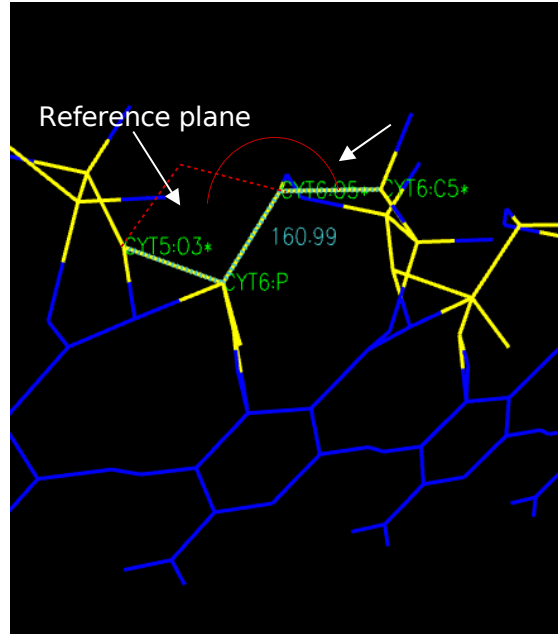
Figure 4. Measure of dihedral angles.

## 2.3 potential for MD simulations

MD simulations calculate the trajectories of $N$ interacting atoms by numerically solving Newton's equations of motion for each atom. To do this, one must have an accurate description of the forces acting on each atom. Since atomic forces are conservative, they can be described by a potential function. There are a variety of interactions that need to be considered which we outline below. The first two forces, which exist between atoms that do not share a chemical bond, are the electrostatic and the van der Waals forces. These interactions are described by the following potentials.

$$electrostatic = \frac{q_i q_j}{4\pi\epsilon_0 r_{ij}}$$

$$van\,der\,Waals = 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6\right]$$

There are additional forces that act on atoms sharing a chemical bond. These forces describe bond stretching (bond force), bond bending (angle force) and bond twisting (torsion force). These interactions are given by the following potentials.

$$bond = \frac{1}{2}k_r(r-r_0)^2$$

$$angle = \frac{1}{2}k_\theta(\theta-\theta_0)^2$$

$$torsion = \frac{1}{2}k_\phi(1+\cos(n_\phi-\delta))$$
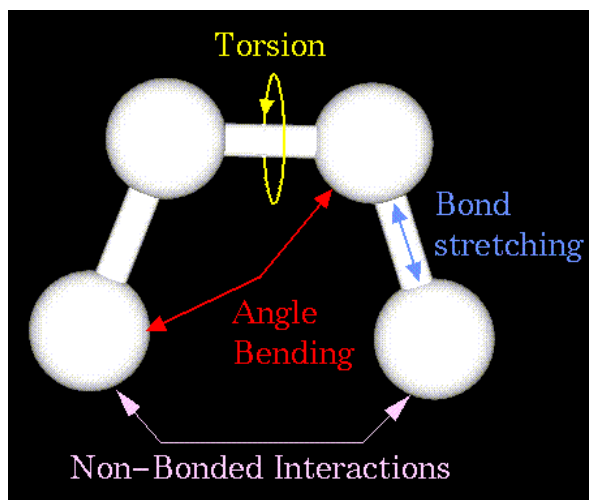
Figure 5 illustrates these various bond interactions.



Figure 5. Description of the forces interacting with the atoms[5].

## 3. **Software and methods**

In this work, we perform molecular dynamics simulations using the **GROMACS** MD package[6]. We obtain ss-DNA structure from *nucleic.x,* which is part of the **Tinker** molecular modeling package[7]. This program generates the coordinates of ss-DNA of a given sequence and structure. Three pre-defined structures are available (A, B, Z) in this program. We also used *Xleap,* which is a sub-program of the **AMBER7** molecular dynamics package[8]. This program enables the user to edit configurations of existing molecules, create structures for new ones and generate *topology* and *coordinate files*. The results of our simulations were analyzed with **VMD. VMD** is a molecular visualization program for displaying, animating and analyzing large biomolecular systems using 3-D graphics and built-in scripting[9]. In the following sections, we outline the procedure for setting up and running our simulations.

### 3.1. **constructing a *coordinate file* for the straight Poly-C**

There are practical limitations on the timescales that can be routinely accessed by all-atom molecular dynamics (MD). Typically timescales on the order of 10's of nanoseconds can be reached with this method. Preliminary simulations suggest that the ssDNA conformation about a CNT reaches equilibrium on timescales that are outside the scope of all-atom MD. However, initial calculations on the binding energies between individual DNA bases and the CNT suggest that it is energetically favorable for each DNA base to stack on the CNT. Therefore, we prepare our system with the assumption that the ssDNA assumes a straight conformation with all bases stacked to the CNT. We then wish to observe how this conformation changes in an MD simulation.

We need to construct a straight Poly C ss-DNA that is not available in  *nucleic.x.* This conformation of ss-DNA can be obtained from specifying a unique set of dihedral angles. These dihedral angles were found by trial-and-error and were implemented in *nucleic.x* by editing the source code. These angles are listed in Table 1. A *coordinate file* (in *PDB* format) for a 10 base long Poly C ss-DNA is then generated using our edited version of *nucleic.x*.

| Dihedral Angle | Angle Measure (degrees) |
|:---:|:---:|
| α | 161 |
| β | -289 |
| γ | 53 |
| δ | 202 |
| ε | 298 |
| ζ | -51 |
| χ | -141 |

Table 1. Dihedral angles of the straight form.

### 3.2. **constructing a *topology file* for the straight Poly-C**

The ss-DNA coordinates were loaded into *Xleap*. A *topology* and an additional *coordinate file* were created by *Xleap* by executing the following command:

```
saveamberparm <unit> <topology.top> <coordinates.crd>
```

Since these files are written using the **AMBER7** format, we convert them to the **GROMACS** format with the *Conv_7.x* program.

### 3.3. **constructing a *coordinate file* for a CNT in a box**

3.3.1. *constructing the coordinate file for the CNT and measuring its length*

We then use the program *nanotubegen* created by Robert Johnson to generate a coordinate file of CNT of a given length and chirality. With this program, we generate a zigzag (*n=11, m=0*) CNT *120 Å* in length. We then load these coordinates into **VMD** and measure the length of the tube by opening **VMD**'s *Tk console* and executing the following command:

```
set CNT [atomselect 0 "all"]
measure minmax $CNT
```

These instructions print the minimum and the maximum coordinates of the CNT. These coordinates are measured in *Å,* but we need *nm* so we divided this result by *10*.

3.3.2. *putting the CNT into a box*

After we have the the measure of the CNT, we need to center the CNT in a box of correct dimension. To make the nanotube box compatible with periodic boundary conditions, we choose a box that has a length along the *z-direction* of *L-tube +* $\dfrac{a_{cc}}{2}$ *,* where $a_{cc}$ = 0.1418 nm is the C-C bond length in the nanotube and the factor of ½ ensures that the nanotube bond lengths are uniform across the periodic boundary. Centering the nanotube coordinates is done with the **GROMACS** program *editconf.* The command for this is:

```
editconf -f <CNT-coordinateFile>.pdb -o <CNT-newCoorFile>.g96 -c -box X Y Z
```

The `-box` flag generates a box of `X Y Z` dimensions and the `-c` flag centers all coordinates in the middle of the box.

### 3.4. **constructing a topology file for the CNT**

After we have the CNT centered in a box and have the compatible coordinate files for **GROMACS** programs, we can generate the nanotube *topology file* with the program *X2top*. The command to do this is:

```
x2top -f <CNT-newCoorFile>.g96 -o <CNT-topologyFile>.top -pbc -nopairs
        -name <name> -nexcl 5
```

The `-pbc` flag indicates that the topology file has periodic boundary conditions (thus, the nanotube will be infinitely long along the z-direction), the `-nopairs` flag eliminates an unnecessary section in the topology, the `-name <name>` flag specifies the name of the nanotube, and `-nexcl 5` allows van der Waals interactions between nanotube atoms separated by less than 5 bonded neighbors. A declaration to include the *position restraints file* is then added at the bottom of this *topology file*. We then save this file and change its extension to *.itp*. This extension is commonly used for *topology files* that pertain to one particular molecule in a many-molecule system. Since our system consists of a nanotube, water, ss-DNA and counterions we generate separate *.itp* files for each.

### 3.5. **build the composite system of CNT, ss-DNA, and ions**

First, we load the *PDB files* for the ss-DNA and the CNT as separate units in *Xleap.* Then we import the ss-DNA unit into a copy of the CNT. The ss-DNA is then oriented using *Xleap's* graphical user interface so that all DNA bases rest flat on the CNT with the *O4** atoms facing towards the CNT. We then determine the total charge of the system by typing:

```
charge <unit>
```

Where `<unit>` is the name of the unit containing the CNT-ssDNA system. This command returns an integer which we refer to as `<number>`.

If the charge its non-zero, counterions are added to neutralize the ss-DNA charge. This is done with the command:

```
addions <unit> Na+ <number>
```

Now the charge of the the system will be zero. A coordinate file of the neutralized system is then saved.

### 3.6. **hydrating the system**

The composite system is then centered in a box of water by entering:

```
editconf -f <unit>.pdb -o <centered>.g96 -c -box X Y Z
genbox -cp <centered>.g96 -cs spc216.gro -o <init>.g96
```

The program *genbox* is a **GROMACS** program that solvates the system from the template `spc216.gro` which contains the coordinates of a box of 216 water molecules. This file was obtained in the $GMXLIB library of **GROMACS**.

### 3.7. **removing water  from the inside of the tube**

By default, *genbox* will place water molecules inside the nanotube. In the real system, the nanotube is presumably hollow. Thus. we wish to remove these water molecules. This is done from the *TK console* in **VMD** by executing a script written by Robert Johnson.  Algorithm 1 shows the script.

```
#!/usr/bin/tclsh


set nt [atomselect 0 "resname CNT"]

lassign [measure center $nt] x y z


set outside [atomselect 0 "not same residue as (water and sqrt((x-
$x)*(x-$x)+(y-$y)*(y-$y)) < 5.0)"]

$outside writepdb "hollowPDB"


puts "hollow.pdb was written!"


# clean up

$nt delete

$outside delete

unset nt outside x y z
```
Algorithm 1. Script to remove the water inside of the CNT.

This script writes a new *coordinate file* called `hollow.pdb`. This file format is then converted to **GROMACS** format using *editconf*.

### 3.8. **making the index file**

**GROMACS** can write the energies between different groups of atoms. For example, in our system we wish to compute energies between the following groups: nanotube, ss-DNA, counterions, water. These groups are defined in an *index (.ndx) file*. This file is created with the **GROMACS** program *make_ndx*. The command to do this is:

```
make_ndx -f <init>.g96 -o <index>.ndx
```

Here, `<init>.g96` is the final coordinate file obtained in step 3.7.

### 3.9. **making the CNT position restraints file**

Since the nanotube is very rigid and we are not interested in intra-nanotube bond distortion, we restrain the positions of all nanotube atoms by placing each atom in a harmonic potential. This is done by generating a *position restraints file* for the CNT with

a script. This file only contains the index numbers of the nanotube atoms as well as the force constants for the harmonic potential. Algorithm 2 shows the script.

```awk
#!/usr/bin/awk -f


BEGIN{atom_num=<quantityOfAtoms>;
fx = 1000;
fy = 1000;
fz = 1000;
for(i=1;i<=atom_num;i++)
print i, "1", fx, fy ,fz}
```

<div align="center">Algorithm 2. Script to generate the <em>position restraints file</em>.</div>

The header "[ `position_restraints` ]" is then added to the top of this file.

### 3.10. energy minimization

Before starting the MD simulation, we run an energy minimization of the system using the Steepest Descents algorithm to allow the system to relax. See Appendix A for a copy of the **GROMACS** input file. Typically we run this algorithm for 1000 steps.

### 3.11. running the simulation

See Appendix B for a copy of the **GROMACS** input file. The major changes from the energy minimzation input file include specifying "`integrator = md`" in "*Calculation type" section* and "`constraints = hbonds`" in the "*Constraints section".*

Then, we run the pre-processor **GROMACS** program *grompp* with the following arguments: *input file* (*.mdp*), *coordinates file* (*.g96*), *index file* (*.ndx*) and *topology file* (*.top*). This program combines all of these files into a single *.tpr* file as well as checks the input files for consistency (e.g. verifies that atom names and numbers in coordinate and topology files match, checks .mdp file for syntax errors, etc). The simulation is then started by executing the **GROMACS** program *mdrun.* The commands for the previously described steps are:

```
grompp -f <inputFile>.mdp -c <init>.g96 -n <index>.ndx

        -p <topologyFile>.top

mdrun -s <topol>.tpr -deffnm <outputName> -g <outputName>.g96
```

### 3.12. post processing

When the MD simulation is finished, the trajectory is viewed in **VMD**. First, the `<init>.g96` file is loaded into **VMD**. The trajectory is loaded on top of these coordinates by right clicking on the molecule name in **VMD**'s Main window, clicking the menu item "l*oad data into molecule",* and then selecting `<outputName>.trr` from the browser window.

## 4. Discussion of Results and Conclusions

Figure 6 shows a graphical representation of the final frame of the MD simulation of a 10-bases Poly-C on a CNT.  It shows how the C-rings are placed just over the surface of the tube.
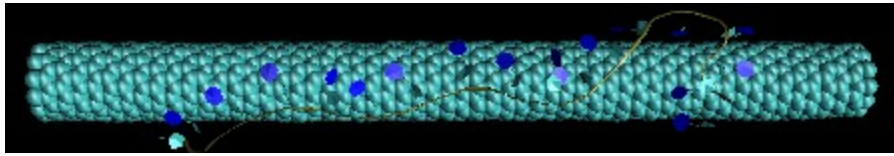


Figure 6.  Poly-C adsorbed onto a CNT.

A simple statistical measurement gives an idea of how the Poly-C conforms onto the CNT surface by measuring how far apart are the C-rings to the CNT.  We measure the distance of the nitrogen (N4) of the C-ring that is to the opposite side of the ss-DNA backbone.  Then we wrote a program that computes the distances between the atom N4* and all the atoms of the CNT. The program selects the minimum  distance.  This is called the Minkowsky distance.  Then, for the Poly-C, we compute the minimum, average and maximum Minkowsky distances of the N4's to the CNT.  This statistics are computed for each frame of the `.trr` file.  When we have this numbers we make the graph of these distances with the program **GNUPLOT**.  Figure 7, 8 an 9 show he resulting graphs for ss-DNA of 10, 19 and 25 bases.
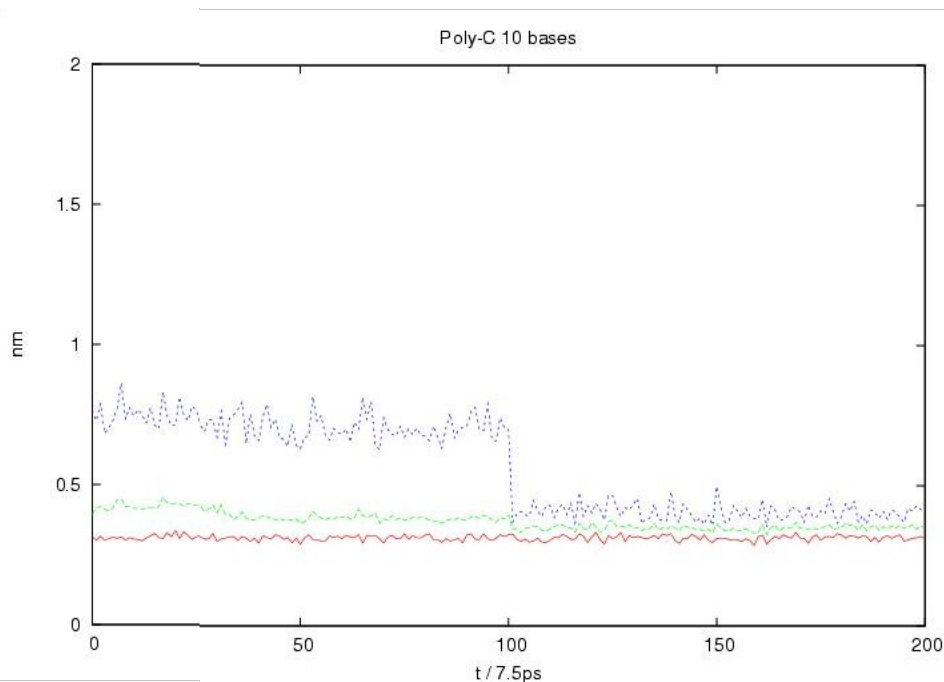


Figure 7.  Minimum (red), average (green) and maximum (blue) Minkowsky distances of the C-rings for a 10-bases Poly-C.
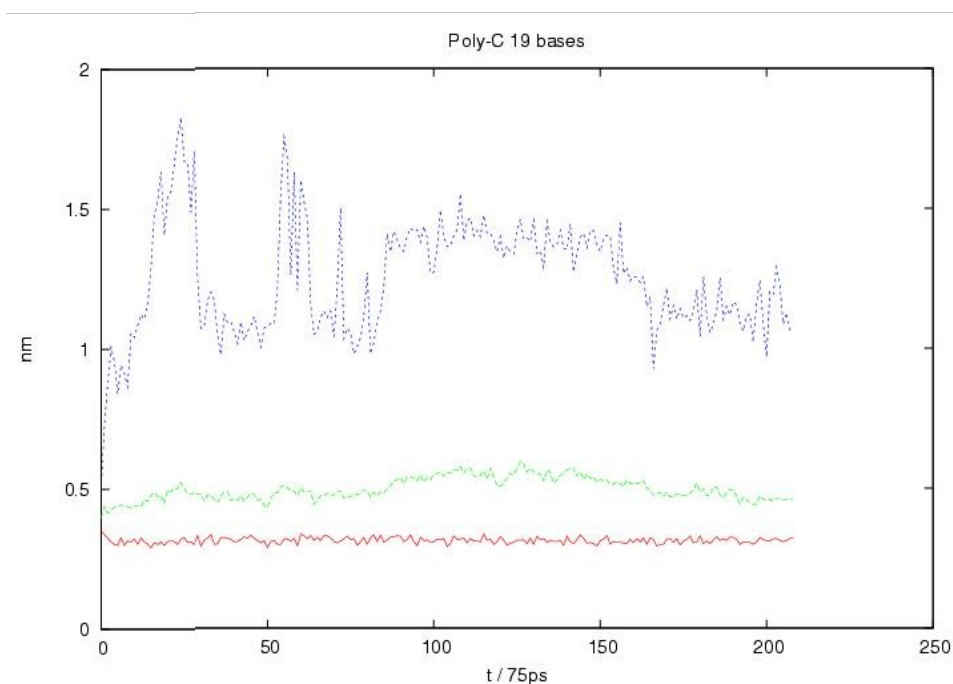
Figure 8. Minimum (red), average (green) and maximum (blue) Minkowsky distances of the C-rings for a 19-bases Poly-C.
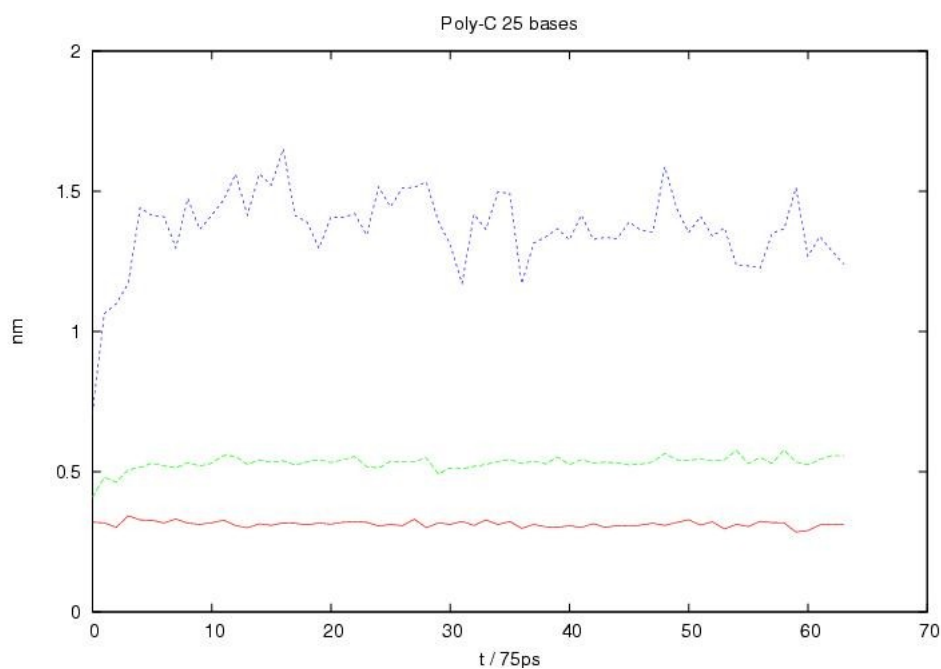


Figure 9. Minimum (red), average (green) and maximum (blue) Minkowsky distances of the C-rings for a 25-bases Poly-C.

From these graph we may draw some interesting preliminary observations that may serve as a starting point for future work. First, we observe that for the graphs corresponding to 19 and 25 bases the average distance of the rings is much closer to the minimum distance than to the maximum distance. This is evidence that not many rings are separated from the CNT. Second, the maximal separation in all graphs

stabilize at different distances, being the 10-bases case the most evident. In this case we observe that the difference between the minimal and maximal separation is very small and is between 3 and 4 Amstrongs. This indicates that all the cytosine rings of the Poly-C remain adsorbed directly onto the CNT.

## 5. **Future work**

1. Perform additional MD simulations to determine how the length of Poly C ss-DNA affects its conformation about the CNT. A computation of the radial density function may show in more detail how the cytosine rings at accommodate at different levels.

2. Calculate adsorption energy differences of analytes interacting with the nanotube vs. interacting with the ss-DNA.

3. Determine how the ss-DNA affects binding orientations and locations.

## 6. **Acknowledgments**

## 7. **Reference**

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