The Improved Lennard-Jones (ILJ) potential is given by

$$V_{ILJ}(r) = \epsilon \left[\frac{m}{n(r) - m} \cdot \left(\frac{r_0}{r} \right)^{n(r)} - \frac{n(r)}{n(r) - m} \cdot \left(\frac{r_0}{r} \right)^{m} \right], \qquad (1)$$

where

$$n(r) = \beta + 4.0 \cdot \left(\frac{r}{r_0} \right)^2 \qquad (2)$$

and $r = R_{i,j}$ is the distance between carbon atom i and nitrogen atom j. The parameters r_0, ϵ and β are set according to the atoms interacting, while m is set according the to the partial charges of the interacting species. The induction potential term for a N_3^- anion interacting with carbon atoms is given by (in meV)

$$V_{ind}(R_{i,1}, R_{i,2}, R_{i,3}) = -7200 \cdot \alpha_c \cdot \frac{n_2(R_{i,2})}{n_2(R_{i,2}) - 4} \left[\frac{q_1}{R_{i,1}^2} + \frac{q_2}{R_{i,2}^2} + \frac{q_3}{R_{i,3}^2} \right]^2, \qquad (3)$$

where $R_{i,1}$, $R_{i,2}$ and $R_{i,3}$ are the distances between the carbon atom i and the three nitrogen atoms, q_1, q_2 and q_3 are the partial charges on the nitrogen atoms, α_c is the polarizability of the carbon atoms and $n_2(R_{i,2})$ is equal to $n(r)$ using r_0 according to the interaction between $C - N_2$. The interaction energy between a trinitrogen anion confined inside a carbon nanotube is given by

$$E_{int} = \sum_{i=1}^{N_C} V_{ILJ}^{C-N_{1,3}}(R_{i,1}) + V_{ILJ}^{C-N_2}(R_{i,2}) V_{ILJ}^{C-N_{1,3}}(R_{i,3}) + V_{ind}(R_{i,1}, R_{i,2}, R_{i,3}), \qquad (4)$$

where N_C corresponds to the total number of carbon atoms, the ILJ potentials $V_{ILJ}^{C-N_{1,3}}$ and $V_{ILJ}^{C-N_2}$ are defined according to the parameters given in **??** and the polarizability α_c appearing in V_{ind} is set to 1.2, the partial charges as $q_1 = q_3 = -0.56$ and $q_2 = 0.12$ and finally the term $\frac{n_2}{n_2 - 4}$ is simplified to 1.0 for the time being. In case of large polarization (large partial charges),

atom types	ϵ	r_0	β	m
C-N$_{1,3}$	5.205	3.994	6–9	6.0
C-N$_2$	3.536	3.828	6–9	6.0

Table 1: ILJ parameters for the interaction of N_3^- confined inside a carbon nanotube. Different values of β are tested.

the electrostatic interaction between interaction centers has to be taken into account. The fact that we have a charged species (N_3^-), enhances the polarization and it really needs to be taken into account.

Since the aim is to fit the potential to the max interaction energy only (i.e. to fit the well depth ϵ), a very accurate value for this interaction energy is required. In order to do so, an elaborate scheme is required, which involves several steps.

1. Geometry relaxation of the complex system and the monomers. The nanotube length is only 3 units, otherwise there are too many basis functions

   (a) Using one pure functional among PBE, B97 and TPSS

(b) Using Grimme dispersion with Becke and Johnson damping (D3BJ)

(c) Using the cc-pvtz basis set on the CNT and the aug-cc-pvtz on the nitrogen (diffuse functions also on the tube lead to linear dependence)

(d) Now testing density fitting in Gaussian, if much faster, we use also that for the pure functional with the universal def2/j basis set

(e) Using one hybrid functional among B3LYP, APFD, what else?

2. All the geometry calculations are performed in Gaussian

3. To obtain accurate interaction energies, there is a total of 7 single point calculations to be performed

   (a) Complex at the complex geometry in the full basis

   (b) First monomer at the complex geometry in the full basis

   (c) First monomer at the complex geometry in the monomer basis

   (d) First monomer at the monomer geometry in the monomer basis

   (e) Second monomer at the complex geometry in the full basis

   (f) Second monomer at the complex geometry in the monomer basis

   (g) Second monomer at the monomer geometry in the monomer basis

4. The series of 7 calculations just listed has to be done for two basis sets, to be able to extrapolate the results at CBS limit

5. The extrapolation schemes are different for SCF and correlated calculations, therefore they can be done separately

6. For the SCF extrapolation, we can compute in Gaussian using triple and quadruple zeta basis sets

7. For the correlated extrapolation, we can compute in ORCA using double and triple zeta basis sets (which will give us also dz scf points)

8. The SCF in this case does not use the RI approximation for both Gaussian and ORCA

9. The correlated method is the DLPNO-CCSD(T)

10. Partial charges have to be obtained and there are many ways to do it. First of all, we need to decide which density to use

    (a) The density (relaxed, unrelaxed, linearized?) of the DLPNO-CCSD(T) method (I do not know how much expensive it is)

    (b) Find a DFT functional in which we can trust (how?) and use its density

    (c) Use the density of DLPNO-SCS-MP2 if it reproduces well the CCSD(T) one. But the same problem as above (relaxed, unrelaxed, linearized? Expensive?)

11. Once we know which density we want to use, calculate the charges

    (a) NPA charges from NBO analysis

    (b) MESP derived charges

    (c) Many other possibilities...

Method	r_{NN}	$Q_{1,3}$	Q_2
Expt.[1]	1.1884	-	-

12. Calculate multipole moments with the charges obtained and compare them with the moments obtained from the calculation

The above computational scheme will provide a very accurate interaction energy and can be ideally applied to different systems. The major pitfall of the above procedure, is the very first step, i.e. the geometry optimization.

1. The functional used for the geometry optimization might give wrong conformations

2. One should optimize the geometry using a wf method, but if it is too expensive we cannot

3. Moreover there are a plethora of minima in the PES, several starting geometries have to be relaxed and compared with each other

With the interaction energy and the partial charges, we can tune the ILJ potential such that it reproduces the interaction energy obtained with the above scheme.

There is a large amount of arbitrariness in this procedure to obtain the ILJ potential. The partial charges calculated are in principle arbitrary and considering them explicitly enhances the complexity of the problem. In particular, the charges will certainly vary depending on the length of the nanotube. This means that if we would like to use longer CNTs in the MD simulation, then the tuned ILJ potential which includes explicitly the charges might not be valid anymore. I believe that therefore we cannot pursue this approach.
A possible solution would be to fit the ILJ potential to a series of calculations of the complex system at different conformations. In this way, the electrostatic effects would be implicitly taken care of in the fitting procedure. Nonetheless, for such a fit, the above procedure is certainly to expensive and one should come up with a reasonable approximation.
Another possibility is to neglect completely the electrostatic term in the potential and tune it just according dispersion and induction forces. This is basically the same as the above solution, but without fitting the entire potential and only relying on the single interaction energy value.
A last idea is to assume that in the limit of a very long nanotube, the polarization far away from the nanotube ends is minimal and has to be taken care only locally around the azide anion. This would mean that the partial charges are assigned only locally around the azide anion and they would need to be approximated in some way. One such way is to compute them for a nanotube of increasing length and observe how they change. If the change is minimal, they can be safely assumed to remain so for any length, if this is not the case, then probably this idea is not feasible.

1 Azide Anion

References

[1] Mark Polak, Martin Gruebele, and Richard J. Saykally. Velocity Modulation Laser Spectroscopy of Negative Ions: The ν_3 Band of Azide (N_3^-). *J. Am. Chem. Soc.*, 109(10):2884–2887, may 1987.

Model	3-CNT	5-CNT	7-CNT
B97D3/cc-pvdz	-72	$-$	$-$
B97D3/cc-pvtz	-77	-39	$-$

Table 2: Unrelaxed interaction energies of N_3^- confined inside a $(5,5)$ SWCNT of increasing length. The basis set used on the anion is always aug-cc-pvtz, while the basis set used on the carbon nanotube is specified in the table entries. All energies are given in kcal/mol.