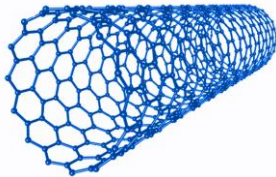


A- Analysis of some results of an article (8 points)

Some people studied a few years ago the behavior of water inside carbon nanotubes.

<i>J. Phys. Chem. A</i> 2009, 113, 2103–2108	2103	
Structure and Dynamics of Water Confined in Single-Wall Nanotubes Tanin Nanok, ^{†,‡,§} Nongnuch Artrith, ^{†,‡,} Piboon Pantu, ^{†,‡} Philippe A. Bopp, [⊥] and Jumras Limtrakul ^{*,†,‡}		

In this study, the water molecules and the various carbon nanotubes were assumed to be rigid. Different nanotubes of different diameters have been studied as described in the following table :

TABLE 1: Details for the MD Simulation Runs of Water in Carbon- and Boron-Nitride Nanotubes in This Work^a

tube	effective inner diameter (Å)	no. of water molecules	simulation time (ns)
(9,9)-nanotubes	8.86	77	4
(10,10)-nanotubes	10.22	102	4
(12,12)-nanotubes	12.92	162	1
(14,14)-nanotubes	15.62	237	1
(16,16)-nanotubes	18.34	327	1
(20,20)-nanotubes	23.74	547	1

^a The length is 36.89 Å in all cases.

- 1) Specify a set of parameters (i.e. an interaction model) to study such systems in MD (or MC) simulations.
- 2) In the paper the atoms of the carbon nanotubes are considered to be electrically neutral (no partial charges). Is it nevertheless necessary to consider the partial charges (qO and qH) on the water molecules ? State your arguments.

The nanotubes have cylindrical symmetry, not spherical symmetry. One thus studies the densities $g(r)$, (not $g(r)$ like in a liquid) where r is the distance between molecules to the centre of the nanotube. The figures next page show the densities of the water molecules (in fact the positions of the oxygen atom) as a function of the radius of the nanotube for tubes of different diameters (called e.g. (9,9)-nanotubes, (10,10)-nanotubes...).

- 3) What do you learn from these plots concerning the filling of these nanotubes with water?
- 4) Draw some conclusions from this.

- 5) For the systems with two peaks close to the surface (except (9,9)-nanotubes,) the distance between these two peaks is 2.9 Å. This value is larger than the distance between the first and the second maximum in $g_{OO}(r)$ for bulk water with the same water model (2.76 Å). Comment on this.
- 6) You will note that the curves are noisier at small r -values than at larger r -values. Please explain this.
- 7) Could the authors have done 'better' work and avoid this noisiness around $r = 0$? How ?
- 8) Use the available data to calculate for each system the distance from the first layer (position of the first maxima) and the surface of the nanotube. Do these distances depend on the filling of the nanotubes ? Comment this result.

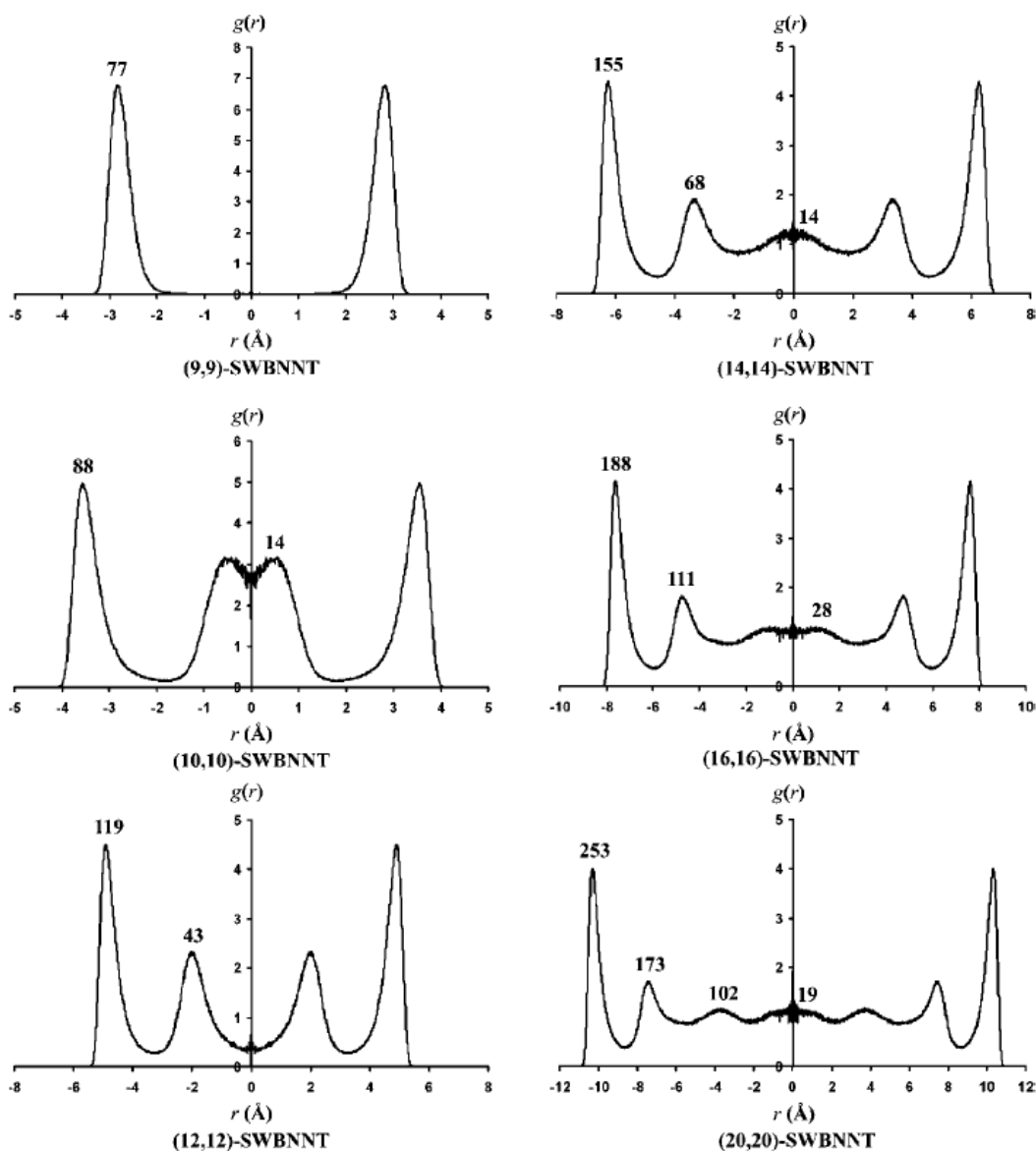


Figure 1. Local density distribution functions, in cylindrical coordinates, for the water molecules in the SWBNNTs. The numbers above the curves indicate the number of molecules present, on the average, in the various regions.

B- Principles (7 points)

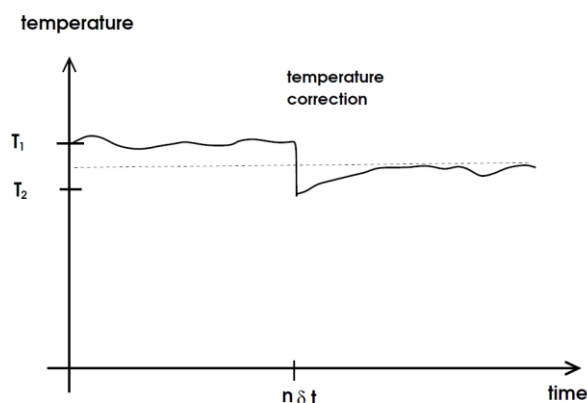
- 1) Two molecular simulation methods have been discussed in this class: the Molecular Dynamics (MD) method and the Monte Carlo (MC) method. Describe what you think to be the fundamental goal of these two methods.
- 2) Method of Molecular Dynamics: on which principle(s) is based this method. How does it achieve the objective that you described in the first question ?
- 3) Monte Carlo method: on which principle(s) is based this method. How does it achieve the objective that you have described in the first question ?
- 4) Comment shortly on the main similarities and differences between these two techniques.
- 5) The Lennard-Jones (LJ) potential is widely used in classical simulations.
 - a) Give the expression of this potential, describe the terms and draw its general appearance.
 - b) Mathematically determine the position (r and E) of the minimum energy of this potential.
 - c) Explain what determines that a potential is repulsive or attractive.
 - d) Determine the distance domains where this LJ potential is repulsive and attractive.

C- Adjusting the temperature of a simulated system in an MD simulation (5 points)

We know that the temperature T of a system is related to the mean square velocity $\langle v^2 \rangle$ of the particles. We study a system of N identical particles of mass m , so we have for the translations (k_B is Boltzmann's constant):

$$\frac{3}{2} N k_B T = N \frac{1}{2} m \langle v^2 \rangle$$

We have equilibrated (inside a NVE MD simulation) our system of N interacting particles so that it has, at some time-step $n \cdot \delta t$, the temperature T_1 (see figure below). We want to cool the system (lower the temperature) to a temperature $T_2 = 0.9 T_1$ in the simplest possible way by multiplying the velocities with a factor α .



- 1) Calculate the factor α to obtain the 10 % reduction in temperature.

However, things are not so simple... After the temperature correction at time-step $n \cdot \delta t$, we observe in the simulation that the system increases its temperature again until it reaches a temperature of $T_3 \approx 0.5 (T_1 + T_2)$.

- 2) Can you think of a reason for this ? Demonstrate why the final temperature T_3 will tend towards $0.5 (T_1 + T_2)$. (Help: consider the equipartition of energies, in average, of the system : $\langle E^{kin} \rangle = \langle E^{pot} \rangle$. Now you scale the velocities and change $E^{kin} \dots$).
- 3) Is this problem of temperature control transferable to a Monte Carlo simulation ?

D- Simulation of an ionic solution (10 points)

We want to simulate the properties of a solution of KBr in methanol, i.e. a system containing three species : CH_3OH , K^+ and Br^- .

The interactions will be represented by charges and Lennard-Jones (LJ) terms on all the atoms.

- 1) If we wish to study 8 pairs of K^+ and Br^- ions in 1600 molecules of methanol, what should be the dimensions of the simulation box (choose cubic) so that the density of the system is 0.876 g/cm^3 ?

$$\begin{array}{lll} M_{\text{O}} = 16 \text{ g/mol} & M_{\text{C}} = 12 \text{ g/mol}, & M_{\text{H}} = 1 \text{ g/mol}, \\ M_{\text{K}} = 39.1 \text{ g/mol} & M_{\text{Br}} = 79.9 \text{ g/mol} & \text{Navogadro} = 6.022 \cdot 10^{23} / \text{mol} \end{array}$$

- 2) Calculate the concentration in moles of solute per liter of this solution.
- 3) The radial distribution functions $g_{\alpha\beta}(r)$ characterize the structure of the system.
- What exactly do these functions mean ?
 - Towards what value do these long-distance functions tend ?
 - In the present case, up to what distance can we calculate these functions ?
 - How many distinct functions $g_{\alpha\beta}(r)$ are needed to fully characterize the structure of our system ? List it.
- 4) Draw in particular on a diagram the expected appearance of the functions $g_{\text{OK}^+}(r)$ and $g_{\text{OBr}^-}(r)$. Pay particular attention to the relative positions of the functions according to r and justify your diagram.
- 5) Write the part of the FORTRAN code to calculate the total potential energy of a configuration.
- Remember that there is a LJ site and a charge on each atom of the system (C, H, O, K^+ , Br^-).
 - Think about LJ parameters of atom species vs those used for interaction calculations
 - Do not declare variables but use explicit names.
 - You will be very careful to properly describe the different contributions, the associated nested loops and the ranges of variation of these nested loops.