université de BORDEAUX	**FALL/WNTER TERM 2021 - DST**	
	Semestre 9	**Code UE : 4TCH914U** **Molecular simulations** **Prof. : J-C. Soetens**
	Date : 10/01/2022 **Without documents**	**You have 3h** **Number of points : 20**

A- Analysis of an article *(9 points)*

Some people studied recently the effect of temperature on concentrated electrolytes.

Effect of temperature on concentrated electrolytes for advanced lithium ion batteries

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A-1) Extract from the article all the information describing the technical parameters of the simulations.

A-2) Detail and explain the protocol used by the authors to build the systems (i.e. the configurations) and then perform the simulations.

A-3) This study was done using Molecular Dynamics (MD) simulations. List all the calculated properties presented in this article and say (yes or no) if these properties could have been calculated using Monte Carlo (MC) type simulations.

A-4) Use the *Figure 1* and the *Equation 2* to find the values that should be in the *Table 1* (in kcal/mol as mentioned in the caption). As the curves are parallel, we will consider for each concentration that the results are identical for Li^+ and PF_6^-. Therefore only one result per concentration.

In part III-B Structural properties, the authors explain how to calculate the coordination number.
A-5) Explain what means this property.
A-6) Comment the *Equation 10* (in respect with *Equation 9*) at first glance used to calculate this property ?

After reading this article you want to simulate a system consisting of 816 molecules of PC ($C_4H_6O_3$) and 20 $LiPF_6$ at a density of 1.3 g/cm^3.

A-7) What should be the size (in Angström) of the cubic simulation box to correspond to this density ?

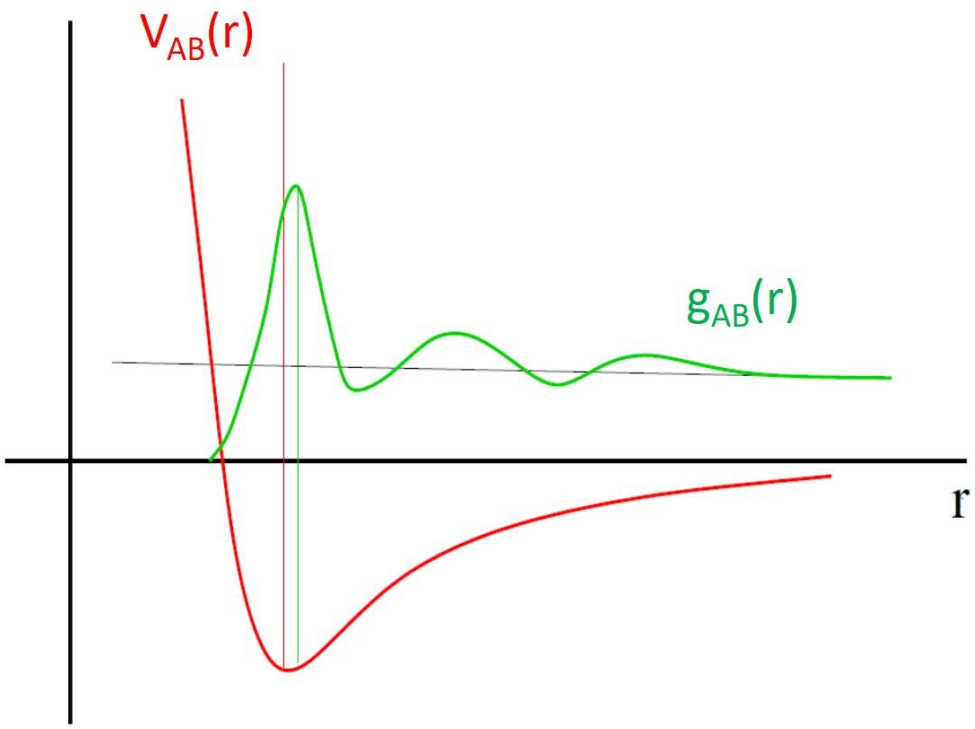
A-8) Along the article the authors use the term concentration. In fact it is Molality, a measure of the number of moles of solute in a solution corresponding to 1 kg of solvent.
→ Calculate the Molality of this system (in mol/kg) ?

A-9) Molarity is a measure of the number of moles of solute according to the volume of the solution.
→ What is the molarity of this system (in mol/l) ?

B- Basics of Statistical Mechanics *(5 points)*

The figure below shows (in red) a rough sketch of a PES (Potential Energy Surface) for the interactions between two particles (say A and B : $V_{AB}(r)$) and a sketch (in green) of the g-function $g_{AB}(r)$ obtained from a MD simulation of a liquid (i.e. dense) mixture of A and B.

The MD simulation has been performed at temperature T_1.
The mass of the particle A is m_A and the mass of the particle B is m_B with $m_A < m_B$.



B-1) Does $g_{AB}(r)$ depends on temperature : Yes / No ? Why ?

B-2) Does $V_{AB}(r)$ depends on temperature : Yes / No ? Why ?

B-3) Does $g_{AB}(r)$ will be the same from a Monte Carlo (MC) simulation : Same/Different ? Why ?

B-4) One sees that the first maximum of $g_{AB}(r)$ does (in general) not coincide exactly with the minimum of the PES. What is the reason(s) for this ?

B-5) Explain why $V_{AB}(r)$ has a continuous evolution at long distance while g(r) presents several oscillations.

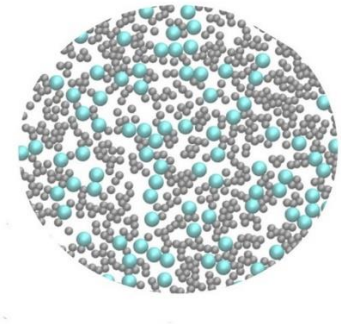
B-6) Imagine and draw the evolution of the g-function $g_{AB}(r)$ plotted above if the MD simulation is performed with :

(a) The temperature of the simulation is still T_1 but we change the masses : now $m_A = m_B$.

(b) $m_A < m_B$ (original masses) but the temperature of the simulation is now T_2 with $T_2 < T_1$.

C- Algorithms programming *(6 points)*

Consider a cluster in gas phase made of two atomic species A and B. The system consists of **NA atoms of type A** and **NB atoms of type B**. As this system is in gas phase, neither the PBC (Periodic Boundary Conditions) nor a cutoff will be applied.



Your job is to complete an existing FORTRAN program :

In this program, the positions of atoms A and B are stored in two tables, respectively `RA(3,maxA)` *and* `RB(3,maxB)`*, with the first dimension (3) for (x,y,z) and the second dimension(maxA and maxB) for the maximum number of each types of atoms (A and B).*

In this program, there are already three functions to calculate the interaction potential energy. You just have to call them : `VAA(r)` *between two atoms of type A,* `VAB(r)` *between two atoms A and B and* `VBB(r)` *between two atoms of type B,.* `r` *being the distance between two atoms.*

Write the following codes as precisely as possible and use comments to illuminate your work. You will pay a particular attention to the necessary loops but you will not declare the variables.

C-1) Write the part of the FORTRAN code allowing to calculate the total potential energy of a configuration of this system. Let us call this energy VTOT.

C-2) Write the part of the FORTRAN code allowing to calculate the distribution of the distances between atoms of type A and B for one configuration.

Thanks to the question C-1) you may consider addressing the following question that you have a function that gives the total interaction potential energy of the system (VTOT) for any configuration.

C-3) Write the Metropolis algorithm allowing to perform a Monte Carlo-type simulation on this system. We are talking here about an algorithm, so a logical sequence of tasks, not of a FORTRAN code.

Useful data :

k_B=1.38 10^{-23} J/K
$N_{Avogadro}$ = 6.02 10^{23}
1 cal = 4.18 J

M(H) = 1 g/mol, M(C) = 12 g/mol, M(O) = 16 g/mol
M(Li) = 7 g/mol, M(P) = 31 g/mol, M(F) = 19 g/mol

Documents : Start programming in fortran.
Mahesh *et al*, J. Chem. Phys. **154**, 214503 (2021).