université de BORDEAUX	**FALL/WNTER TERM 2020 - DST**	
	Semestre 9	**Code UE : 4TCH914U** **Molecular simulations** **Prof. : J-C. Soetens**
	Date : 11/01/2021 **Without documents**	**You have 3h** **Number of points : 20**

A- Analysis of an article *(8 points)*

Some people studied a few years ago the properties of water molecules near an oxide surface.

Cite this: *Phys. Chem. Chem. Phys.*, 2012, **14**, 15593–15605

www.rsc.org/pccp **PAPER**

Atomic scale characterization of interfacial water near an oxide surface using molecular dynamics simulations

Sanket A. Deshmukh and Subramanian K. R. S. Sankaranarayanan*

A-1) Extract from the article all the information describing the interactions taken into account. Clearly describe the mathematical expressions, the species involved, and the physical nature of the interactions associated within these mathematical expressions. But important, do not give back the values of the parameters.

A-2) Extract from the article all the information describing the technical parameters of the simulations.

A-3) Explain the reasons for the differences between figures 3a and 3b.

A-4) This study was done using Molecular Dynamics (MD) simulations. List all the calculated properties presented in this article and say if these properties could have been calculated using Monte Carlo (MC) type simulations.

B- MD simulation of an ionic system : preparation of the simulation box *(4 points)*

We want to simulate a solution of KCl in methanol (CH_3OH). According to the desired concentration, the simulated system will contain the following species in a cubic box : 512 molecules CH_3OH, 12 ions K^+ and 12 ions Cl^-.

Data : molar masses in g/mol : $M_O = 16$, $M_H = 1$, $M_C = 12$, $M_K = 39.1$ and $M_{Cl} = 35.5$
$N_{avogadro} = 6.02\ 10^{23}$ /mol

B-1) What should be the dimensions (in A) of the simulation box so that the density of the system is 0.82 g/cm^3 ?

B-2) Calculate the molarity (in mol/l) of this solution.

The radial distribution functions $g_{ab}(r)$ are used to characterize the structure of liquids and mixtures.

B-3) Recall the expression of the formula to calculate gab(r).

B-4) Toward which value do these functions tend at large r ? Why ?

B-5) In the present study, how far can these functions be calculated ?

B-6) How many site-site functions must be known to fully characterize the structure of the present system ? Give the list of these functions.

C- Adjusting the temperature of a simulated system in an MD simulation *(4 points)*

We know that the temperature T of a system is related to the mean square velocity $< v^2 >$ 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):

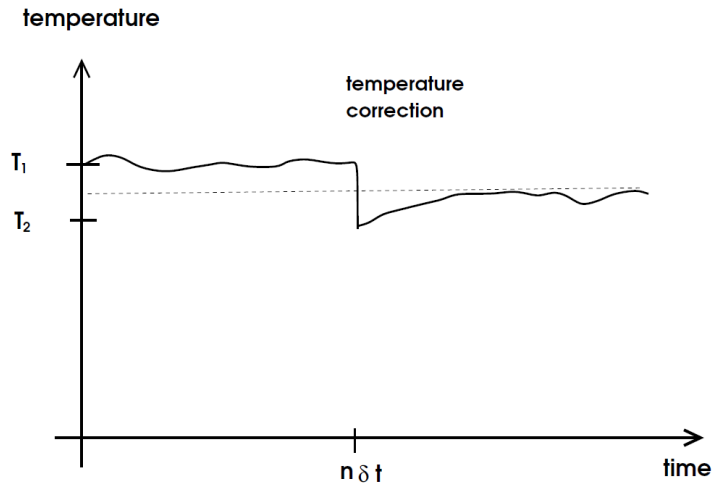
$$\frac{3}{2}Nk_BT = N\frac{1}{2}m < v^2 >$$

We have equilibrated (inside a NEV MD simulation) our system of N interacting particles so that it has, at some time-step n.δt, 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.

C-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.δt, we observe that the system increases its temperature again until it reaches a temperature of $T_3 \approx 0.5\ (T_1 + T_2)$.

C-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 : $< E^{kin} > = < E^{pot} >$. Now you scale the velocities and change E^{kin} ...*).

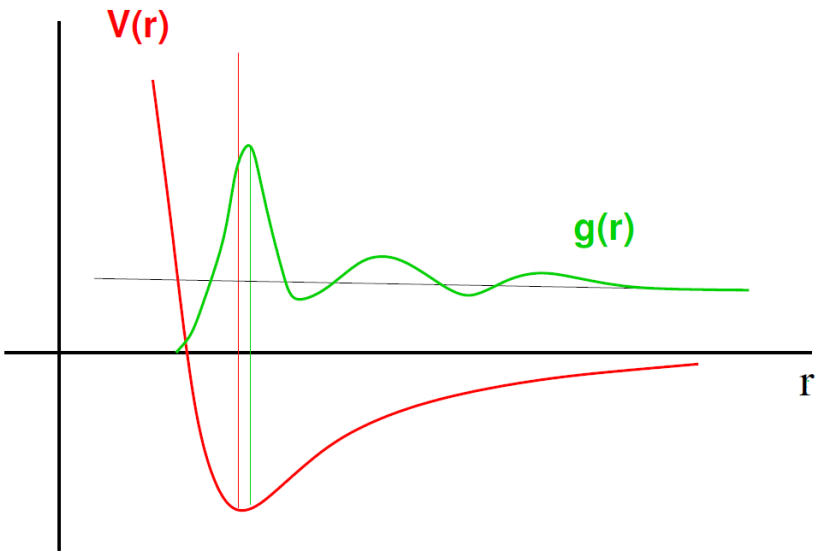


C-3) Is this problem of temperature control transferable to a Monte Carlo simulation ?

D- Basics of Statistical Mechanics *(4 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 $m_A < m_B$.



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

D-2) Does V(r) depends on temperature : Yes / No ? Why.

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

D-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 ?

D-5) Explain why V(r) has a continuous evolution at long distance while g(r) presents several oscillations.

D-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 $T_2 < T_1$.