université de BORDEAUX	**FALL/WNTER TERM 2022 - DST**	
	Semestre 9	**Code UE : 4TCH914U** **Molecular simulations** **Prof. : J-C. Soetens**
	Date : 9/01/2023 **Without documents**	**You have 3h** **Number of points : 30**

A- Analysis of an article *(12 points)*

Few years ago some people published the following article :

THE JOURNAL OF PHYSICAL CHEMISTRY B

Article

Cite This: *J. Phys. Chem. B* 2018, 122, 10783−10792

pubs.acs.org/JPCB

Molecular Dynamics Simulations of Ion Selectivity in a Claudin-15 Paracellular Channel

Giulio Alberini,[†,‡] Fabio Benfenati,[*,†,§] and Luca Maragliano[*,†,§]

[†]Center for Synaptic Neuroscience and Technology (NSYN@UniGe), Istituto Italiano di Tecnologia, Largo Rosanna Benzi, 10, 16132 Genova, Italy

[‡]Department of Experimental Medicine, Università degli Studi di Genova, Viale Benedetto XV, 3, 16132 Genova, Italy

[§]IRCCS Ospedale Policlinico San Martino, Largo Rosanna Benzi, 10, 16132 Genova, Italy

Work to do : read this article and explain (in 4 pages maximum) how these authors used simulations to find a microscopic explanation for the ion selectivity of channels.

Among all the arguments to be developed, you will address in particular the following two points :

- concerning the energy aspect of the transfer of ions by these channels, you will explain why it is necessary to calculate the free energy (and not be satisfied with potential energy) and how particular methods are implemented.

- concerning the hydration of ions, explain how the coordination numbers of figures 7 and 8 are calculated and what these properties reveal about the ion transfer mechanism.

B- Simulation techniques *(6 points)*

B-1) Draw as accurate as possible a flowchart of how a Monte Carlo (MC) simulation works.

B-2) Explain what the "periodic boundary conditions" and the "minimum image convention" are. What is the use of it?

B-3) You begin the study of a system at equilibrium by molecular dynamics. A colleague gives you an interaction potential, an initial configuration and all the useful details (temperature, ensemble, etc.). Propose a series of tests to verify that the system is in equilibrium and that the simulation can be used to calculate representative properties ?

C- Case study *(12 points)*

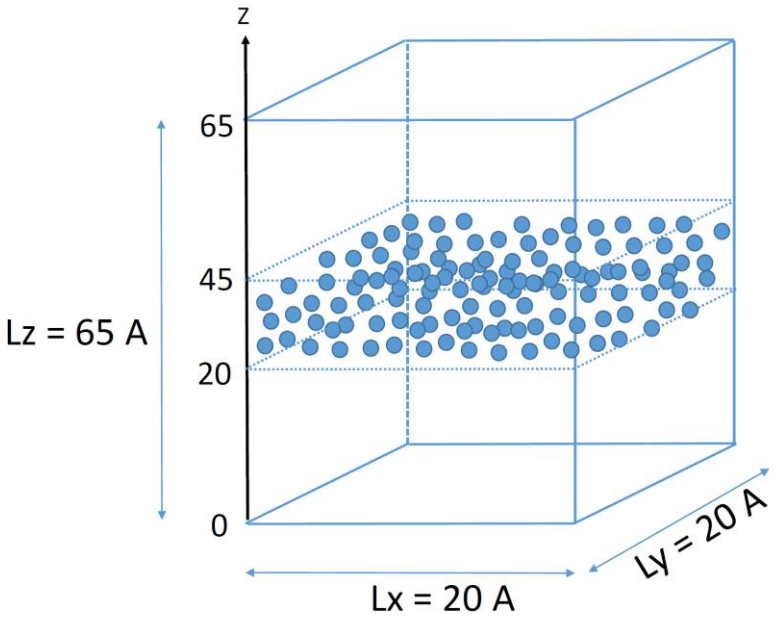
Molecular dynamics study of an iodide an a lithium ion at the water-liquid mercury interface
G. Toth and K. Heinzinger, Chemical Physics Letter (1995).

These authors notably studied by molecular dynamics (MD) the behavior of an aqueous solution of LiCl at the interface with mercury (liquid Hg: an electrode) at room temperature. Mercury atoms and ions are represented by one site each and water molecules by three sites.

C-1) Propose a set of intermolecular interaction potentials to study this system.

C-2) What are the different possibilities to describe the intramolecular interactions of the water molecule. Discuss the impact of the various possible choices on the properties accessible or not and on the conduct of the simulations.

The authors used the simulation box shown below. The edge lengths are Lx = Ly = 20 Å and Lz = 65 Å. The mercury electrode is simulated by 400 Hg atoms on several layers between z=20 and z=45 Å. The rest of the box is filled with water and LiCl.



C-3) Calculate the density (in g/cm^3) of the electrode.

C-4) If we want to simulate pure water in contact with the electrode, how many water molecules should we put into the box to obtain a density of 1 g/cm^3 ?

C-5) Now we want to study a LiCl solution in contact with the electrode (1 LiCl for 10 molecules of water). How many molecules of water and LiCl must be put into the box to obtain (as close as possible) a density of 1 g/cm^3 ?

C-6) Calculate the concentration (in mol/l of solution) of Li^+ ions in the solution.

C-7) The MD simulation is carried out under the usual conditions (periodic boundary conditions and minimum image convention). Propose a cutoff radius adapted to the simulation box.

C-8) We want to describe the structure of this system, list all the radial distribution functions $g_{\alpha\beta}(r)$ necessary for this purpose.

C-9) The authors have calculated the probability density of the presence of species α as a function of z (from z=0 to z=65 Å): $g_\alpha(z)$. Draw approximately (without worrying about the scale for the probability density) the shape for the oxygen atoms of the water molecules, that is $g_O(z)$.

Useful data :

$k_B = 1.38\ 10^{-23}$ J/K
$N_{Avogadro} = 6.02\ 10^{23}$ /mole

M(H) = 1 g/mol
M(O) = 16 g/mol

M(Li) = 7 g/mol,
M(Cl) = 35.5 g/mol

M(Hg) = 200.6 g/mol