	FALL/WINTER TERM 2019 - EXAM	
	Semestre 9 Date : 13/01/2020 <u>Without documents</u>	Code UE : 4TCH914U Molecular simulations Prof. : J-C. Soetens You have 3h Number of points : 20

A- Analysis of an article (7 points)

Some people studied a few years ago the hydration entropy of some hydrophobic solutes :

THE JOURNAL OF
PHYSICAL CHEMISTRY B

Article
pubs.acs.org/JPCB

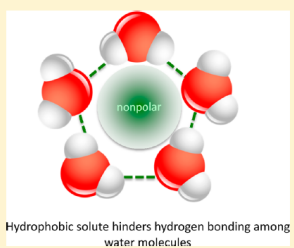
Thermodynamic and Structural Evidence for Reduced Hydrogen Bonding among Water Molecules near Small Hydrophobic Solutes

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[Supporting Information](#)

ABSTRACT: The structure of water molecules near a hydrophobic solute remains elusive despite a long history of scrutiny. Here, we re-examine the subtle issue by a combination of thermodynamic analysis for Henry's constants of several nonpolar gases over a broad range of temperatures and molecular dynamic simulations for the water structure in the hydration shell using several popular semiempirical models of liquid water. Both the structural and thermodynamic data indicate that hydrophobic hydration reduces the degree of the hydrogen bonding among water molecules, and the effect becomes more prominent at high temperatures. Hydrogen-bond formation is slightly hindered near a hydrophobic solute due to the restriction of the degree of freedom for water molecules in the solvation shell, and the confinement effect becomes more significant as temperature increases. Reduction in the extent of hydrogen bonding is fully consistent with a positive contribution of a small hydrophobic solute to the solution heat capacity. As predicted by the scaled-particle theory, both Henry's constants and simulation results suggest that the hydration entropy is determined primarily by cavity formation in liquid water, with its magnitude rising with the solute size but declining with temperature.



Hydrophobic solute hinders hydrogen bonding among water molecules

Read this article and answer to the following questions :

- A-1) Which program is used to perform the MD simulations ? Give the useful technical details of the MD simulations (ensemble, temperature, etc.).
- A-2) Comment specifically on the choice of the ensemble by these authors : explain if it is essential or if another ensemble could have agreed.
- A-3) How many and which hydrophobic solutes have been studied ? Sort these solutes according to their 'size' ?
- A-4) The interactions between solutes are not specified in the article. Why ?
- A-5) Special attention is paid to hydrogen bonds (HBs). How are the HBs between water molecules determined in this study ?
- A-6) The van der Waals energy between water molecules and a solute makes use of the 'WCA' potential. Draw approximately the shape of this potential. Comment on the choice and the origin of the value $\sigma^{1/6}$ for r which split this potential in two parts.
- A-7) About the Figure 1 : What could the authors have calculated and added to this figure to indicate the number of water molecules within the solvation cages ?
- A-8) Could this study have been done using Monte Carlo simulations ? Explain...

B- Principles (5 points)

B-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.

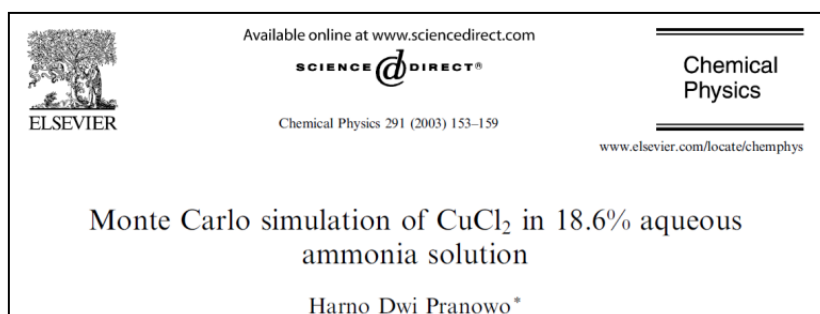
B-2) Method of Molecular Dynamics: on which principle(s) is based this method. Draw a flowchart as precise as possible of how this method works.

B-3) Monte Carlo method: on which principle(s) is based this method. Draw a flowchart as precise as possible of how this method works.

B-4) Comment on the main similarities and differences between these two techniques (MC and MD).

B-5) Describe what is a GCMC simulation : what does 'GCMC' mean, the corresponding ensemble, how it works in few sentences. Give an exemple of application of this method.

C- MC simulation of an ionic system (5 points)



The article cited above presents a simulation of a CuCl_2 solution in a mixture of water and ammonia. Reading the article indicates that the simulated system contains the following species :

171 molecules H_2O , 39 molecules NH_3 , 5 ions Cu^{2+} and 10 ions Cl^- .

C-1) Among the species present in the studied system, what is the solvent, what is the solute ?

C-2) Justify why the mixture is advertised at 18.6 % in the title of the article.

C-3) What should be the dimensions of the simulation box (cubic box) so that the density of the system is 0.809 g/cm^3 ?

C-4) Calculate the molarity (mol/l) of this solution.

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

C-5) Toward which value do these functions tend at large r ? Why ?

C-6) In the present study, how far can these functions be calculated ?

C-7) How many site-site functions must be known to fully characterize the structure of the present system ?
Give a full list of these functions.

C-8) Draw on the same graph the expected curves for $g_{\text{Cu-O}}(r)$ and $g_{\text{Cu-Hw}}(r)$. Same question for $g_{\text{Cu-N}}(r)$ and $g_{\text{Cu-Ha}}(r)$. (Hw refer to the hydrogen atoms of water and Ha the hydrogen atoms of ammonia).

Molar masses in g/mol : $M_{\text{O}} = 16$, $M_{\text{H}} = 1$, $M_{\text{N}} = 14$, $M_{\text{Cu}} = 63.54$ and $M_{\text{Cl}} = 35.45$. $N_{\text{avogadro}} = 6.02 \cdot 10^{23}$

D- Adjusting the temperature of a simulated system in an MD simulation (3 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):

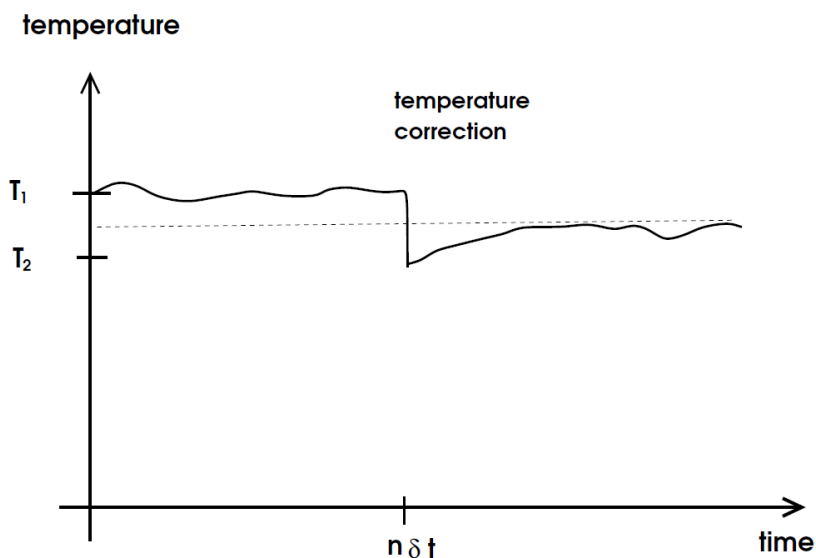
$$\frac{3}{2}Nk_B T = N\frac{1}{2}m \langle v^2 \rangle$$

We have equilibrated (inside a NEV 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 .

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

D-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} ...).



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