université de BORDEAUX	**FALL/WNTER TERM 2018 - EXAM**	
	Semestre 9	**Code UE : 4TCH914U** **Molecular simulations** **J-C. Soetens**
	Date : 15/01/2019 **Without documents**	**You have 3h** **Number of points : 25/25**

A- Potential models *(8 points)*

The potential energy surface (PES) that describes the interactions between atoms inside molecules (the so-called intramolecular interactions) and between molecules (intermolecular interactions) in condensed phases is (or can be) derived from quantum-chemical calculations of the electronic energies.

Questions:

A-1) Which approximation(s) must be made to derive such PES ?
A-2) Describe in a few sentences the procedure "how to do it".
A-3) Which mathematical expression(s) do you know that often describe such PES :
- for intramolecular interactions ?
- for intermolecular interactions ?

In molecular simulations, the following potential is sometimes used to describe an interaction between two particles : $U(r) = -1/r + 2/r^4$

Questions:

A-4) Draw approximately the evolution of this potential U(r).
A-5) Calculate the position and the energy of the minimum of U(r).
A-6) Give the expression for the force F accompanying this potential as a function of r.
A-7) Draw the evolution of the force F(r) on the previous plot in A-5). Be rigorous about the positions of the characteristic points.
A-8) Give the domains in r where this potential is attractive and repulsive

Influence of the description of an interaction model on the computation time.

Questions :

A-9) Describe which and how the various characteristics of classical force fields can have an influence on the computation time in a molecular simulation of a condensed phase.

B- Principles of classical molecular simulations *(3 points)*

B-1) What is a 'microstate' in (classical) statistical mechanics ?
(a) A set given by constant parameters ?
(b) A point in phase space ?
(c) A surface in phase space ?
(d) All accessible points at a given temperature T in phase space ?
(e) All accessible points at a given total energy E in phase space ?

B-2) Method of Molecular Dynamics: on which principle(s) is based this method. What is the fundamental goal of this method ?

B-3) How the temperature can be controlled in a Molecular Dynamics (MD) simulation ?

B-4) How the temperature can be controlled in a Monte Carlo simulation ?

B-5) What can one obtain from analyzing the particles velocities in an equilibrium MD system (many possible responses) ? Explain...

(a) The temperature ?
(b) An infrared spectrum ?
(c) The radial distribution functions (rdf) g(r) ?
(e) The Maxwell-Boltzmann distribution of velocities ?
(f) The kinetic energy ?
(g) The intramolecular potential energies ?

C- Molecular interactions *(2 points)*

Some Japanese people studied a few years ago the intermolecular interactions of CHF_3 dimer using ab initio calculations.

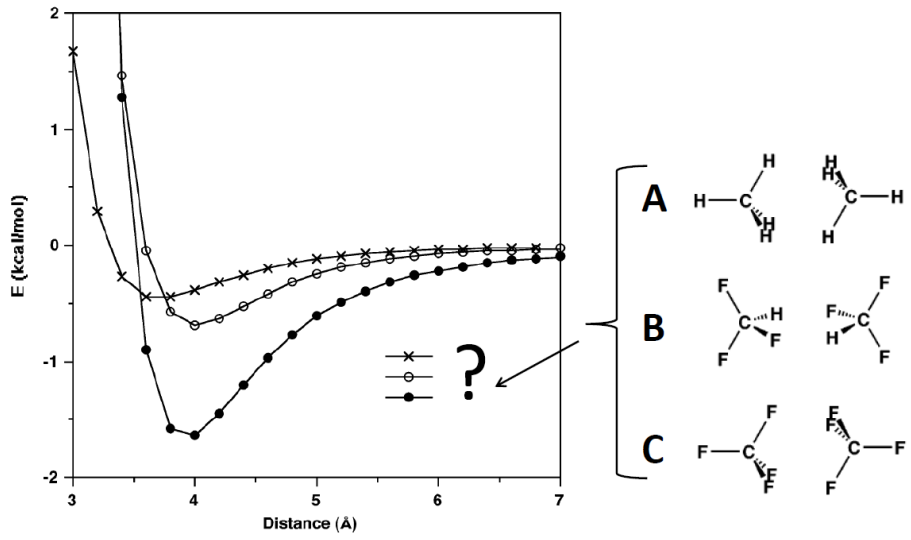
7962 *J. Phys. Chem. A* **2003,** *107,* 7962−7968

Ab Initio Calculations of Intermolecular Interaction of CHF_3 Dimer: Origin of Attraction and Magnitude of CH/F Interaction

Seiji Tsuzuki,*,†,§ Tadafumi Uchimaru,† Masuhiro Mikami,†,§ and Shingo Urata‡

National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba, Ibaraki 305-8568, Japan, and Research Center, Asahi Glass Co., Ltd. (AGC), 1150 Hazawa-cho, Kanagawa-ku, Yokohama, Kanagawa 221-8755, Japan

In this paper, we can especially see the following figure which represents the interaction energies of the dimers A / CH_4-CH_4, B / CHF_3-CHF_3 and C / CF_4-CF_4 as a function of the carbon-carbon distance :



and the following table :

dimer	distance (Å)[b]	E_{total}[c]	E_{es}[d]	E_{rep}[e]	E_{corr}[f]
?	3.8	−0.44	0.04	0.24	−0.72
?	4.0	−0.69	0.17	0.36	−1.22
?	4.0	−1.63	−0.94	0.05	−0.74

where the energies are in kcal/mol. E_{total} in the total interaction energy, E_{es} the electrostatic contribution, E_{rep} the repulsion contribution and E_{corr} the electronic correlation contribution. We also know the boiling points of the differents species under 1 bar : 112 K for CH_4, 191 K for CHF_3 and 145 K for CF_4.

Questions :

C-1) Use these informations to assign the three curves to the three dimers (I mean A, B, C with x, o and •).

C-2) Explain these results through an analysis of the nature of the intermolecular interactions inside these dimers.

D- Molecular Dynamics simulation of an ionic system *(6 points)*

We want to simulate an aqueous solution of LiCl. Thus, three species will be present in the system : Li^+, Cl^- and H2O.

System size

D-1) We want to build a simulation box with 400 water molecules and 2 pairs LiCl. What should be the dimensions of this box (cubic box) so that the density of the system is 1.05 g/cm^3 ?

D-2) Calculate the molarity (in mol/l) of this solution ?

Structure : the radial distribution functions $g_{ab}(r)$ are used to characterize the structure of disorderd systems.

D-3) Toward which value do these functions tend at large r ? Why ?

D-4) In the present study, how far can these functions be calculated ?

D-5) How many site-site $g_{ab}(r)$ functions must be calculate to fully characterize the structure of the present system ? Give a full list of these functions.

D-6) Draw in particular on a first diagram the appearance of the functions $gOLi^+(r)$, $gHLi^+(r)$ and on a second diagram the appearance of the functions $gOCl^-(r)$, $gHCl^-(r)$. Pay a particular attention to the relative positions of the functions according to r.

Data : *Molar masses in g/mol : M_O = 16, M_H = 1, M_{Li} = 7 and M_{Cl} = 35.45, $N_{avogadro}$ = 6.02 10^{23}*

E- Analyze an article *(6 points)*

THE JOURNAL OF PHYSICAL CHEMISTRY B

Article

pubs.acs.org/JPCB

Transfer of the K^+ Cation Across a Water/Dichloromethane Interface: A Steered Molecular Dynamics Study with Implications in Cation Extraction

Mário Valente, Sérgio Filipe Sousa, A. L. Magalhães,* and Cristina Freire*

REQUIMTE - Departamento de Química e Bioquímica, Faculdade de Ciências, Universidade do Porto, Rua Campo Alegre s/n, 4169-007, Porto, Portugal

Read this article and answer to the following questions :

E-1) Which program is used ?

E-2) How many and which molecular species constitute the studied systems ?

E-3) Give the useful technical details of the molecular dynamics simulations (ensemble, temperature, cutoff, etc.)

E-4) Is the potential model used polarizable or nonpolarizable ?

E-5) Why the question of the polarizable or nonpolarizable characteristic of the potential is particularly important for the simulated system in this study ?

E-6) About Figure 4A, the authors write : « (this figure) shows that the cation considerably increases its velocity toward the aqueous phase ca. 10 Å before it reaches the GDS… ».

What do you think of this observation?