

CLAYFF FORCE FIELD VERSUS TIP3P WATER MODEL IN MOLECULAR SIMULATIONS: VALIDATION FOR MONTMORILLONITE CLAY MODEL

CAMPO DE FUERZAS CLAYFF VERSUS MODELO DE AGUA TIP3P EN SIMULACIONES MOLECULARES: VALIDACIÓN PARA EL MODELO DE ARCILLA MONTMORILLONITA

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Recibido 12/10/2022; Aceptado 25/11/2022

Molecular simulations have been useful tools in the research of the host-guest interactions in clays. It has been possible due to the implementation of appropriate force fields to simulate clays, as the CLAYFF. It uses the SPC potential to reproduce the water interactions. However, this is a limitation when combined with the most commonly used organic force fields, AMBER and CHARMM, that use the TIP3P water potential. In the present paper, molecular dynamics simulations of the water-clay model system was done using a combination of CLAYFF with SPC and TIP3P water force fields in order to validate the use of TIP3P water model with the CLAYFF. The results shows very good agreement between radial distribution functions and diffusion coefficients using both water potentials combined with CLAYFF. This fact opens the possibility of using this clay force field with the CHARMM and AMBER force fields.

Las simulaciones moleculares han sido herramientas útiles en la investigación de las interacciones hospedero-huésped en arcillas. Esto ha sido posible gracias a la implementación de campos de fuerza apropiados para simular arcillas, como el CLAYFF. En el mismo, las interacciones de las moléculas de agua son modeladas usando el potencial SPC. Sin embargo, esta es una limitación para combinar con los campos de fuerza orgánicos más utilizados, AMBER y CHARMM, que utilizan el potencial TIP3P del agua. En el presente trabajo realizamos simulaciones de Dinámica Molecular en un sistema arcilla-agua utilizando los potenciales CLAYFF-SPC y CLAYFF-TIP3P en aras de validar el uso de esta última combinación de potenciales. Los resultados muestran una muy buena concordancia entre las funciones de distribución radial y los coeficientes de difusión utilizando ambos potenciales del agua combinados con CLAYFF. Este hecho abre la posibilidad de utilizar este campo de fuerza de arcilla con los campos de fuerza CHARMM y AMBER.

PACS: Molecular dynamics calculations (cálculos de dinámica molecular), 31.15.xv; Solvent effects (efectos solventes), 31.70.Dk; Potential energy surfaces (superficies de energía potencial), 31.50.Bc.

I. INTRODUCTION

Clays and clay minerals are materials with many applications in agriculture, construction, the pharmaceutical and cosmetic industries, oil refining, and many chemical processes. They were widely studied in the 20 century, while their research in the XXI century is focusing on their connection with emergent fields, such as environmental remediation and biopharmaceutical applications [1,2].

In the last two decades, theoretical methods have been useful and essential tools in the research of the host-guest interactions in clays. Important advances in the simulation of different processes in these materials have been achieved. Quantum and classical calculations have allowed to deepen our understanding of the interactions between clays and different guest molecules [3,4]. It has been possible due to the implementation of appropriate force fields (FFs) to simulate clays using Molecular Dynamics (MD) and other classical simulations.

Force Fields with quality and transferability, are essential

for MD. The FFs are mathematical functions that have been adjusted to certain conditions (temperatures, composition, pressure, etc.) for some compounds. And in many cases, they are used on other materials and in a wide range of conditions. That is why the selection of the appropriate FFs is a challenge for computational materials science. A more in-depth discussion of this topic can be found in reference [5].

CLAYFF has been one of the most used force fields to model clay structures [6]. It uses the SPC potential [7] to reproduce water interactions. However, it poses limitations when combined with the most used organic force fields, AMBER [8] and CHARMM [9], which use the TIP3P potential [10] to model water molecules. Choosing appropriate force fields combinations to simulate inorganic-organic interactions is essential in order to understand the molecular mechanisms present in the drug-clay or protein-clay interactions. For example, Wright & Walsh tested the transferability of TIP3P to CLAYFF for quartz [11]. They did not observe any difference between the radial distribution function (rdf) Si-Ow between both water potentials. Recently, we reported MD simulations of ciprofloxacin and montmorillonite clay

models interactions using CLAYFF and Universal Force Field potential (UFF) [12]. However, the possibility to combine CLAYFF with the most used force field for drugs and proteins, CHARMM and AMBER, starts with the correct validation of the use of TIP3P water model with the CLAYFF. In the present paper, MD simulations of the lithium fluorhectorite clay model with water were done using a combination of the CLAYFF model and SPC and TIP3P water force fields. The aim is to validate the use of the TIP3P water potential with the CLAYFF force field for clays. This will open the possibility to combine both force fields to simulate the interactions of clays with drugs, proteins and others organic molecules.

II. METHODOLOGY

The clay model used is a supercell of 5x5x3 unit cell of Lithium fluorhectorite that contains 900 water molecules in the interlayer spaces and was built as described in ref. [12]. Also the periodicity in the 010 direction was cleaved and a slab of 30 Å with 1493 water molecules ($\rho \sim 0,95 \text{ g/cm}^3$) was inserted in the simulation box to reproduce the interaction of the clay model with the outer solution. The density of the outer water slab is very near to the liquid water and to the previously reported for other water simulations [13,14]. The valences of Si and O atoms of the surface were compensated adding OH and H, respectively, ending the tetrahedral clay edges with OH groups. Meanwhile, octahedral ions (Mg^{2+} , Li^+ and F^-) were not balanced.

CLAYFF was the potential used to describe the clay interaction [6]. The Morse potentials terms for OH clay edge surfaces proposed by Pouvreau et al [15] was used instead the ones used in reference [12]. However, the angle term and water potential suggested by Prouveau was not possible to adapt to our model. When they were used, the simulation results evolved to water cluster formation and the separation of the H in the OH terminal group. The parameters of Li^+ compensating cation were taken from Koneshan et. al. [16].

In order to compare the two water potentials, SPC [7] and TIP3P [10], were used to simulate the water interactions.

The intermolecular interactions, i.e., the van der Waals and electrostatic forces between the atoms of the clay and water molecules, have been treated with the parameters proposed by the different force fields. More details about Lennard Jones potential and the combination rules used to determine its parameters, and the potentials, parameters and atomic charges used in the simulations are discussed and presented in our Supporting Information.

MD simulations were performed with the DL_POLY software [17]. Different simulations steps were done to equilibrate the system. Firstly, the clay framework and water were fixed and only the clay terminal OH was relaxing during 1 ps at 300 K in the NVE simulation with a time step 10^{-16} s. Second, the water and the OH terminal were relaxed, keeping fixed the clay framework, in the NVT simulation of 2 ps at 300 K with time step of 5×10^{-16} s. After that, in the third step, all atoms were relaxed, except those Li and F of the octahedral sheets that are in the cleaved surface in contact with the water

solution. These ions were fixed during the simulations in order to avoid possible diffusion. A NPT simulation of 100 ps at 300 K, 1 atm and time step 1 fs was done. Once the system was perfectly equilibrated, a production run of 1 ns in the NPT system with the same details of the third step was performed. The Nosé-Hoover thermostat and barostat were used, each with a 100 fs relaxation time, respectively. In all simulations, periodic boundary conditions were applied, with a time step of 1 fs. The Ewald summation method was used to calculate the electrostatic interactions of the system. The cutoff of the long range interactions, the Coulomb and the Lennard-Jones potentials, were set to 10 Å. The trajectory of the atoms in the NPT simulations was collected each 5000 steps for dynamics and structural analysis.

III. RESULTS

Fig. 1 shows the evolution of Volume (V), Temperature (T) and Total Configurational Energy (E) during the simulation for the two modeled systems.

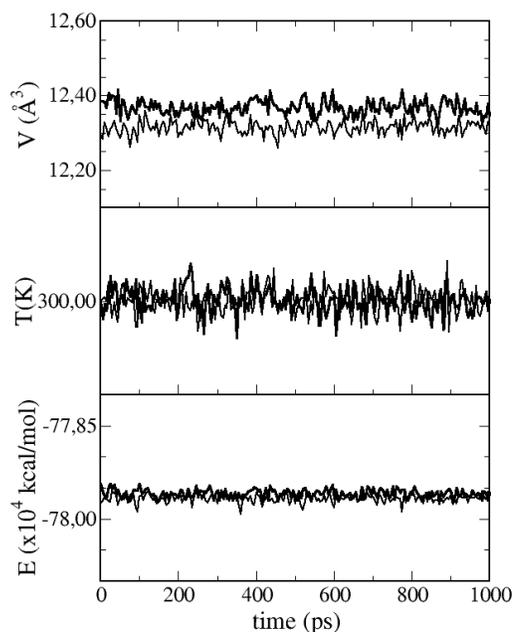


Figure 1. Volume, Temperature and Total Configurational Energy values recorded each 5000 steps during the simulation. The thickest line is the CLAYFF-SPC water system, while the thinnest line is the CLAYFF-TIP3P water system.

As can be seen, the three properties are controlled during the 1ns of simulation. The graphics also show good agreement between the results of the SPC and TIP3P water potential simulations. The Average values (A_v) and the standard deviation (s) of the V, T and E can be found in Table SI2 from Supporting information. It is important to remark that the standard deviation of T only represents the 0.92 % of the A_v , instead for the V and E, which are 0.16 and 0.01 %, respectively. These results support the fact that the simulated systems are well equilibrated.

The property used to compare the results of the simulation of the clay-SPC water and clay-TIP3P water systems was the

radial distribution function (rdf) of the principal clay atoms (Si, O, Li⁺) and the oxygens of the water (OW). They are shown in Fig. 2. As can be seen, there is very good agreement in the position and the amplitude of the different peaks for both modeled systems. This fact supports the possibility of combining the TIP3P water potential with the CLAYFF force field to simulate similar clay models, opening the possibility to combine CLAYFF with the CHARMM and the AMBER force field using TIP3P water.

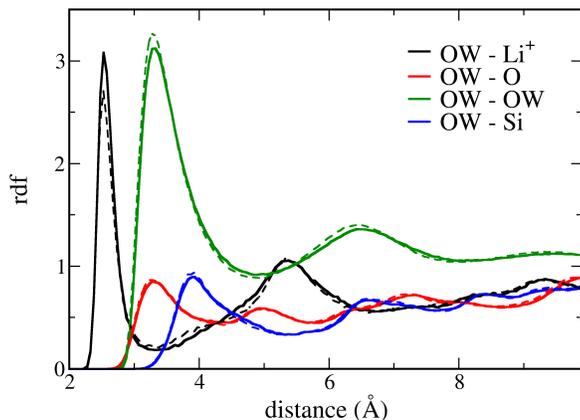


Figure 2. Radial distribution function of the OW-Li⁺, OW-O, OW-OW and OW-Si pairs. The continuous lines are from the CLAYFF-SPC water system, while the dashed lines belong to the CLAYFF-TIP3P water system.

Important information can be determined by analyzing the radial distribution function. The first peak of the Li⁺-OW rdf begins at 2.29 Å, has a maximum between 2.52 and 2.53 Å, and decays around 3.1 Å, indicating the average distance of the first hydration sphere of the compensating cation in these kind of systems.

The OW-OW rdfs reported for liquid water simulations with SPC and TIP3P have the first peaks at 2.78 and 2.77 Å, respectively [18]. In the present simulation the first OW-OW rdf peaks can be found at bigger distances (3.31 and 3.28 Å, respectively) and it could correspond to the number of water molecules that are occluded inside the clay interlayer. At the beginning of the simulations there were 900 water molecules in the interlayers and 1493 in the outer solution. These framework water molecules have space limitations to interact between them, due to the confinement effect inside the clay. And they are also interacting with the Li⁺, favoring the formation of the hydration sphere, which affects the molecule arrangement of the liquid water. These facts can be the cause of the displacement of the OW-OW first peak of the rdf.

The OW-Si and OW-O radial distribution functions indicate the distance between water molecules and the framework atoms. The SPC and TIP3P potentials locate the water molecules at the same distance of the clay atom (3.30 and 3.92 Å, respectively), indicating that both can reproduce appropriately these interactions.

Now we discuss the Diffusion coefficients (D). Table 1 shows the most outstanding D coefficients of the different atoms. As

expected, the clay framework atoms have D values four orders of magnitude smaller than those in water atoms and the Li⁺ compensating cations have diffusion coefficient three orders of magnitude smaller than those of water. They are the clay species with largest motion during the simulation, according to the fact that compensating cations and water molecules have freedom of motion in these materials. It was possible to observe during the simulation the interlayer movement of some Li⁺ cations using both types of water parameters.

The D value obtained for OW and HW (see Table 1) are of the same order of those reported for liquid water modeled with SPC and TIP3P. It is important to note that the D values calculated for SPC-clay are in good agreement with the D values of liquid SPC water and very similar to those of TIP3P water [18]. Moreover, the D water values can be compared with those reported by González Sánchez et al. for water in fully hydrated (f.h.) Na⁺ and Ca²⁺ Montmorillonite (m) [19]. These are important facts that validate our simulations.

Finally, Infrared (IR) spectra were obtained from the Fourier transform of the velocity autocorrelation functions [20, 21] of the CLAYFF-SPC and the CLAYFF-TIP3P simulations. However, a complete interpretation of the spectra in clays is impossible because of the high number of atoms in the unit cell and its disorder, so a clear correlation between structure and vibrational data does not exist.

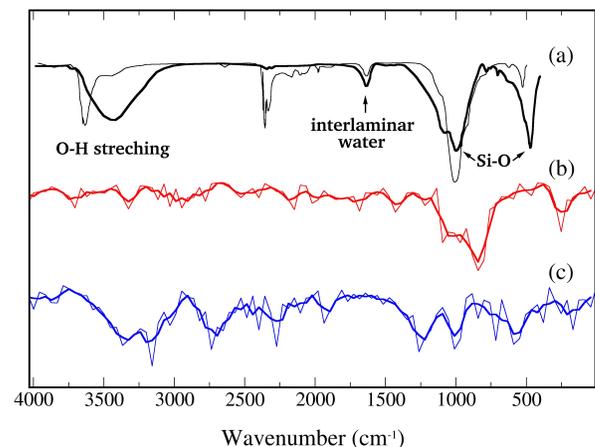


Figure 3. IR spectra. (a) Experimental FTIR: thinner and thicker lines correspond to dehydrated synthetic montmorillonite [22], and experimental FTIR obtained for lithium fluorohectorite with water [23], respectively. (b) CLAYFF-SPC (c) CLAYFF-TIP3P. In (b) and (c), thinner lines correspond to the Fourier transform of the velocity autocorrelation functions, and the thicker lines are the smoothed spectra, respectively.

Fig. 3 shows the simulated and experimental FTIR spectra [22, 23]. As can be seen in the experimental spectra, four important bands associated with the Si-O and H-O vibration normal modes are present. The anti-symmetric and symmetric stretching of Si-O can be observed at 1091 and 997 cm⁻¹. Also the out-of-plane Si-O bending band at 710 cm⁻¹ and the in-plane bending at 472 cm⁻¹ are also identified. These bands also appear in the simulated spectra, and are more defined in CLAYFF-SPC. However, the band at 1643 cm⁻¹, associated to the bending in the plane of the water molecules in the interlayer space (δ H₂O), are not observed in the simulations: This is because for the SPC and TIP3P potentials,

the water molecules are regarded as rigid particles and the O-H vibrations are not taken into account. The band at 3448 cm^{-1} associated to the stretching vibration O-H is reproduced in both simulated spectra, better defined in TIP3P, and it corresponds to the vibration of the OH groups of the clay edges.

Table 1. Diffusion coefficients of the atoms present in the simulated systems using SPC and TIP3P water models.

Atoms	D ($10^{-9}\text{m}^2\text{s}^{-1}$)	
	CLAYFF-SPC	CLAYFF-TIP3P
Si	3.4523×10^{-4}	4.2634×10^{-4}
Oo	3.443×10^{-4}	4.2210×10^{-4}
O	3.5463×10^{-4}	4.1261×10^{-4}
Mg	3.3943×10^{-4}	4.1586×10^{-4}
Li	2.8841×10^{-4}	3.7062×10^{-4}
F	2.9459×10^{-4}	3.3898×10^{-4}
Li ⁺	3.0641×10^{-3}	3.0262×10^{-3}
Oh	4.2045×10^{-4}	8.3572×10^{-4}
H	4.4879×10^{-4}	7.4912×10^{-4}
OW	4.0251	3.9112
HW	4.0255	3.9121
Liquid water [15]	4.22	5.67
Water [19]	2.37 ± 0.12	
Na-m (f.h.) [19]	1.21 ± 0.12	
Ca-m (f.h.) [19]	1.22 ± 0.08	

IV. CONCLUSIONS

The good agreement between the radial distribution functions of the water oxygens (OW) and the principal atoms of the clay and the OW-OW using both SPC and TIP3P water potentials with CLAYFF force field was demonstrated. The interaction between the oxygens of the framework water and Li^+ compensating cations produces a displacement of the OW-OW rdf first peak, suggesting an organization of the solvent molecule which is different from that observed in liquid water.

The calculated diffusion coefficients support the fact that the compensating cation and water molecules have freedom of motion inside the clay materials. They are the atoms with bigger values of D, specially the atoms of water molecules, in comparison with framework atoms, that exhibited lower D values. The D values calculated for the water atoms are in good agreement with the estimated for liquid water using the SPC and TIP3P force fields.

In the simulations it is possible to reproduce the normal Si-O and H-O vibration modes of the clay framework and the terminal OH groups. However, the vibration normal modes of the water molecules are not observed, due to the limitations of the water potentials.

The simulations carried out using CLAYFF in combination with SPC and TIP3P water models and the further comparison of the results validate the possibility of combining CLAYFF

with TIP3P water, opening the possibility of using this clay force field with CHARMM and AMBER force fields.

The supplementary information document is available online at the Rev. Cubana Fis. website and/or upon request to the authors. It includes details about Lennard Jones's potential and the combination rules used to determine its parameters, and the potentials, parameters and atomic charges used in the simulations; the average values (Av) and the standard deviation (s) of the V, T and E.

ACKNOWLEDGMENTS

A. L. and G. R-L. would like to thank Cuban National Programs PN211LH008-027 and PN223LH010-017 for financial support.

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