# A computational study of hydrogen bonding of water confined in nanoporous materials

P. Gómez-Álvarez* and S. Calero
*Departamento de Sistemas Físicos, Químicos y Naturales.*
*Universidad Pablo de Olavide. Ctra. Utrera km. 1, 41013, Sevilla*

The hydrogen bonding[1] in associated liquids has been systematically studied for many years, either experimentally or computationally. Although several techniques such as neutron and x-ray diffraction have considerably increased our knowledge of their structural properties, no accurate and unambiguous information can be extracted from experimental data. On the other hand, Molecular Simulation (MS) represents a powerful tool to complement the experimental approaches and overcome their deficiencies. Thus, the increasing computation power available to scientists has made MS a very useful alternative to gain further insight into the details of the hydrogen-bonding structure of these systems. Of course, this great interest is obviously due to the fact that hydrogen-bonded interactions play a crucial role in a variety of fields, and are responsible of a number of peculiar properties observed in associated substances. In this respect, water[2] is unarguably the most significant case. Hence, it has been studied more extensively than any other liquid. Most of the reported works are focused on analysing bulk water. It shows a complicated tetrahedral H-bonding network, the variation of which as a function of temperature and pressure provokes a considerably singular macroscopic behaviour. On the other hand, the molecular-level characterization of its structure in confining environments is also key to understanding many chemical and biological processes of relevance, from a fundamental point of view to industrial applications such as biological membrane transport, the removal of pollutants from water or water/alcohol separations, among others. In recent years, the number of available porous materials has increased substantially, with new material classes such as Metal-Organic Frameworks joining the traditional adsorbents, which include activated carbons and zeolites.

In spite of being currently of great interest, little is known about the structure of water within the nanopore. Therefore, this work is concerned with the hydrogen bond properties at room temperature of water confined in two different types of crystalline porous materials that show high stability to water: zeolites and Zeolitic Imidazolate Frameworks (ZIFs). The reason of this choice is twofold. On one hand, while zeolites are hydrophobic in their pure siliceous form, ZIFs are hydrophilic due to the metal centers. On the other hand, the pore sizes of the latter are approximately twice as large as those of their zeolite counterparts by virtue of the longer IM linking units. Specifically, we considered five industrially important zeolites with quite different pore arrangement, and their respective Zn and imidazole-based ZIFs, namely: FAU, FER, MFI, MOR, and RHO. Adsorption of water in these structures was computed via Monte Carlo simulations in the grand-canonical ensemble using previously validated force fields. The hydrogen-bonding behaviour of confined water has been described in terms of the Radial Function Distributions (RDFs) and the HB statistics. Particularly, a specific geometric criterion of HB formation[3] was applied over the generated configurations and allowed the computation of the fraction of associated molecules as well as the fraction of which with $i$ H-bonds, $f_i$, and the average number of hydrogen bonds per molecule $\langle n_{\mathrm{HB}} \rangle$.

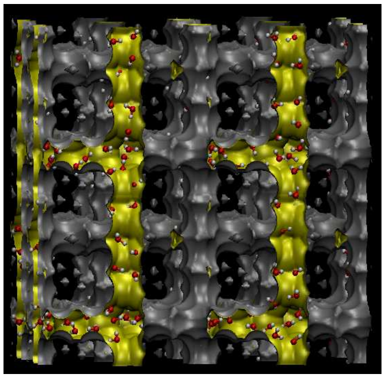

FIG. 1. Snapshot from a simulation. The interior of the energy surfaces (in yellow color) delimits the pore volume where molecules can be adsorbed.

As expected, an enhancement of hydrogen bonding with water loading within the nanopores until reaching bulk-like densities was observed. At these states, our simulations reveal that, although association is still important, the confinement prevents the tetrahedrally coordinated structure characteristic of bulk liquid water. Instead, water molecules form mainly aggregates, whose nature was found notably sensitive to the type of confining material.

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