Molecular dynamics simulation study on the structure and the dynamic properties of nano-confined alcohols between graphene surfaces

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A B S T R A C T

Molecular dynamics simulation was conducted to study the structure and dynamics of hydrogen bonds in alcohols (methanol, ethanol, and 1-propanol) confined within graphene nanopores at a constant parallel component of pressure, 101.3 kPa, and at constant temperatures, ranging from 260 to 340 K. The results indicated that, while confined alcohol molecules orient themselves with the hydrophobic methyl groups exposing to the two plates, the polar hydroxyl groups stand away from surface to preserve a hydrogen-bonding with adjacent layer. Contrary to confined water, the average of hydrogen-bond values of confined alcohol molecules is found to be the same as bulk. Decreasing diffusion coefficient, increasing the relaxation time and, accordingly, decreasing hydrogen bond exchange dynamics occur by increasing the size of alkyl group in alcohol molecules in bulk and confined fluids. Our findings in this work indicate that the effect of confining surfaces on the confined fluid increase at lower temperatures compared to the higher temperatures.

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1. Introduction

Methanol and ethanol are among the most promising renewable fuels that can replace petrochemicals [1]. Due to the intensive use of fossil fuels, there has been an ever increasing trend in the production of polluting gases released into the atmosphere, which has caused climate changes on the earth. Since ethanol is not toxic, it does not contaminate water resources, does not change the natural balance of carbon dioxide in the atmosphere in contrast to the fossil fuels [2], and can be produced in large amounts from the agriculture products or biomass [3]. It is a green fuel that can be applied directly as a fuel or as a gasoline enhancer among the renewable energy resources.

A profound realization of the microscopic behavior of Hydrogen bonded (H-bonded) liquids is essential for many biological and chemical processes. However, the influence of H-bonds on the static and dynamic properties of associated liquids is not well realized. Due to the importance of water in biological systems, a large body of experimental and theoretical studies is aimed at clarifying the details of their structural and dynamical properties in

the bulk and in the vicinity of organic [4—9] or inorganic [10—17] materials. Indeed, the other H-bonded liquids such as alcohols remain underexplored. Alcohols with one hydroxyl group are specified by H-bonding patterns which may be regarded, mostly, as cyclic and, partly, as linear structures [18,19] that are very different from the tridimensional network generic of water because of their hydrophobic groups. Also, by changing the alkyl chain length or by going from primary to secondary or tertiary alcohols, the size and shape of alcohol molecules can be changed easily; this, highlights the effect of the hydrophobic parts in the HB network. Finally, against water, alcohols are miscible with a variety of both nonpolar and polar solvents.

The behavior of molecules confined in the pore with nanometric dimensions is currently a subject of great interest because it plays an important role in many technological applications such as crevice corrosion processes in boilers [20], the characteristic of steams within geothermal reservoirs [21], the attainment of oil trapped within porous rocks [22], the hydration in highly concentrated sugar solutions [23] and problems with fundamental biological relationship such as the solvation at the surface of proteins [24]. The behavior of ethanol molecules in nanopores has considerable impacts on many chemical and biological processes. It is found that ethanol molecules place themselves near the

hydrophobic domain of the pore [25] and block the ion flux within the channel, affording many of the well-known effects of ethanol in humans, such as behavior disorder or anesthesia. Moreover, the behavior of ethanol within the nanopore is significant for the manufacture of fuel-grade ethanol [26], where the nanoporous material is widely used. A suitable physical explanation of the modifications operated in the confined liquid, compared to what is acquired in more usual bulk systems, is necessary to realize how finite size effects influence the behavior of trapped phases.

Recently, numerous attempts have been made to clarify the properties of fluids at the interface. Gubbins and his co-workers studied the adsorption and phase equilibrium of simple gas [27,28], water [29–31], and mixtures [32,33] within different nanopores using molecular simulation. Above cited literature and other studies [9,16,34–36] demonstrated that the behavior of confined fluids is essentially specified by the anisotropic fluid-fluid and wall-fluid interactions. The change of interactions could result in significant changes in behavior of the confined fluids. In the case of alcohol molecules, the coexistence of alkyl chain (nonpolar and hydrophobic) and hydroxyl (polar and hydrophilic) groups make the fluid-fluid and wall-fluid interactions more anisotropic. Zhang and his co-workers [37] studied the transport diffusion of water and methanol molecules inside the hydrophobic and hydrophilic pores with MD simulations. They found that methanol has a much higher flux than that of water in the hydrophobic pore. Thus, the separation of water−methanol mixtures in hydrophobic pores is expected. Morineau and his coworkers studied the methanol molecules confined in silica nanopores with MD simulations [38]. Their results demonstrated that H-bonding interaction of methanol and surface significantly affects the local structure of the interfacial methanol. Kaneko and his co-workers [39–41] studied the structure of methanol, ethanol, and 1-propanol confined in carbon nanopores using in situ X-ray diffraction. They found that, although all molecules could form ordered structures within the nanopore, only ethanol had a remarkable preferred orientation.

While experimental studies use rather indirect methods to investigate H-bonding, a direct experimental measurement about the microscopic properties of confined molecules remains usually difficult [42]. However, computer simulation is a method widely used to obtain direct microscopic information on the statistics and the dynamics of H-bonds and studying the confined behavior within nanoscale [43–45]. From a fundamental point of view, it is interesting to explore similarities and differences between methanol, ethanol and 1-propanol placed in confinements. In this work, we conduct MD simulations at ambient pressures, over a wide range of temperatures to study the structural behavior, diffusion coefficient, the H-bonding statistics and the mean lifetime of H-bonds of alcohols including methanol, ethanol and 1- propanol at the interface, and its comparison to the bulk.

2. Simulation

In the present work, we have employed our new simulation method [46] in the *NAPT* ensemble to simulate a constant number N of alcohol molecules confined between graphene surfaces of constant surface area A at constant parallel component of pressure and constant temperature. It should be noted that in this simulation only the confined region is simulated. It is shown that in the NAPT ensemble method, we do not need to simulate in the grand canonicalensemble to establish equilibrium between bulk and confined fluids. Therefore, we simply impose the parallel pressure to 1 bar (the pressure of the bulk sample) [46–50]. Also, the calculation of chemical potentials for LJ fluid in confinement and bulk fluid indicates that the NAPT ensemble guarantees the existence of equilibrium between the bulk sample and the fluid in

confinement, unless the pore is very narrow [51]. In this method the system is coupled to a Berendsen thermostat [52] and a barostat by changing the distance between the surfaces dynamically to achieve a constant parallel component of pressure, $P_{||}$, defined as [46]:

$$
\begin{aligned}
P_{||} &= \frac{P_{xx} + P_{yy}}{2} \\
&= \frac{1}{3V} \sum_i m_i v_i^2 + \frac{1}{2V} \left[\sum_i \sum_{j>i} (X_{ij} \cdot F_{x,ij} + Y_{ij} \cdot F_{y,ij}) + \sum_i \right. \\
&\quad \times \left. \sum_s (X_{is} \cdot F_{x,is} + Y_{is} \cdot F_{y,is}) \right]
\end{aligned}
\tag{3}
$$

where P_{xx} and P_{yy} are the x- and y-components of pressure tensor, respectively; m is the atomic mass; v is the velocity; V is the volume; subscripts i and j show the atoms in the confining region; subscripts s stands for the surface atoms, X and Y are the relative distances between particles in the x and y directions, respectively, and F_x and F_y are their corresponding forces.

In order to keep the parallel component of pressure fixed, a proportional scaling of the z-coordinates of all particles per time step from z to μz is necessary. The scaling constant μ is defined as:

$$
\mu = 1 - \beta \Delta t \, \frac{\left(P_{0||} - P_{||} \right)}{\tau_P}
\tag{4}
$$

where β is the isothermal compressibility, Δt is the time step, $P_{0||}$ is the target value of the parallel component of pressure, and τ_P is the time constant for pressure coupling, determining the strength of coupling to the barostat. That is, in this method, the distance between the surfaces is changed to keep $P_{||}$ fixed, but the x and y dimensions of the simulation box remain fixed. Since the C atoms involved in graphene surface are immobile, the change in the volume of the simulation box is done by the shifting the z-coordinates of C atoms from z to μz.

Here, $P_{||}$ is fixed to the corresponding bulk pressure. From the surface force apparatus measurements, it is known that the external field, created by the configuration of confined surfaces, varies very slowly from the center of confined region to the bulk [53,54]. Since variation of $P_{||}$ from the bulk fluid to the confined region depends on the gradient of fluid-surface interactions parallel to the surface, as already reported [55], $P_{||}$ is essentially the same as the bulk pressure.

The three-site LJ plus Coulombic potentials were used to describe the non-bonded interactions of the force field. A reaction field model [56] was used to evaluate the coulombic interactions, i. e.,

$$
U_{ij} = 4\varepsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] + \frac{q_i q_j}{4\pi\varepsilon_0} \left(\frac{1}{r_{ij}} + \frac{\varepsilon_{rf} - 1}{2\varepsilon_{rf} + 1} \frac{r_{ij}^2}{r_c^3} \right)
$$

where ε_{ij} is the potential well-depth, σ_{ij} is the position at which the LJ potential is equal to zero, r_{ij} is the distance between centers of spheres i and j, q is charge, ε_0 is the permittivity of vacuum, ε_{rf} is the reaction field dielectric, and r_c is the cut-off distance.

To keep the balance between the available computing time and atomic detail, the united-atom approach is applied: a molecule is represented as a collection of cites, some of which represent a group of atoms, instead of a collection of atoms. An alcohol molecule consists of a hydrogen site, an oxygen site (together forming the hydroxyl group −OH), and subsequent sites representing