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Joël Puibasset, R.J.-M. Pellenq. Confinement effect on thermodynamic and structural properties of water in hydrophilic mesoporous silica. *European Physical Journal E: Soft matter and biological physics*, 2003, 12 (S1), pp.67 - 70. 10.1140/epjed/e2003-01-017-1 . hal-03563006

HAL Id: hal-03563006

<https://hal.science/hal-03563006>

Submitted on 25 Jul 2022

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Confinement effect on thermodynamic and structural properties of water in hydrophilic mesoporous silica.

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Received: date / Revised version: date

Abstract. The adsorption of water on porous silica surfaces at 300 K, has been qualitatively reproduced by Grand Canonical Monte Carlo simulations (GCMC) without any adjustment of adsorbate/substrate potential parameter. The simulated adsorption isotherm and isosteric differential enthalpy of adsorption compare well to experimental data for Vycor, showing the ability of the model in describing hydrophilic properties of silica surfaces. The analysis of fluid structure in the mesoporous glass gives detailed insights into confinement and disorder effects on water adsorbed on the hydrophilic surface of a porous glass. It is shown that hydrophilic properties are not simply related to surface hydroxyl density but are also related to local structure of the silica surface.

PACS. 68.43.De Statistical mechanics of adsorbates – 61.43.Gt Powders, porous materials

1 Introduction

Previous simulation works focused on dynamical and structural properties of water confined in geometrically simple pores (slit [1,2], or cylinders cut in an initial cubic silica [3,4]), supposed to mimic real mesoporous materials. The aim of this work is to investigate, by way of Grand Canonical Monte Carlo simulations, the adsorption properties of water confined in a more realistic disordered mesoporous material previously obtained by off lattice reconstruction [5]. It has been shown [6] that the sample reproduces quite well the geometrical complexity of real high specific surface Vycor, in terms of surface area, chord distribution, and correlation peak in small angle neutron scattering spectra [7].

The interactions between water and substrate is derived from the PN-TrAZ potential [8], and the SPC model is used for water-water interaction. Adsorption isotherm, and isosteric heat of adsorption have been calculated and compared to experimental data found in literature. The good agreement shows that the model is able to give a satisfactory description of hydrophilic properties of Vycor glass. To understand the effect of surface on water structure, oxygen-oxygen radial distribution functions have been determined.

2 Computational details

In order to study adsorption properties in a Controlled Porous Glass (Vycor 7930 like) by molecular simulation, an off-lattice reconstruction algorithm has been used to generate an atomistic Vycor-like mesoporous structure. Portions of an initial cubic crystal of cristobalite 106.95 Å of edge are cut out by applying the off-lattice functional representing the gaussian field associated to the volume autocorrelation function of the studied porous structure [5, 7]. Periodic boundary conditions are applied to the gaussian field, so as to generate the periodic structure shown in figure 1. In order to obtain a realistic description of the surface chemistry, all silicon atoms in an incomplete tetrahedral environment are removed, and all oxygen dangling bonds are saturated with hydrogen atoms placed at 1 Å from oxygen perpendicular to the surface. The porosity of the sample is 0.28, the density 1.56 g/cm³, the specific surface area 210 m²/g, the mean pore diameter 36 Å, and OH surface density 7 OH/nm², all in agreement with experimental values : 0.28, 1.50 g/cm³, 200 m²/g, and around 7 OH/nm² if out-gassed around 400°C [9,10] except for the pore size slightly smaller in our pseudo-vycor compared to real one (40 Å). Although the box size is only three times the pore size, it has been previously shown that this numerical sample reproduces quite well micro and meso textural properties of real Vycor [5–7]. It is thought that this sample will be large enough to capture the behavior of water in mesoporous materials.

The water adsorbed on the surface is described by the SPC

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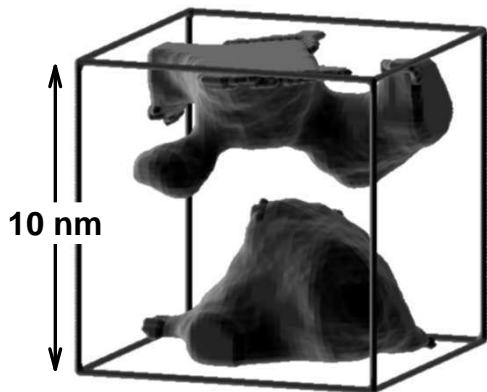


Fig. 1. 3D representation of the numerical sample of Vycor used in this study. Porosity (in gray) : 28%, specific surface area $210 \text{ m}^2/\text{g}$, mean pore size 3.6 nm.

model [11]. This fast computable model is well suited for very large systems, as it reproduces quite well the thermodynamic properties of water around ambient temperature [12]. The interaction between water molecules and silica substrate is described in the framework of the PN-TrAZ model [8] which has proven to model successfully the adsorption of simple adsorbates on various zeolites [13] and mesoporous glass [14,15]. In this model, the pair potential decomposes in two parts : a repulsion term due to electronic clouds and the attractive dispersion terms. The electrostatic contributions are calculated for water-water and water-silica interactions. The partial charges for water species are from SPC model. Those for silica species are taken equal, for consistency, to the charges used in the framework of the PN-TrAZ model to calculate the dispersion terms (Si : $+2e$, O : $-e$, and H : $+0.5e$).

Minimal image convention is adopted to calculate all interactions (cut off equal to half the simulation box, *ie* 5 nm). The electrostatic contribution is evaluated by summing on neutral subgroups of atoms. Implementation of Ewald summation procedure [16] has proven to be of little improvement, probably due to the large box size (107 Å), absence of isolated charges, and zero total dipolar moment of the substrate. Calculations show that most of the substrate contribution to electrostatics comes from the surface dipoles (hydroxyls), the tetrahedral SiO_4 giving rise to weak quadrupolar term only.

3 Adsorption properties

The amount of water adsorbed at 300 K has been determined by way of Grand Canonical Monte Carlo Simulation. An equal number of translation, rotation, creation or destruction of molecules has been chosen, around 2.10^4 per water molecule at full saturation, up to 10^5 at low coverage. The acceptance level for creation or destruction

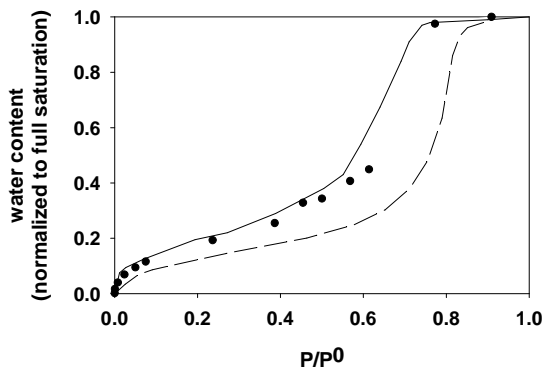


Fig. 2. Circles : GCMC adsorption isotherm in the numerical pseudo-Vycor. Experimental curves : solid line : T. Takei et al. [20] (gravimetry in Vycor; pore size : 4.72 nm). dashed line : N. Markova et al. [21] (micro-calorimetry in Vycor; pore size : 4 to 7 nm).

is quite low, around 1% of trials. The full saturation is reached at the vapor pressure at 300 K, which can be determined by Gibbs Ensemble Monte Carlo method[17]. The value we obtained for SPC model is about 0.044 ± 0.003 bar at 300 K, in agreement with calculation obtained by other groups[18,19]. At this saturating pressure, the density is between 0.91 and 0.95 g/cm^3 , the uncertainty coming from the very slow convergence at full saturation due to very low acceptance level at high density. Nevertheless, this value is only 4% lower than the density of bulk SPC water at 300 K under saturating pressure (0.97 g/cm^3 , by GEMC method).

The amount of water adsorbed, normalized to full saturation, is given in figure 2 as a function of pressure normalized to the saturating pressure for SPC model (0.044 bar). The isotherm is of type IV in IUPAC classification, showing a rapid increase at low pressure characteristic of high adsorbent-substrate interaction. This is expected for hydrophilic surfaces. The steep rise in adsorption at a pressure around 80% of the saturating pressure is related to capillary condensation in the mesoporosity of the sample. For comparison, two experimental adsorption isotherms are shown. The first one is a gravimetric measurement by T. Takei, *et al.* [20] in a 7930 Vycor sample characterized by nitrogen adsorption (pore size around 4.72 nm in diameter). The other one has been obtained by N. Markova, *et al.* [21] with a double twin microcalorimeter, in a 7930 Vycor glass (pore size between 4 and 7 nm). Our simulation results are in good agreement with experimental data, specially at low pressure where water/substrate interactions are predominant. This shows the ability of the PN-TrAZ potential to describe water silica interaction with parameters identical to those deduced from previous studies of adsorption in zeolites.

The heat of adsorption at very low coverage (75 kJ/mol [22]) is well above the heat of liquefaction of bulk water (44 kJ/mol). This means that the surface is hydrophilic, as previously deduced from the shape of adsorption isotherm

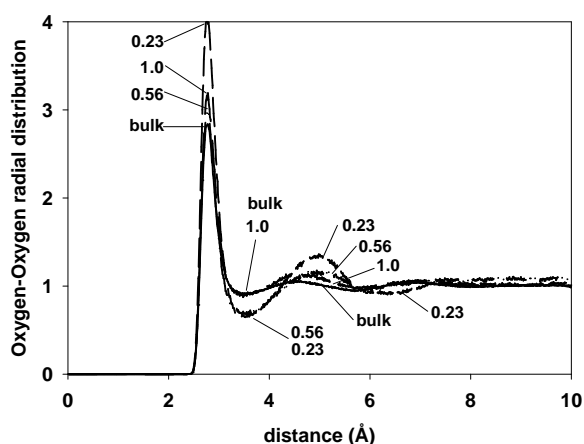


Fig. 3. Oxygen-Oxygen radial distribution function for bulk water and water in Vycor for three different relative pressure given on the figure.

at low pressure. The agreement with the experimental value (65 kJ/mol) [21] is quite good.

4 Structural analysis

To get more insight in the hydrophilic properties of silica surfaces, the structure of water in our mesoporous sample has been studied by way of site-site radial distribution functions. To evidence the effect of the silica surface, the distributions have been determined for three different pressures ($P/P^0=0.23, 0.56, 1.$), corresponding to less than mono-layer coverage up to saturation (20%, 35%, 100% respectively). Particular attention was paid to normalization in order to make distributions comparable. As usual, the first step is to calculate the average number of sites $n(r)$ at a distance r from a defined site. It is then normalized to the number of molecules of an ideal gas at the same density and at the same distance r from the fixed site and contained in the Vycor porosity. This procedure is applied directly in the case of the Vycor saturated by water. But in the case of mono-layer coverage, the normalization procedure is slightly modified to take into account the bi-dimensional character of the thin water film. The number of sites $n(r)$ at a distance r from a defined site is normalized to the number of molecules of an ideal bi-dimensional gas at the same density and same distance r from the fixed site. In this way, all site-site distribution functions tend to unity for large radii. The oxygen-oxygen radial distribution functions are shown in figure 3 for the three different pressures and 300 K in Vycor, and, for comparison, in bulk water at saturating pressure at the same temperature.

As can be seen on the figure all distributions converge to unity for large distances, which validates the normalization procedure. The oxygen-oxygen distribution function obtained in bulk water at saturating pressure is in agreement with literature. The first maximum is at 2.77 Å and

the second maximum at 4.5 Å. The integral of the first peak gives a coordination number of 5.3 in agreement with literature. The structure of water confined in Vycor is slightly more structured, in qualitative agreement with experiment [23,24]. As can be seen on figure 3, the positions of the first and second maximum and first minimum are almost identical to the bulk water. However the peaks are around 10% higher in the case of water confined in Vycor glass, whereas the minimums are almost identical. This is the signature of larger structure of water in presence of confinement. On the other hand, the integral of the first peak gives a coordination number of 5.0, slightly lower than in the bulk water case. This decrease is mainly related to the 4% lower density of water in Vycor compared to bulk water.

The main effect of confinement on the distribution functions comes from near the silica surfaces as can be seen on the distribution function for a water mono-layer adsorbed on the Vycor surface, obtained for a relative pressure equal to 0.56 (figure 3). In this case the structure of water is stronger as shown by the larger first peak and lower first minimum. The integral of the first peak, taking care of the bi-dimensional normalization, gives a coordination number of 2.2. This coordination number shows that some water molecules are absent from the first hydration sphere, and probably replaced by hydrogen bonding with the silica surface (under study). Another interesting point is to note the broadening of the first minimum and the displacement of the second maximum to larger distances (5 Å). It corresponds to the formation of chains of water molecules each having two neighbors. Such a structure is imposed by the substrate and the bi-dimensional character of the thin film. The displacement of this second maximum to larger distances was first observed by Brovchenko *et al.*[25,26] and also reported by Gallo *et al.*[4]. Furthermore, it has been shown [25,26] that the height of this displaced second peak depends on the strength of water-substrate interaction. This shows that the second peak at 5 Å is strongly related to bi-dimensional character of adsorbed water film: the stronger the interaction, the higher the peak, and the higher the confinement of water to a thin layer.

For a relative pressure equal to 0.23, the average coverage corresponds to less than a mono-layer. At this pressure, water molecules are not homogeneously distributed on the surface, but group on large size bi-dimensional patches containing several tens of molecules. The pair distribution function obtained for such configurations, shown in figure 3, is rather different from the one corresponding to mono-layer coverage. The first and second peak are much higher, and the second shell structure is visible. The area of the first peak gives a coordination number equal to 1.6, slightly lower than for mono-layer, which can be related to the presence of water molecules in the periphery of the patches which have only one neighbor instead of two, and isolated molecules. A noticeable point is that the second maximum is still located at 5 Å, showing that the structure of water is close to the mono-layer structure. However, this second peak is much higher in the low pressure

case, and the second minimum more pronounced. The water is then structured at larger extend, which can be understood considering the two following points. First, at low pressure, only very attractive localized sites are occupied, which freezes partially the water structure by reducing its mobility. Secondly, the structure of the silica surface varies in the 3D porous sample (zones of higher hydroxyl density); this explains that the distribution function depends on water pressure.

5 Conclusion

A Grand Canonical Monte Carlo simulation study of water adsorption on Vycor has been presented. The large size mesoporous numerical sample previously obtained by off-lattice reconstruction method, has proven to mimic quite well the geometric complexity of real Vycor, like its specific surface area, pore size, chord distribution and correlation peak in small angle neutron scattering spectra. Its surface chemistry is obtained in a realistic way since all dangling oxygen bonds are saturated with hydrogen which gives 7 OH/nm² in agreement with experiment. The interaction between SPC water and silica is entirely derived in the framework of the PN-TrAZ model with the intrinsic parameters for silica previously deduced from simulation study of adsorption of rare gases in Vycor.

The adsorption isotherm calculated is of type IV in IUPAC classification, showing a rapid increase at low pressure as expected for hydrophilic surfaces. The steep rise in adsorption around $P/P^0 = 0.8$ is due to capillary condensation in the mesoporous solid. The result is comparable to two available experimental adsorption isotherms of water measured by very different techniques (gravimetry and calorimetry). This result, and the good agreement of the simulated isosteric heat of adsorption at very low coverage (75 kJ/mol) with experimental data, show that the model presented is able to describe quantitatively the hydrophilicity of the Vycor surface with no adjustable parameters.

The structure analysis shows a strong structuration of water close to the silica surface. This effect is evidenced at low coverage where long distance correlations are visible. In particular, a correlation at 5 Å appears at low coverage, which is characteristic of two-dimensional arrangement of water molecules. In the case of Vycor fully saturated with water, the oxygen-oxygen distribution function shows a higher structure than for bulk water, the contribution being probably mainly due to the contribution of water molecules close to the surface. A further analysis at different distances from the silica surface will enable us to discriminate surface effects from structuration of water within the pores.

6 Acknowledgements

A. Delville, P. Porion and P. E. Levitz are gratefully acknowledged for fruitful discussions. We also thank the

Institut du Développement et des Ressources en Informatique Scientifique (CNRS, Orsay, France) for the IBM computing grant 021153.

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