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Molecular simulations of water in hydrophobic microporous solids

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Abstract This work reports Grand Canonical Monte-Carlo molecular simulation (GCMC) results of water adsorption in *a priori* hydrophobic microporous solids such as silicalite, a purely siliceous zeolite ($Ø_{\mathrm{pore}} \sim 5$ Å) and C-Y, a pure carbon replica of zeolite Y ($Ø_{\mathrm{pore}} \sim 1$ nm). At a first step, in both cases, the water-water interactions are described with the SPC model (calibrated for bulk liquid water) while water-substrate interactions are calculated within the framework of the PN-TrAZ model. This adsorbate-zeolite potential decomposes into short range (repulsive, inductive and dispersive) interaction terms with transferable parameters plus, in the case of silicalite, an electrostatic interaction term based on SPC partial charges for water and *ab initio* charges for silicalite. With such a standard approach, we found that water fills the microporous volume in both materials at pressure value well below P_0; hence does not show a strong hydrophobic behaviour at variance with reference experiments (V. Eroshenko et al. in C. R. Phys. 3:111, 2002). This indicates that common models used to describe confined polar molecules are far from being operative. We show on the basis of periodic *ab initio* calculations that confined water molecules in silicate have a dipole value ∼10% smaller than that in the 3D liquid phase indicating that the environment felt by a confined water molecule in silicalite pores is not equivalent to that in the bulk liquid. This implies that classical simulations of polar molecules in ultra confining environment should rely on polarizable potentials (K.S. Smirnov, D. Bougeard in Chem. Phys. 292:53, 2003) if one wishes to capture the underlying physics. Reducing the SPC water dipole moment by 5% in GCMC calculations does allow reproducing experimental data.

Keywords Grand canonical Monte-Carlo · *Ab initio* periodic calculations · Water · Adsorption · Silicalite · Zeolite carbon replica

1 Introduction

Understanding hydrophobicity of porous materials at a molecular level has triggered a great deal of research for many years (Lum et al. 1999; Giaya and Thompson 2002a). Siliceous zeolites are known as being hydrophobic media (Patarin and Gies 2005). This means that water invades their microporosity from the liquid phase under pressure (i.e. a relative pressure larger than unity). Trzpit et al. recently reported an experimental and molecular simulation study of water condensation in silicalite-1 zeolite (Trzpit et al. 2007). A first sample was synthesized using the so-called "fluoride route" and contains no defects. A second sample synthesized using the "hydroxide route" was found to contain a small amount of silanol groups using spectroscopy technique such as H-NMR. The thermodynamics of water condensation was studied in these two samples, as well as in a commercial sample, in order to understand the effect of local defects on water adsorption. The main results of this work was to shown that whatever the samples (defective or defect-free), water condensation was still observed above the water saturation vapor pressure P_0. Both experiments and simulations agree on the fact that a small water uptake can be observed at very low pressure on the defective sample

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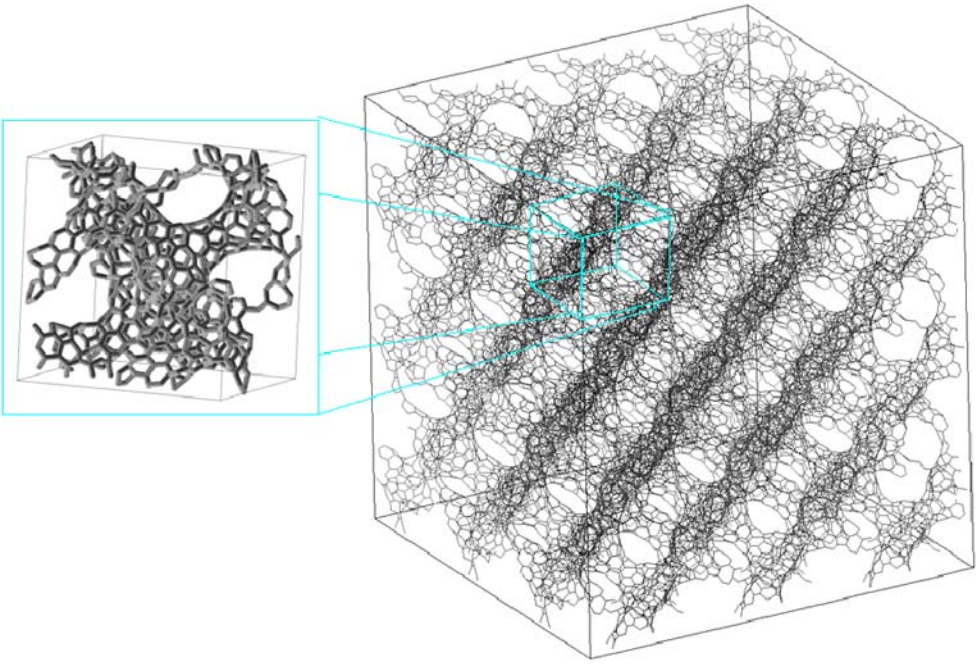

Fig. 1 A single unit cell of the carbon replica of Y zeolite extracted from a 5^3 unit cell C-Y crystal (grey bonds link two carbon atoms, the C-Y structure being made essentially of sp_2 carbon atoms)

due to hydrophilic "patches", but that the bulk liquid does not form from the gas phase below P_0. Possible applications are storage or dissipation of mechanical energy as shown by Eroshenko et al. preforming water intrusion/extrusion cycles in silicalite zeolite, the siliceous analog of the ZSM-5 zeolite (Eroshenko et al. 2001, 2002).

Microporous carbon are also known to exhibit an hydrophobic behavior that is less marked since water absorbed at room temperature around a relative pressure of 0.7 (McCallum et al. 1999; Jorge et al. 2002). Recently, new ordered forms of carbon have been produced by casting the voids of zeolite structures such as $AlPO_4$-5 or Y faujasite (Ma et al. 2000; Wang et al. 2000). These carbon substrates thought as being almost pure carbon phases, should have an enhanced hydrophobic behavior.

Molecular simulations is a well suitable to gain a profound understanding of dynamical, structural or thermodynamic properties of polar and non polar fluids confined in nanopores (Auerbach et al. 2003; Bussai et al., 2001, 2002, 2003; Demontis et al. 2003; Fleys et al. 2004; Desbiens et al. 2005; Douguet et al. 1996; Fleys and Thompson 2005; Ramachandran et al. 2006; Puibasset and Pellenq 2003a).

The aim of this study is to gain insights on the origin of the hydrophobic character of two porous substrates, namely silicalite zeolite and the carbon replica of faujasite Y zeolite at a molecular level using the well-established Grand Canonical Monte-Carlo simulation technique. These calculations are based on an interaction model which was successfully used in predicting water adsorption in disordered mesoporous silica substrate like Vycor glass (Puibasset and Pellenq 2003a, 2003b, 2005).

2 Numerical details

The first atomistic simulated adsorbent is made of the 3*3*3 repetition of one unit cell of the silicalite. The spatial dimensions of the simulation box are then 60.21*59.76*40.26 Å^3. Periodic boundary conditions are applied in the 3 directions. The second adsorbent is a simulated sample of C-Y, a pure carbon replica of zeolite Y ($Ø_{\text{pore}} = 1$ nm) obtained from Grand Canonical Monte-Carlo simulation (see below) of carbon vapour deposition in the zeolitic host using both the REBO potential for carbon interactions and the PN-TrAZ approach to describe the carbon-matrix interactions (Roussel et al. 2007). The simulation box dimensions are 24.85 Å in two directions and 74.55 Å in the third direction (Fig. 1). The adsorbed water is described by the SPC model (Berendsen et al. 1981), because it is a fast computable model which reproduces well the thermodynamic and structural properties of bulk water around ambient temperature, like vapor pressure, enthalpy of vaporization, and radial distribution functions (Jorgensen et al. 1983). In the Grand Canonical Monte-Carlo simulation technique, the temperature, volume and chemical potential (related to the pressure of the gas) are kept constant. An equal number of trials for translation, rotation, and creation or destruction of molecules has been chosen for each run at fixed pressure. No bias procedure was introduced since the density is generally relatively low. As in experiments, the repetition of the calculation for different vapor pressures enables to calculate the complete adsorption isotherm. For each Monte-Carlo run, the configurations are considered for visual examination and statistical calculations every block of 10^4 Monte-Carlo steps along the Markov chain, so that they are de-correlated.

Table 1 PN-TrAZ parameters for water and vycor species in atomic units

Atoms	Water		Silicalite		Carbon replica
	O	H	Si	O	C
q (e)	−0.82	0.41	+2	−1	0
A (E_h)	247.7	1.338	6163.4	1543.5	35.7
b (a_0^{-1})	2.075	2.11	2.395	2.19	1.681
Polarizabilities (a_0^3)	7.56	2.655	2.36	8.03	11.89
N_{eff}	4.476	0.414	1.52	4.656	2.65

$a_0 = 0.529177$ Å, $1 E_h = 3.1578 \times 10^5$ K

Table 2 Dispersion and repulsion parameters obtained in the framework of the PN-TrAZ model in atomic units

Water species	Adsorbent species	C_6 ($E_h a_0^6$)	C_8 ($E_h a_0^8$)	C_{10} ($E_h a_0^{10}$)	A (E_h)	b (a_0^{-1})
H	O	8.3157	151.22	2668.6	45.444	2.149
H	Si	2.4874	32.919	–	90.811	2.243
H	C	10.882	256.30	–	6.9120	1.838
O	O	34.850	735.319	13540.4	618.3	2.131
O	Si	10.513	172.72	–	1235.5	2.223
O	C	42.0537	1141.057	25300.76	94.01	1.878

Water/substrate interactions are assumed to remain weak, in the physisorption energy range. In this work, we have used a TrAZ form of the original PN-type potential function as reported for adsorption of rare gases and nitrogen in silicalite-1 (Pellenq and Nicholson 1994). The PN-TrAZ potential function is based on the usual partition of the adsorption intermolecular energy restricted to two body terms only: it includes a dispersion interaction term, a repulsive short range contribution, an induction term and a coulombic term. The choice of this particular model to describe the water/adsorbent potential was motivated by the good degree of parameter transferability. Indeed, in a previous study (Puibasset and Pellenq 2003c), we found that using a set of potential parameters previously derived for adsorption in silica zeolite augmented to take into account hydroxyl groups, the TrAZ model allows reproducing both low coverage experimental adsorption isotherm (amount adsorbed versus pressure at constant temperature) and isosteric heat curve with no further adjustment. In the case of water interacting with silicalite, one has to parameterize four different adsorbate/adsorbent-species potentials; two in the case of water confined in C-Y. All atomic and potential parameters and coefficients are given in Tables 1 and 2. Note that repulsive parameters for like-pairs are taken from a previous work on the simulation of rare gases in silicalite (Pellenq and Nicholson 1994) using Bohm and Ahlrichs (1982) combination rules based on *ab initio* results at the Hartree-Fock level approximation which only describes the repulsive energy term in the case of non charged and polar species. This type of potential function based on the PN-TrAZ parameterization method was used in various studies of molecular and covalent fluids at interfaces from open surfaces (Marinelli et al. 1999; Puibasset and Pellenq 2003a, 2003b) to microporous zeolites (Lachet et al. 1998; Nicholson and Pellenq 1998; Fuchs and Cheetham 2001; Bichara et al. 2002; Grey et al. 2002) and more recently in the case of mesoporous Vycor-like materials (Pellenq et al. 2000, 2001; Pellenq and Levitz 2002; Puibasset and Pellenq 2002, 2003a, 2003b, 2003c, 2005; Coasne and Pellenq 2004).

Minimal image convention is adopted to calculate all interactions. Long range mean-field correction to dispersion terms cannot be precisely calculated because the density is not uniform. Actually, the size of the box is large enough so that large distance contributions are negligible. The electrostatic contribution is evaluated by summing on neutral subgroups of atoms of highest symmetry (tetrahedral silicon SiO_4). Implementation of Ewald summation procedure (Ewald 1921; Heyes 1994) has proven to be of little improvement, probably due to the large box size, and absence of isolated charges.

3 Simulation results

The amount of water adsorbed at 300 K has been determined by way of standard Grand Canonical Monte-Carlo Simulation (Nicholson and Parsonage 1982) (GCMC), which mimics a real adsorption experiment. The Fig. 2 shows a typical equilibration run (enlarged around its equilibrium value) at a relative pressure of 0.16 from an initial configuration at relative pressure 0.07 in the zeolite carbon replica. The

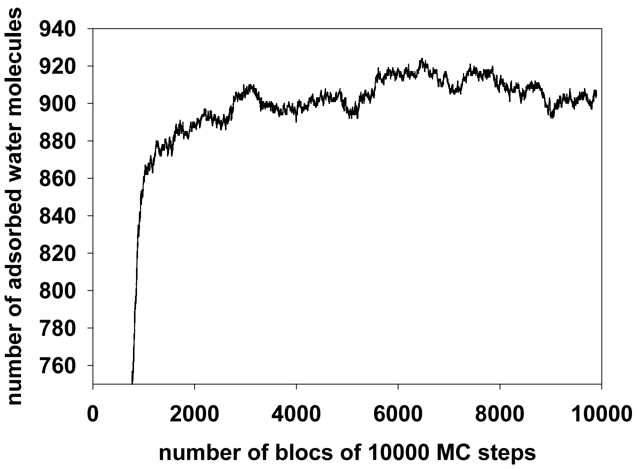

Fig. 2 Example of equilibration run showing the amount of water adsorbed at $P/P_0 = 0.34$ from an initial configuration at $P/P_0 = 0.23$, as a function of the number of blocks of 10^4 Monte-Carlo step

number of particles is drawn as a function of the number of blocks of 10^4 MC steps. As can be seen, the evolution is initially very rapid, and then slows down. Good equilibration is reached after 10^4 blocks, that is to say around 10^5 trials per water molecule. Similar behavior is observed for water in silicalite. To acquire data, another 5×10^5 trials per molecule were run, where the number of particles fluctuates around a constant value. After the complete saturation of the samples is reached for high chemical potential μ or reduced pressure, one can start decreasing μ to acquire the desorption branch and locate a possible hysteresis loop (if there is).

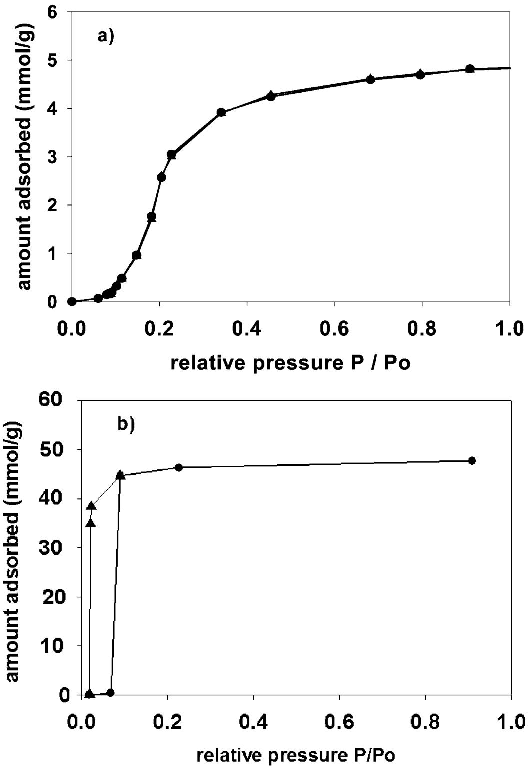

Fig. 3 Water adsorption (*circles*)/desorption (*triangles*) isotherms in silicalite-1 (**a**) and carbon replica (**b**) as a function of relative pressure. Note that at pore completion, the carbon structure can adsorb ten times more water than silicalite

The adsorption/desorption isotherms obtained in the two samples at 300 K are given is Fig. 3 as a function of the relative pressure P/P_0 where $P_0 = 0.044$ bar is the saturating vapor pressure of SPC water at 300 K (Errington and Panagiotopoulos 1998; Vorholz et al. 2000). As can be seen the curve is reversible for silicalite, as expected for a microporous adsorbent. The curve shows low initial adsorption for $P/P_0 < 0.1$, as for a hydrophobic surface. This is in qualitative agreement with experimental data. However, the substrate saturates for pressure lower than the saturating vapor pressure, which indicates a noticeable affinity of our simulated substrate for water which is confirmed by the isosteric heat of adsorption (see later). This excessive hydrophilic character was previously observed by other authors reporting simulation results for confined water in silicalite with the same kind of approach based on a bulk water potential with a physisorption water-host potential (Desbiens et al. 2005). Note that this is also in disagreement with experimental data, which show stronger hydrophobicity (Fubini et al. 1989; Kenny and Sing 1990; Zhao et al. 1997; Giaya and Thompson 2002b). In carbon replica the isotherms present a hysteresis, which may be interpreted by the fact that the pores are larger than in silicalite. It was noticed that the hysteresis width slightly decreases with the system size and may be due to an artifact of the Monte-Carlo method. The important point however is that, here again, the system presents a rather large adsorption at low pressure, which is not expected in hydrophobic carbon adsorbents. However, such behavior also observed by other authors: for instance Birkett and Do report GCMC simulation results of water adsorption of a graphitic surface based on standard water-water and water-carbon potentials showing the same large affinity of the simulated water for the carbon surface that sharply contrast with available experimental data (Birkett and Do 2007; Striolo et al. 2005)

Figure 4 shows molecular configurations of water adsorbed in the numerical sample for different pressures. For clarity, the substrate is not shown. For low pressure ($P/P_0 = 0.0886$) the system is made of isolated water molecules and clusters containing few molecules adsorbed on the substrate. For a relative pressure 1.67 times larger ($P/P_0 = 0.1477$) the amount of water adsorbed is 4.5 times larger, and essentially all molecules are implied in a cluster (no isolated molecules left). At $P/P_0 = 0.2045$, the system is almost saturated, and the clusters merge into large size ones. The last snapshot shows the $P/P_0 = 0.341$ configuration almost completely filled, with few adsorption sites left. Figure 5

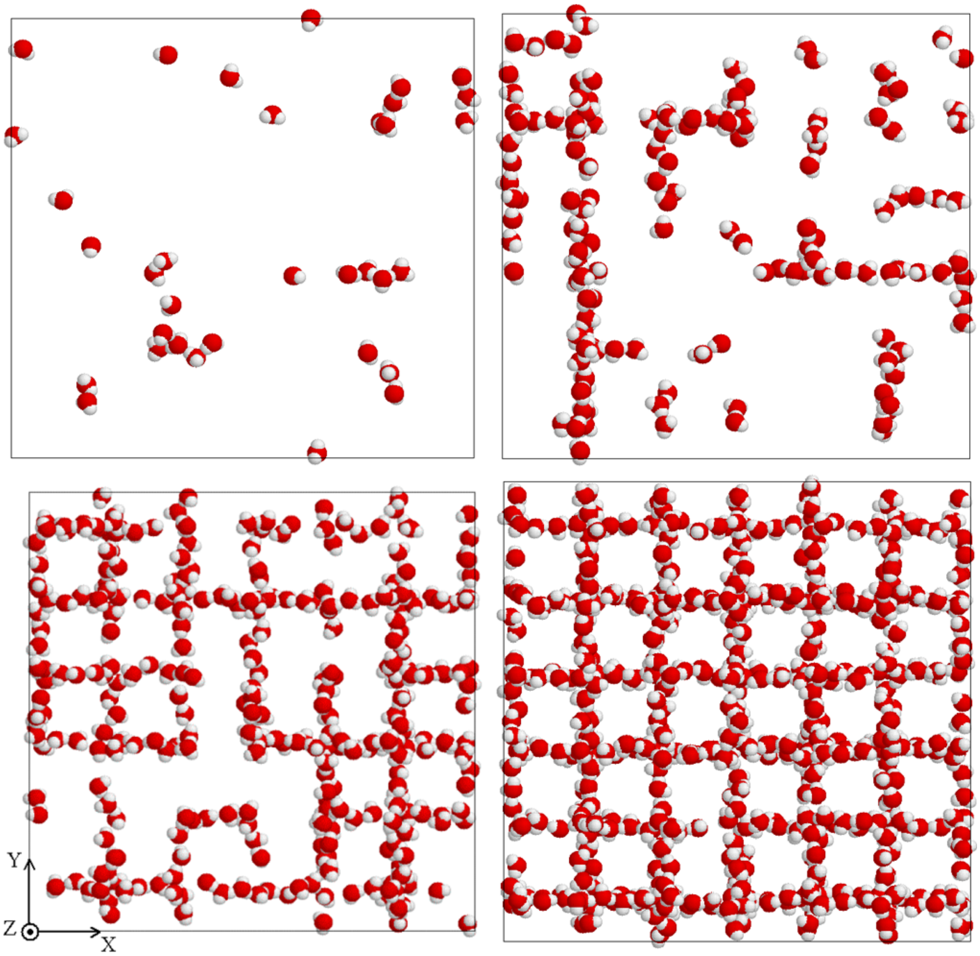

Fig. 4 Water molecular configurations in silicalite for four relative pressures ($P/P_0 = 0.0886$, 0.1477, 0.2045, 0.3409). The silicalite species are not represented

shows a molecular configuration for water confined in the carbon sample. For clarity, water confined in one single carbon replica is shown (the entire simulation box is made of three successive boxes). As can be seen, water forms one single cluster. If the pressure is decreased, the system immediately jumps to the gas-like state (few isolated molecules), since the configuration corresponds to the limit of the desorption curve (lowest average density). There is no intermediate situation with water clusters as observed in silicalite. The same happens upon adsorption, where a single large water cluster forms in one step.

Figure 6 gives the molecular configurational energy (in kJ per mol of water molecules) at 300 K as a function of the relative pressure in silicalite. The general trend shows that the configurational energy decreases with pressure or coverage: the water-silicalite interactions are then weaker than water-water interactions, which is characteristic of a hydrophobic adsorbent. More precisely, the evolution of the configurational energy with coverage shows essentially two behaviors. For relative pressure lower than 0.2 the energy decreases rapidly with relative pressure, whereas above $P/P_0 = 0.2$ the configurational energy hardly decreases with pressure. The first range of pressure corresponds to the initial adsorption of molecules on small and disconnected clusters previously adsorbed (see Fig. 4). On the other hand, for larger pressure essentially only one (infinite) cluster per-

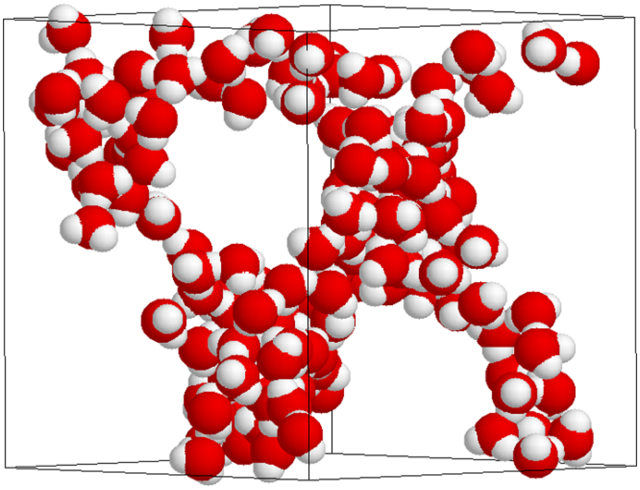

Fig. 5 Water molecular configuration in one single (for clarity) carbon replica for $P/P_0 = 0.0205$ (the simulation box is made of 3 such replicas, see text)

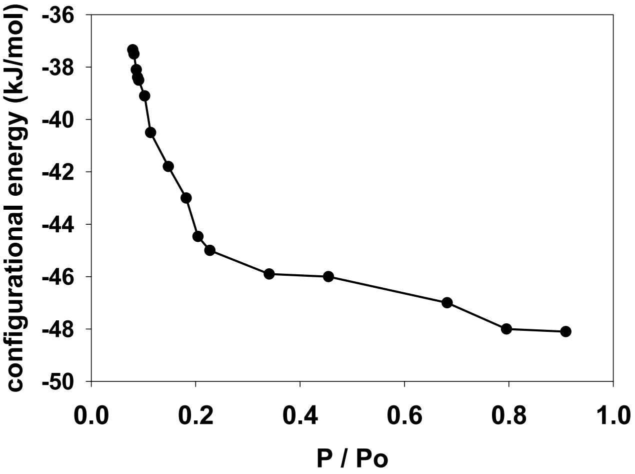

Fig. 6 Configurational energy of water adsorbed in silicalite-1 as a function of relative pressure

sists, and the number of free sites decreases significantly. Interestingly, the opposite behavior was observed in the case of water adsorption in hydrophilic mesoporous Vycor material (Puibasset and Pellenq 2005).

In the case of water adsorbed in carbon replica, the energetic behavior is much simpler. Essentially, the configurational energy of water along the gas-like branch (low adsorption region) is around −44 kJ/mol. The value is almost constant and corresponds to the water/substrate contribution. As expected, water/water contributions are almost zero due to the extremely low amount adsorbed. Along the saturating liquidlike branch, the energetic contribution reaches −52 to −54 kJ/mol. The value is again almost constant. However, the fluid/wall contribution now reduces to −13 kJ/mol, while the water/water contribution reaches −40 kJ/mol. This behavior is compatible with the fact that water molecules form a single liquid-like aggregate confined in the carbon porosity.

The configurational energy is not a directly accessible quantity, from an experimental point of view. The measurable quantity is the isosteric heat of adsorption, which measures the heat released by the adsorption of a given amount of fluid, as a function of the total amount of fluid previously adsorbed in the substrate. Numerically, this quantity is deduced from cross-fluctuations in energy (U) and adsorbed quantity (N) through the formula (Nicholson and Parsonage 1982):

$$q_{\mathrm{st}} = -\frac{\langle UN\rangle - \langle U\rangle\langle N\rangle}{\langle N^2\rangle - \langle N\rangle^2} + RT. \tag{1}$$

The general trend is an increase of the isosteric heat of adsorption, from 43 kJ/mol at low coverage, up to 52 kJ/mol at saturation. This is typical of hydrophobic adsorbent. The low coverage value gives information on the strength of the adsorbate/adsorbent interaction. The value (43 kJ/mol) is close to the latent heat of vaporization of water. The water/silicalite interactions are then comparable in intensity to the water/water interactions, which is drastically different from hydrophilic substrate like silica surfaces presenting hydroxyl groups (Puibasset and Pellenq 2003a, 2003b), for which the water/silica interactions are much stronger than water/water interactions. However, the higher the coverage the higher the heat released. The contribution from the substrate (around 40 kJ/mol) is almost constant, due to the small size of the pores, while the contribution from water/water interactions increases (up to 10 kJ/mol) with the pore filling. However, the water/water contribution can never reach its bulk value because the structure of water in silicalite is strongly distorted. Inspection shows that, at saturation, most of the molecules establish two hydrogen bonds instead of four in bulk water, which explains the increase of 10 kJ/mol in isosteric heat.

For water confined in the carbon samples, the amount adsorbed in the low pressure region was too small to extract precise values for the isosteric heat of adsorption. However, the values are of the order of the latent heat of bulk water within error bars, as for silicalite. The substrate is then slightly hydrophobic. As for silicalite, the hydrophobicity character is again much too low compared to what is expected for a pure carbon substrate (Birkett and Do 2007).

4 Influence of water dipole

This section focuses on a quantitative comparison of the simulation results with experiments. Various conventions are used to give the adsorption isotherms (relative pressure, absolute pressure or chemical potential, depending on the range of pressure considered in the experiments). We decided to report our simulation results and the experimental data found in the literature for silicalite in Fig. 7 as a function of the chemical potential of water. Various techniques are used: gravimetric or calorimetric measurements (Fubini et al. 1989; Kenny and Sing 1990; Zhao et al. 1997; Giaya and Thompson 2002b). In each case, the water uptake is very low, showing that silicalite is hydrophobic. Inspection of experimental data show large variations, probably due to differences in sample preparation. Above the bulk saturating point, conventional techniques fail. Eroshenko et al. (2001, 2002) developed intrusion experiments to measure the amount of water introduced in the porous material as a function of the liquid water pressure. The results show a linear volume variation of the system with pressure, with a rapid water uptake around 100 MPa. Two water intrusion points from the above mentioned experiments are reported in Fig. 7, corresponding to $P/P_0 = 0.5$ and $P = 100$ MPa. The water pressures have been converted to chemical potential using the fact that the gas state is almost

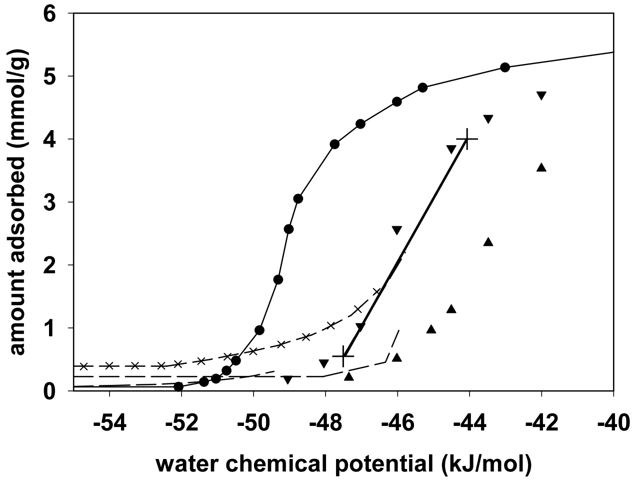

Fig. 7 Water adsorption isotherm in silicalite as a function of the chemical potential. *Dashed line*: experimental data of Kenny and Sing (1990). *Dashed-crossed line*: experimental data of Zhao et al. (1997). Solid line: experimental data of Eroshenko et al. (2001). *Circles*: PN-TrAZ model + original SPC water model. *Down triangles*: PN-TrAZ model + SPC water model with water partial charges reduced by 5 percents. *Up triangles*: PN-TrAZ model + SPC water model with water partial charges reduced by 10 percents

ideal, and by integrating the water equation of state above the saturating point, which is a standard procedure. As previously mentioned, the simulation results are in qualitative agreement with experimental results. However, the adsorption isotherm, as predicted by the model, is shifted towards low chemical potential as compared to experimental data: the pore filling occurs around $P/P_0 = 0.2$ in simulation ($\mu = -49$ kJ/mol), whereas it is expected to occur around $\mu = -44$ kJ/mol. Similar results where obtained by Desbiens et al. (2005) when using the same electrostatic partial charges as we did for silicalite species. In order to reconcile simulation results with experimental data, we propose to re-consider the electrostatic contributions. Desbiens et al. (2005) proposed to decrease the partial charges of the silicalite species ($q_{\mathrm{Si}} = 1.4$ instead of 2.0). Another way to modify electrostatic contributions is guided by the fact that the water model used in the simulation (SPC) might not be optimal to describe low density water. As a matter of fact, it is expected that the partial charges on a water molecule are greatly influenced by the environment seen by this molecule. In most cases, water simulation models are parameterized in the liquid state. In such a situation, the water molecules are surrounded by a highly polarizing media. It is then questionable whether such models are efficient to quantitatively describe the water clusters observed in silicalite. It is then suggested to evaluate the influence of water partial charges on water adsorption isotherm in silicalite.

To this end, we performed full *ab initio* Hartree-Fock calculations of water in the liquid bulk phase and confined to silicalite pores using the CRYSTAL98 code that allows periodic calculations. The choice of atomic basis sets is of central importance for such calculations. We have chosen 6-31G* orbital sets for hydrogen and oxygen species; silicon was modeled using a Durand pseudo-potential (http://www.crystal.unito.it/Basis_Sets/Ptable.html). This type of calculations allows obtaining (Mulliken) partial charges of all atoms in the considered periodic simulation box, hence characterizing the nature of bonding processes (ionic, covalent, ioni-covalent). Note however that these calculations were carried out at the Hartree Fock level of approximation thus ignoring electronic correlation effects hence dispersion interactions. As expected from Pauling's rule for electronegativity, we found that the partial charges of zeolitic species are half their formal values ($q_{\mathrm{oZ}} = -1.05$, $q_{\mathrm{Si}} = +2.1$) in agreement with previous *ab initio* calculations on quartz (Nada et al. 1990). As shown in Fig. 8 with such relatively atomic large basis sets, a single water molecule having the SPC geometry (HOH = 109.45°, OH = 1 Å) has a dipole moment norm at 1.67 D (9% smaller than the experimental value, 1.85 D, note that the SPC value is fixed at 2.245 D). Such a discrepancy indicates that difficulty in calculating *ab initio* such an electronic property that is indeed very dependent on the basis sets (Martin and Zipse 2005); for instance the use of minimal STO3G basis sets lead to a dipole moment norm of 0.7 D for the SPC water molecule geometry. Note that the recent work of Dyer and Cummings (2006) shows that DFT-CPMD (Car-Parrinello *ab initio* molecular dynamics) calculations of the dipole moment distribution for water bulk liquid is also very dependent on the analysis technique: electron density partitioning among molecules following the Bader approach to determine partial charges leads to a dipole moment mean value of 2.5 D at 300 K rather close to the experimental value while the use of localized Wannier functions leads to dipole moment mean value of 3.1 D.

In this work, we first consider a molecular configuration of bulk water at 300 K (density 1 g/cc) generated from a Gibbs ensemble simulation. The *ab initio* distribution of dipole (see Fig. 8) is centered on a mean value of 2.0 D (again smaller than the experimental value of 2.6 D). Now considering a confined phase of 25 water molecules in a unit cell of silicalite (loading relatively close to maximum), we found that the water dipole moment distribution is downshifted to a mean value at 1.83 D i.e. 9.5% smaller than the bulk value. This is an interesting result that shows that the electric field felt by a given water molecule due the zeolite species and neighbouring water molecules is not as intense as in the bulk. The same result was recently obtained by Coudert et al. (2006) performing DFT-CPMD calculations of water molecule confined to LTA zeolite. In

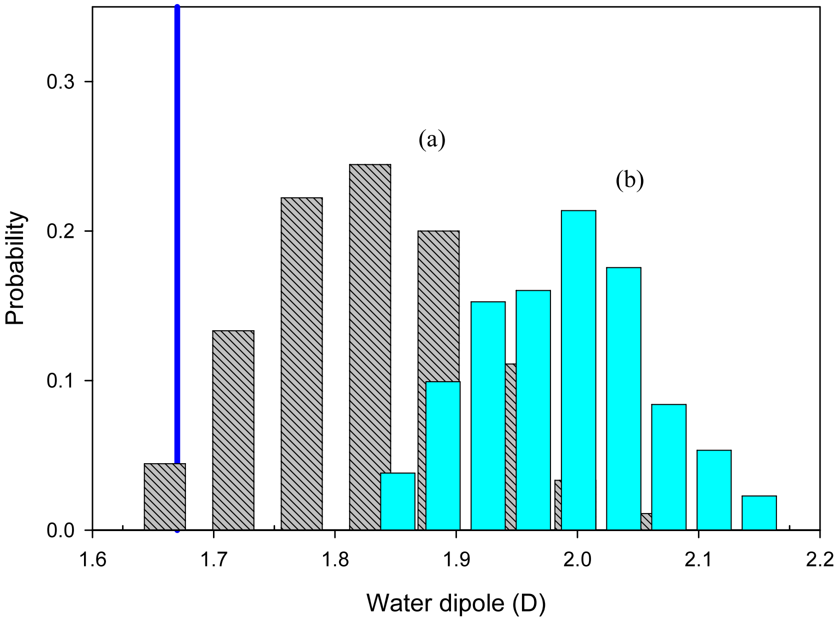

Fig. 8 Water dipole distribution calculated *ab initio* (see text) from (**a**) a 300 K GCMC molecular configuration of 25 H_2O molecule confined in a silicalite unit cell (**b**) a bulk liquid configuration at room temperature (1 g/cc). The *vertical line* shows the *ab initio* value of water dipole for a single molecule (gas phase)

addition, they show that the dipole moment shift is loading-dependent. Note that our *ab initio* results confirm the elegant results of Smirnov and Bougeard who performed classical molecular dynamics with charge-adaptative potentials of water confined in silicalite (Smirnov and Bougeard 2003). The trivial and technical consequence of our results is that classical simulations of confined polar fluid have to be performed with polarizable potentials to capture correctly the underlying the physics. The main physical conclusion is this work is that the reduction of the dipole moment of confined water molecules in siliceous zeolite (such as silicalite) is at the origin of the hydrophobic behavior of these materials. One may also infer that aluminum-containing-zeolites have a hydrophilic character that is due to the strong electric field created by counter-ions in the zeolitic voids in direct contact with the water adsorbed phase. Finally, this type of calculation in the 25 water molecules confined in a unit cell of silicalite (192 oxygen atoms + 96 silicon atoms) requires very a large hard disk temporary storage capacity (∼200 Go: number of atoms in the simulation cell = 363 i.e. 4152 atomic orbitals and 2160 electrons).

Figure 7 also shows the simulation results obtained with a dipole moment of water molecules equal to 95 and 90 percent of that for the original SPC model. As can be seen, quantitative agreement with the experimental data is obtained for 5 percent reduction of the partial charges, i.e. the pore filling occurs around a chemical potential $\mu = -44$ kJ/mol. A more accurate description would take into account the molecule environment, and make the partial charges hence the dipole moment dependent on it "on the flight" as reported in Smirnov and Bougeard (2003) paper.

5 Conclusion

Water adsorption/desorption isotherms at 300 K in two ordered microporous samples (silicalite-1 and a carbon replica of zeolite Y) calculated by GCMC are reported. The water-substrate interactions were calculated in the framework of the PN-TrAZ model while water-water interactions were modelled using the SPC potential model. For silicalite, the adsorption isotherm at 300 K is of type V without hysteresis, in qualitative agreement with experimental data. The isosteric heat of adsorption is also calculated, and shown to increase as a function of water coverage, as expected in a hydrophobic system. Visual inspection of molecular configurations shows that water molecules form aggregates of larger and larger size as the chemical potential or relative pressure increases. In the case of carbon replica, the adsorption/desorption isotherm at 300 K presents a hysteresis loop. The isosteric heat of adsorption at low coverage is compatible with a slightly hydrophobic surface. However, as for silicalite, the simulation results significantly underestimate the expected hydrophobicity of such carboneous adsorbent.

In order to improve the agreement between GCMC simulation results and experimental data, we decreased the partial charges of the water model hence its dipole moment. This is justified by the fact that the water models are generally parameterized for the bulk liquid phase, taking phenomenologically into account the polarization contributions. These contributions are expected to be lower in silicalite (lower electric fields due to tetrahedral silicon instead of dipolar contributions in bulk liquid water) as shown by quantum calculations of the effective partial charges of water molecules confined in silicalite (molecular configurations taken from the GCMC runs with the SPC model). These calculations suggest that the dipole of water confined in silicalite is around 10 percent lower than in bulk. GCMC calculations performed with a SPC model with reduction of the partial charges by 5% allow a quantitative agreement with experimental data that indeed show a strong hydrophobic character. Further quantum chemical calculations are underway to evaluate the change in the water moment in aluminum-containing zeolites and find the reason of the high-hydrophillicity at a molecular level.

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References

Auerbach, S.M., Carrado, K.A., Dutta, P.K. (eds.): Handbook of Zeolite Science and Technology. Marcel Dekker, New York (2003)

Berendsen, H.J.C., Postma, J.P.M., van Gunsteren, W.F., Hermans, J.: In: Pullman, B. (ed.) Intermolecular Forces, p. 331. Reidel, Dordrecht (1981)

Bichara, C., Raty, J.-Y., Pellenq, R.J.-M.: Adsorption of selenium wires in silicalites-1 zeolite: a first order transition in a microporous system. Phys. Rev. Lett. **89**, 016101 (2002)

Birkett, G.R., Do, D.D.: Simulation study of water adsorption on carbon black the effect of graphite water interaction strength. J. Phys. Chem. C **111**, 5735–5742 (2007)

Bohm, H.J., Ahlrichs, R.: J. Chem. Phys. **77**, 2028 (1982)

Bussai, C., Hannongbua, S., Haberlandt, R.: Understanding the movement, encapsulation, and energy barrier of water molecule diffusion into and in silicalites using Ab initio calculations. J. Phys. Chem. B **105**(17), 3409–3414 (2001)

Bussai, C., Vasenkov, S., Liu, H., Böhlmann, W., Fritzsche, S., Hannongbua, S., Haberlandt, R., Kärger, J.: On the diffusion of water in silicalite-1: MD simulations using ab initio fitted potential and PFG NMR measurements. Appl. Catal. A: Gen. **232**, 59–66 (2002)

Bussai, C., Fritzsche, S., Haberlandt, R., Hannongbua, S.: Formation of low density water clusters in the silicalite 1 cage: a molecular dynamics study. J. Phys. Chem. B **107**, 12444–12450 (2003)

Coasne, B., Pellenq, R.J.-M.: A grand canonical Monte-Carlo study of capillary condensation in mesoporous media: effect of the pore morphology and topology. J. Chem. Phys. **121**(8), 3767–3774 (2004)

Coudert, F.X., Vuilleumier, R., Boutin, A.: Dipole moment, hydrogen bonding and IR spectrum of confined water. Chem. Phys. Chem. **7**, 2464–2467 (2006)

Demontis, P., Stara, G., Suffritti, G.B.: Behavior of water in the hydrophobic zeolite silicalite at different temperatures. A molecular dynamics study. J. Phys. Chem. B **107**(18), 4426–4436 (2003)

Desbiens, N., Boutin, A., Demachy, I.: Water condensation in hydrophobic silicalite-1 zeolite: a molecular simulation study. J. Phys. Chem. B **109**(50), 24071–24076 (2005)

Douguet, D., Pellenq, R.J.-M., Boutin, A.: The adsorption of argon and nitrogen in silicalite-1 zeolite: a grand canonical Monte-Carlo study. Mol. Simul. **17**(4–6), 255–288 (1996)

Dyer, P.J., Cummings, P.T.: Hydrogen bonding and induced dipole moments in water: predictions from the Gaussian charge polarizable model and Car-Parrinello molecular dynamics. J. Chem. Phys. **125**, 144519 (2006)

Eroshenko, V., Regis, R.-C., et al.: Energetics: a new field of applications for hydrophobic zeolites. J. Am. Chem. Soc. **123**, 8129–8130 (2001)

Eroshenko, V., Regis, R.-C., Soulard, M., Patarin, J.: Les systèmes hétérogènes “eau-zéolithe hydrophobe”: de nouveaux ressorts moléculaires. C. R. Phys. **3**, 111–119 (2002)

Errington, J.R., Panagiotopoulos, A.Z.: A fixed point charge model for water optimized to the vapor-liquid coexistence properties. J. Phys. Chem. B **102**, 7470–7475 (1998)

Ewald, P.: Ann. Phys. **64**, 253–257 (1921)

Fleys, M., Thompson, R.W.: Monte-Carlo simulations of water adsorption isotherms in silicalite and dealuminated zeolite Y. J. Chem. Theory Comput. **1**, 453–458 (2005)

Fleys, M., Thompson, R.W., MacDonald, J.C.: Comparison of the behavior of water in silicalite and dealuminated Zeolite Y at different temperatures by molecular dynamics simulations. J. Phys. Chem. B **108**(32), 12197–12203 (2004)

Fubini, B., Bolis, V., Bailes, M., Stone, F.S.: The reactivity of oxides with water vapor. Solid State Ionics **32/33**, 258–272 (1989)

Fuchs, A.H., Cheetham, A.K.: J. Phys. Chem. B **105**, 7375–7387 (2001)

Giaya, A., Thompson, R.W.: Water confined in cylindrical micropores. J. Chem. Phys. **117**, 3464–3475 (2002a)

Giaya, A., Thompson, R.W.: Single-component gas phase adsorption and desorption studies using a tapered element oscillating microbalance. Microporous Mesoporous Mater. **55**(3), 265–274 (2002b)

Grey, T.J., Nicholson, D., Gale, J.: A simulation study of the adsorption of nitrogen in Ca-chabazite. Appl. Surf. Sci. **196**, 105–114 (2002)

Heyes, D.M.: Phys. Rev. B **49**, 755–764 (1994)

Jorge, M., Schumacher, C., Seaton, N.A.: Simulation study of the effect of the chemical heterogeneity of activated carbon on water adsorption. Langmuir **18**, 9296–9306 (2002)

Jorgensen, W.L., Chandrasekhar, J., Madura, J.D., Impey, R.W., Klein, M.L.: Comparison of simple potential functions for simulating liquid water. J. Chem. Phys. **79**(2), 926–935 (1983)

Kenny, M.B., Sing, K.S.W.: The hydrophobicity of silicalite and ZSM-5. Chem. Ind. (London) **2**, 39–40 (1990)

Lachet, V., Boutin, A., Tavitian, B., Fuchs, A.H.: Computational study of p-xylene/m-xylene mixtures adsorbed in NaY zeolite. J. Phys. Chem. B **102**, 9224–9233 (1998)

Lum, K., Chandler, D., Weeks, J.D.: Hydrophobicity at small and large length scales. J. Phys. Chem. B **103**, 4570–4577 (1999)

Ma, Z.X., Kyotani, T., Tomita, A.: Preparation of a high surface area microporous carbon having the structural regularity of Y zeolite. Chem. Commun. **2**, 2365–2376 (2000)

McCallum, C.L., Bandosz, T.J., McGrother, S.C.: A molecular model for adsorption of water on activated carbon: comparison of simulation and experiment. Langmuir **15**(2), 533–544 (1999)

Marinelli, F., Grillet, Y., Pellenq, R.J.-M.: The adsorption of argon on ZnO at 77 K. Mol. Phys. **97**, 1207–1238 (1999)

Martin, F., Zipse, H.: Charge distribution in the water molecule: a comparison of methods. J. Comput. Chem. **26**, 97–105 (2005)

Nada, R., Catlow, C.R.A., Dovesi, R., Pisani, C.: An ab-Initio Hartree-Fock study of α-quartz and stishovite. Phys. Chem. Miner. **17**, 353–362 (1990)

Nicholson, D., Parsonage, N.G.: Computer Simulation and the Statistical Mechanics of Adsorption. Academic Press, London (1982)

Nicholson, D., Pellenq, R.J.-M.: Adsorption in zeolites: intermolecular interactions and computer simulation. Adv. Colloid Interface Sci. **76/77**, 179–189 (1998)

Patarin, J., Gies, H.: Crystalline and organized porous solids. C. R. Chim. **8**, 243–243 (2005). (Thematic issue)

Pellenq, R.J.-M., Levitz, P.E.: Capillary condensation in a disordered mesoporous medium: a grand canonical Monte-Carlo study. Mol. Phys. **100**, 2059–2077 (2002)

Pellenq, R.J.-M., Nicholson, D.: Intermolecular potential function for the physical adsorption of rare gases in silicalite. J. Phys. Chem. **98**, 13339–13349 (1994)

Pellenq, R.J.-M., Rodts, S., Pasquier, V., Levitz, P.: A grand canonical Monte-Carlo simulation study of xenon adsorption in a Vycor like matrix. Adsorption **6**, 241–249 (2000)

Pellenq, R.J.-M., Rousseau, B., Levitz, P.: A grand canonical Monte-Carlo study of argon adsorption/condensation in mesoporous silica glass. Phys. Chem. Chem. Phys. **3**, 1207–1212 (2001)

Puibasset, J., Pellenq, R.J.-M.: In: Reinoso, F.R., McEnaney, B., Rouquerol, J., Unger, K. (eds.) 6th Int. Symp. on the Characterization of Porous Solids. Studies in Surface Science and Catalysis, vol. 144, Alicante, Spain (2002)

Puibasset, J., Pellenq, R.J.-M.: Water adsorption on hydrophilic mesoporous and plane silica substrates: a grand canonical Monte-Carlo simulation study. J. Chem. Phys. **118**, 5613–5622 (2003a)

Puibasset, J., Pellenq, R.J.-M.: Grand canonical Monte-Carlo simulation study of water structure an hydrophilic mesoporous and plane silica substrates. J. Chem. Phys. **119**, 9226–9232 (2003b)

Puibasset, J., Pellenq, R.J.-M.: Confinement effect on thermodynamic and structural properties of water in hydrophilic mesoporous silica. Eur. Phys. J. E **12**(s01), 017 (2003c)

Puibasset, J., Pellenq, R.J.-M.: Water adsorption in disordered mesoporous silica (Vycor) at 300 K and 650 K: a grand canonical Monte-Carlo simulation study of hysteresis. J. Chem. Phys. **122**, 094704 (2005)

Ramachandran, C.E., Chempath, S., Broadbelt, L.J., Snurr, R.Q.: Water adsorption in hydrophobic nanopores: Monte-Carlo simulations of water in silicalite. Microporous Mesoporous Mater. **90**, 293–298 (2006)

Roussel, T., Didion A., R.J.-M., Pellenq, R.J.-M., Gadiou, R., Bichara, C., Vix-Guterl, C.J.: Textural and adsorption properties of carbon replica of Y zeolite: an experimental and simulation study. J. Phys. Chem. C **111**, 15863–15876 (2007)

Smirnov, K.S., Bougeard, D.: Including the polarization in simulations of hydrated aluminosilicates. Model and application to water in silicalite. Chem. Phys. **292**, 53–70 (2003)

Striolo, A., Chialvo, A.A., Gubbins, K.E., Cummings, P.T.: Water in carbon nanotubes: adsorption isotherms and thermodynamic properties from molecular simulation. J. Chem. Phys. **122**, 234712 (2005)

Trzpit, M., Soulard, M., Patarin, J., Desbiens, N., Cailliez, F., Boutin, A., Demachy, I., Fuchs, A.H.: The effect of local defects on water adsorption in silicalite-1 zeolite: a joint experimental and molecular simulation study. Langmuir **23**, 10131–10139 (2007)

Vorholz, J., Harismiadis, V.I., Rumpf, B., Panagiotopoulos, A.Z., Maurer, G.: Vapor + liquid equilibrium of water, carbon dioxide, and the binary system, water + carbon dioxide, from molecular simulation. Fluid Phase Equilibria **170**, 203–234 (2000)

Wang, N., Tang, Z.K., Li, G.D., Chen, J.S.: Materials science—single-walled 4 angstrom carbon nanotube arrays. Nature **408**(6808), 50–51 (2000)

Zhao, X.S., Ma, Q., Lu, G.Q.: VOC removal: comparison of MCM-41 with hydrophobic zeolites and activated carbon. Energy Fuels **12**, 1051–1054 (1997)