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The Effect of Pore Connectivity on Water Adsorption Isotherms in Non-Activated Graphitic Nanopores

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Abstract. The adsorption of water in graphitic carbons is usually simulated via a weighted average of the adsorption isotherms simulated in carbon-slit pore of different widths. By following this procedure, details about pore morphology and pore connectivity may be overlooked. Towards a better match between virtual and real experiments, we present simulated adsorption isotherms for SPC/E model water in porous carbons composed by interconnected carbon-slit pores. The pores are separated from each other by one graphene layer. Imperfections (lack of carbon atoms) in the graphene layers result in interconnections between pores. The grand canonical Monte Carlo algorithm is used here to simulate water adsorption. Our results show that while the qualitative features obtained in the simulation of independent slit-shaped pores are reproduced when interconnected pores are considered, the adsorption isotherms rise more gradually and the adsorption/desorption hysteresis loops are narrower in the latter case.

Keywords: SPC/E water, carbon-slit pores, grand canonical Monte Carlo simulations

1. Introduction

Water adsorption in carbons is known to be strongly affected by the presence and density of oxygenated groups on the carbon surfaces (Brennan et al., 2001; Rouquerol et al., 1999). In the absence of such groups, the adsorption of water is insignificant at low pressures and it is usually accompanied by large adsorption/desorption hysteresis loops (Rudisill et al., 1992). As the surface density of oxygenated groups increases, water adsorption occurs at increasingly lower pressures, and as pressure is increased a continuous pore filling may occur (Jorge et al., 2002). Among available experimental data, Rudisill et al. (1992) reported water adsorption isotherms in carbon fibers at various temperatures and observed large adsorption-desorption hysteresis loops. They showed that the width of the hysteresis loops decrease as temperature increases. The experimental observations alone do not allow us to fully understand water adsorption, because of the small

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pore size that characterizes carbons, their peculiar morphologies, and the frequent appearance of long-lived metastable states for the adsorbed water. In this scenario, molecular simulation becomes a powerful tool to facilitate the microscopic interpretation of the phenomena under investigation (Nicholson, 1996).

Our group studied the adsorption of water in carbon-slit pores and in doped and un-doped SWCNs in a wide temperature range (Striolo et al., 2003, 2004a, 2004b, 2004c). Our results provide an extensive data set for adsorption isotherms as a function of pore width and morphology, as well as a detailed investigation on the effect of temperature and chemical heterogeneity on thermodynamic, structural, and transport properties of confined water. We also provide details on the mechanism of adsorption and desorption with the aid of a large number of intermediate configurational snapshots. However, the models assumed to describe the pores in our earlier work do not consider pore connectivity or pore-opening effects. Our group proposed to use reverse Monte Carlo (RMC) algorithms to compute the microscopic structure of a specific carbon based on experimental pair correlation functions. Thomson and Gubbins (2000) applied the RMC algorithm to develop a model composed of rigid and perfect graphene segments. Applying the RMC procedure to an atomistic description of the solid carbon, and combining the method with simulated annealing techniques, Pikunic et al. (2001, 2003) were able to reconstruct virtual adsorbents that show a better fit to experimental observations. The virtual materials obtained correctly reproduce the TEM images of the original carbons and the pores obtained are characterized by the correct polydispersity and connectivity.

As an intermediate step towards the simulation of water adsorption in realistic carbons obtained by RMC simulations we present here results for the adsorption in connected graphitic carbon-slit pores. Among several equivalent models (Bandosz et al., 2003), the model for the solid carbon that we chose resembles the randomly etched graphite model of Seaton et al. (1997). Other models for connected graphitic carbon-slit pores were not investigated. The goal of this work is to understand if connections between different pores generate differences in the simulated adsorption isotherms for water. Our model does not intend to replicate any realistic representation of a porous material, nevertheless, important insights could be obtained by studying the adsorption of model fluids in simplified models such as that employed here.

2. Simulation Details

To understand the effect of pore connectivity on the features of the simulated adsorption isotherms, we simulated water adsorption isotherms in solid matrices composed of four carbon-slit pores of widths 0.6, 0.6, 1.0, and 2.0 nm. In our representation the carbon-slit pores were separated from each other by one graphite layer. A schematic representation of the independent carbon-slit pores used in this work is shown in Fig. 1. Several carbon atoms are missing from each graphite layer. To simulate a perfect material 3,168 carbon atoms are necessary. The porous adsorbent considered in this work was composed of 2,853 carbon atoms. The simulation box dimensions were 4.69 × 4.43 × 4.20 nm. Periodic boundary conditions were implemented in all three directions to simulate an infinite porous material.

The SPC/E (Berendsen et al., 1987) model was chosen to describe water molecules. Each carbon atom in the system was represented as a Lennard-Jones sphere whose interaction parameters were taken from Steele (1974). The unlike Lennard-Jones parameters were obtained from water-water and carbon-carbon parameters by the Lorentz-Berthelot combining rules. For computational efficiency a grid was built to account for solid-water interactions with 0.018 nm spacing, and

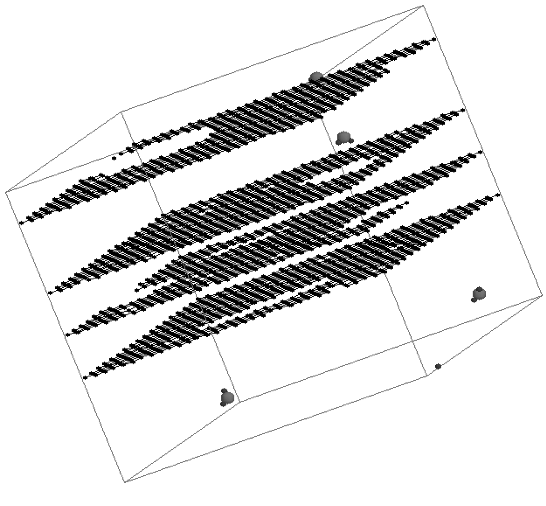

Figure 1. Schematic representation of the interconnected carbon pore model used in this work. The material is composed of four carbon slit pores (two of width 0.6 nm, one of width 1.0 nm, and one of width 2.0 nm). The pores are stacked on top of each other and separated by one graphite layer. The graphite layers are imperfect and several carbon atoms are missing, providing connections between the pores. Periodic boundary conditions are applied in the x, y, and z directions. Several water molecules are included in this picture.

linear interpolation was used to compute the energies between the points in the grid.

The grand canonical Monte Carlo (GCMC) method (Nicholson and Parsonage, 1982) was used to simulate water adsorption. In this ensemble volume, temperature, and adsorbate chemical potential are fixed. The number of adsorbate molecules can vary, as well as the location and the orientation of each adsorbed molecule within the pore. Trial moves considered were translation, rotation, insertion, and deletion of water molecules. The moves were randomly chosen with equal probability to ensure microscopic detailed balance. The maximum translation vector was automatically adjusted to obtain an acceptance ratio of about 0.35. The rotations were obtained with the quaternions method. No limitation was imposed on the maximum rotation angle. The acceptance ratio for rotation trial moves was at least 0.20.

For the adsorption path of the isotherms, mimicking experimental procedures, the pores were first considered empty. Simulation runs were performed at increasing chemical potentials. The resulting simulation configurations at specified conditions were used to initiate the subsequent simulation at higher chemical potentials. Desorption cycles were initiated with a typical configuration of a filled pore. The chemical potential was reduced until the pores were emptied from the previously confined water. To obtain the reduced pressure of the bulk phase in equilibrium with the adsorbate at various chemical potentials, a virial equation of state that employs a known saturation point was used (Müller et al., 1996). Equilibration runs consisting of 0.2 billion (2×10^8) trial moves were used. The production phase involved at least 0.5 billion (5×10^8) trial moves. Approximately 2,000 water molecules are adsorbed in correspondence to pore filling in the pores considered. Because simulated water molecules are fluid at all conditions here considered, the GCMC algorithm ensured fair equilibration for the results reported here. The number of accepted insertion/deletion trial moves ensured that each water molecule confined within the nanotubes was substituted at least 1,000 times during a typical simulation run.

3. Results and Discussion

Simulated water adsorption isotherms in carbon-slit pores have the shape of a type V isotherm in the IUPAC classification (Striolo et al., 2003). At low pressures the amount of water adsorbed is negligible; the pores suddenly and completely fill once a certain pressure threshold is reached; and the corresponding adsorption/desorption loops are characterized by large hysteresis loops. With decreasing pore width, the relative pressure at which pore filling occurs decreases. In qualitative agreement with available experimental observations our results indicate that the size of the hysteresis loops decreases as the pore width decreases. In addition, a molecular sieving effect is found in carbon-slit pores of width 0.6 nm.

When water adsorption is simulated in connected carbon-slit pores different phenomena are observed. In Fig. 2 we report a sequence of snapshots obtained as the relative water pressure of water increases at 498 K. At low relative pressures small clusters of water molecules are observed within the porous structure. As the pressure increases the pore of width 1.0 nm fills. We note that the pore is not entirely filled but the region connected to the pore of width 2.0 nm is depleted of water molecules. As the pressure further increases the pore of width 2.0 nm is completely filled, as well as the pore of width 1.0 nm. Few water molecules can also be observed in the pores of width 0.6 nm, especially in proximity of pore openings. As the pressure increases, a hydrogen-bonded network of adsorbed water molecules is observed within the pores of width 0.6 nm. This network, due to the strong preferential water-water interactions that overcome the weak carbon-water attractions, connects the wider pores through the imperfections in the graphite layers.

Because of this sequence of events, the resulting adsorption isotherm is significantly smoother compared to the adsorption isotherms simulated in isolated carbon-slit pores and resembles experimental adsorption isotherms. In Fig. 3 we report a representative adsorption isotherm simulated for water in the interconnected pore described in Fig. 1 at 498 K. Our results, in qualitative agreement with experimental evidence (Rudisill et al., 1992), show negligible water uptake at low relative pressures, fast but continuous pore filling, and narrow adsorption-desorption hysteresis loop. Our results show that the amount of adsorbed water increases as pressure rises above the water saturation pressure. This result is partially due to the pore sieving effect observed for carbon-slit pores of width 0.6 nm in that large pressures are required to fill such narrow pores. Experimentally, this result may indicate that carbon-slit nanopores are not filled with water unless large external pressures are applied.

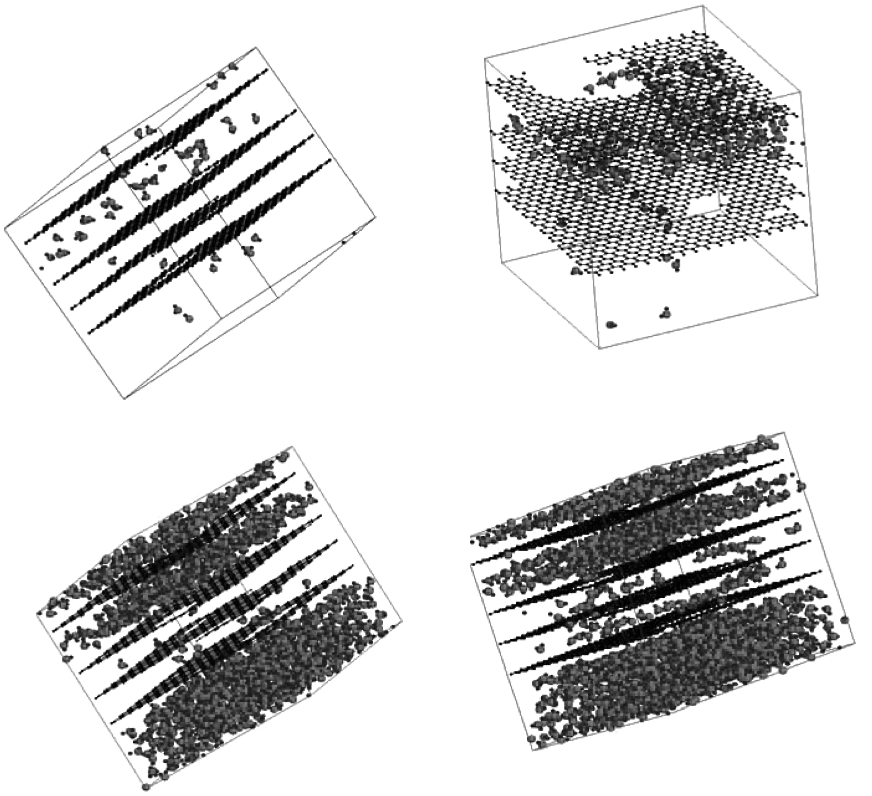

Figure 2. Sequence of simulation snapshots collected at 498 K. The snapshots are obtained as the relative pressure of bulk water increases, in the order left to right, top to bottom.

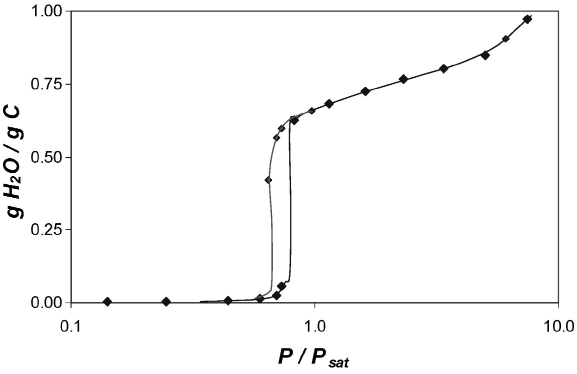

Figure 3. Simulated water adsorption isotherm in the interconnected carbon pore represented in Fig. 1 at 498 K. Black diamonds are results for adsorption, grey symbols are for desorption. Lines are guides to the eye. Statistical uncertainty is less than the size of the symbols.

A complete comparison between adsorption isotherms simulated in independent carbon-slit pores and in connected graphitic carbon pores is currently in preparation.

4. Conclusions

Our results for simulated water adsorption in interconnected graphitic carbon pores demonstrate that pore connectivity can yield isotherms characterized by continuous water uptake as the pressure increases and narrower adsorption-desorption hysteresis loops compared to those simulated in isolated carbon-slit pores. We are currently investigating the effect of chemical heterogeneity on the features of simulated adsorption isotherms by placing carbonyl groups in proximity of pore openings in the carbon model presented here.

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