

# Purification of water through nanoporous carbon membranes: a molecular simulation viewpoint

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Although carbon is generally considered hydrophobic and a poor choice to fabricate membranes, recent developments in nanotechnology have provided nanoporous structures such as nanotubes and graphene sheets, which hold promise as the 'ultimate' membrane materials for water purification. Nonetheless, the behaviour of water through these nanoconfined environments is unique and nonintuitive. This review describes our current understanding and challenges associated with the molecular simulation of the water-carbon interaction. It is expected that simulations can guide the design of water purification membranes with both high selectivity and high permeability.

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## Introduction

Recently, a paper [1] reported the fabrication of supported membranes with a graphene oxide layer of roughly 1  $\mu\text{m}$  in thickness. Apart from the remarkable feat of producing such an ultrathin membrane material, the most striking result described was that the membrane was permeable to water while being essentially impermeable to helium. It is obvious from the above-mentioned report that water has to have a peculiar, nonintuitive transport mechanism through these (and other similar) nanoporous morphologies. Probing such mechanisms from an experimental point of view proves to be challenging, to say the least; and it is here that the application of molecular simulations have started to shed light on the unique mechanisms; which come into play at these reduced length scales. This review focuses on a few of the recent advances and challenges faced in the molecular modelling of the adsorption and transport properties of water in nanoconfined carbon structures.

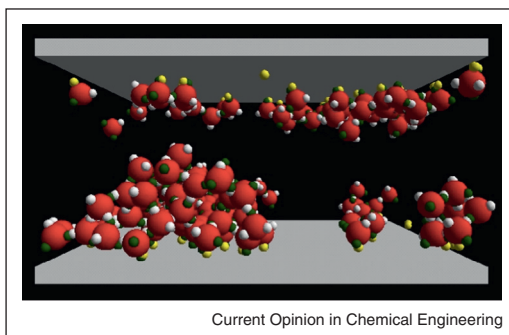
Water, on its own, is a profoundly unusual fluid and a large portion of the scientific literature is concerned with

understanding and describing its exceptional properties. In spite of its chemical simplicity, its peculiar ability to form up to four hydrogen bonds with its neighbours provides it with a myriad of abnormal thermodynamic and transport properties. While the bulk-phase properties of water have been studied extensively and are reasonably well-understood, our comprehension of the water-solid equilibria is much less detailed. For example, the adsorption of water on carbons presents an apparent paradox: on a macroscopic scale, it appears as if carbon surfaces are hydrophobic, thus little or no adsorption of water is to be expected. In spite of this, some of the porous activated carbons seem to strongly adsorb water, even in a preferential manner over more chemically compatible substances, that is, hydrocarbons. Only a complete description of the adsorption and transport process of water on a nanoscale can elucidate these puzzling phenomena.

## The basics: adsorption of water on graphitic surfaces

The apparent ambiguity of carbon towards water can be explained by understanding the hydrogen bonding nature of water and the predominant role it has on its adsorption properties. It has long since been recognized [2], albeit only very recently proven directly, that water must adsorb on activated carbons in a *sui generis* way, that is, in a different fashion as more commonly studied nonassociating molecules such as alkanes do. There are major differences between the strongly polar nature of the water-water interactions and the usually weaker interactions between water and most of the organic substrates. Unlike simple molecules that adsorb forming layers on the surfaces (i.e., a Langmuirian adsorption), water adsorbs forming three-dimensional clusters, nucleating at the nanoscale on a defect (e.g., a step [3] or an edge) and/or an energetical heterogeneity (e.g., a hydroxyl substituent). Experiments aimed at elucidating the actual molecular process are plagued with problems such as properly characterizing the carbon surfaces and the heterogeneities (usually oxygenated radicals), which make up the 'activation' of the surface and by difficulties in interpreting macroscopic behaviour in terms of molecular-level phenomena. Fundamental theories, on the contrary, cannot be successfully developed until a clear physical vision of the process is obtained. Müller *et al.* [4<sup>\*</sup>] gave a clear account of the unique adsorption mechanism of water on graphite, showing how water adsorbs on surfaces as clusters, as opposed to a more conventional Langmuir monolayer. The snapshot in [Figure 1](#) shows how the adsorption

Fig. 1



Snapshot of an equilibrium state of a Monte Carlo simulation of water (red) adsorbed on a 2 nm wide graphitic carbon. The graphitic walls have energetic heterogeneities (yellow) at a density of 2 sites/nm<sup>2</sup>. The ratio of external pressure to the bulk fluid saturation pressure is 0.285, the temperature 300 K. This state point is at a pressure just below the onset of capillary condensation at these conditions, showing a critical clustering of water molecules.

of water is a cooperative fluid-fluid process involving the formation of clusters on the surfaces around energetically heterogeneous sites. The clustering mechanism was later verified experimentally by *in situ* small angle X ray scattering [5,6].

The confining effect of carbon nanopores has a profound nonintuitive influence on the equilibrium adsorption behaviour of water, favouring a series of apparently long-lived metastable states. An example of this is the fact that many of the simulation studies have confirmed that once water is adsorbed within a carbon matrix, it will not easily desorb. This is expressed in very large hysteresis loops found in adsorption isotherms and persistence of adsorbed water in confined carbon nanopores in spite of a more stable de-wetted thermodynamic state. A further macroscopic observation is the depression of the freezing point of nanoconfined water, leading to the observation of ice and ice-like structures at conditions away from those found in bulk.

The discovery in the early 1990s [7] of the synthetic carbon nanotube structures immediately generated excitement in the simulation community as the perspective of being able to study, model and compare with experiments a uniquely well-defined carbon adsorbent. Today, the amount of reported simulation studies on nanotubes exceeds thousands of papers [8]. There are parallels but also differences between the behaviour of water in 2D and 1D carbon geometries [9]. Less-structured carbon materials can usually be modelled by a suitable collection of flat plates (slit-like pores) and cylinders (nanotube-like pores), so these two geometries are excellent starting points for modelling most all carbon materials. Outstandingly, for very small nanotubes, a water nanowire is

observed, with water molecules forming a continually hydrogen-bonded single file.

### The challenge: purification of water through nanoporous carbons

Purification of water by nanoporous membranes has been identified as one of the major challenges of this century [10]. Carbon-based materials would not seem to be the obvious choice for a separation membrane; commercial activated porous carbons are brittle by nature and the fact that they are usually considered a hydrophobic material seem to be detrimental factors. The key problem, of course, is the generalization of these observations to sp<sup>2</sup> carbon materials and the definition of hydrophobicity itself (discussed later). Some of these preconceived ideas have changed fundamentally after a *simulation* report [11<sup>•</sup>] claimed that water was able to adsorb and diffuse through carbon nanotubes. The diffusion through carbon nanotubes is unique in many respects; particularly super-diffusion is seen, where the water transport is several orders of magnitude larger than what would be expected even under bulk conditions. The above-mentioned paper has sparked a very lively and controversial debate about the nature and kinetics of diffusion and adsorption on nanotubes and bundles. The movement of water molecules along the nanotube axis is described as taking place via bursts of hydrogen-bonded clusters of molecules: a detailed study by Striolo clarifies this mechanism [12]. Experimental observations of diffusion of water through bacterial potassium channels seem to confirm these observations [13].

Simulations [14,15] have predicted the fact that carbon nanotubes with their axis aligned in the direction of the water flow could prove to be a plausible material for the separation of solutes from water; they have recognized two key aspects: the ultra-fast diffusion within the pores and the high resistance to mass transport in the entrance and exit of these pristine pores. Following this, the innovative work of Hinds *et al.* [16,17] and Holt *et al.* [18<sup>•</sup>] have reported the fabrication of membranes using aligned carbon nanotubes, the latter exhibiting water permeabilities several orders of magnitude larger than equivalent polycarbonate membranes. Since then, several groups have focused on the experimental fabrication [19,20, 21<sup>•</sup>,22,23<sup>•</sup>], theoretical description [24<sup>•</sup>] and simulation [25–28] of these types of membranes for water purification. An aspect, which has been frequently observed and generally overlooked, is that the flow characteristics will depend crucially on the substituents placed on the entrance/exit of the pores [29–31].

With the recent interest in graphene, a logical extension of the above idea is to explore the capability of a graphene sheet with a defect or nanopore [32] placed orthogonally with respect to a flow, so as to constitute the ultimately thin molecular membrane. A simulation paper by Suk and

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