Water mobility in MoS$_2$ nanopores: effects of the dipole-dipole interaction on the physics of fluid transport

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Nanoscale materials are promising desalination technology. While fast water flow in nanotubes is well understood, this is not the case for water permeability in single-layer membranes. The advances in nanofluidics opened up the possibility to shift the permeability–selectivity tradeoff. The physical-chemical balance between nanopore size, shape, and charge might be the answer. In this work, we investigate the role of the MoS$_2$ nanopore charge distribution in water mobility by tuning its strength. We shed light on the competition between charge and nanopore size. The strong dipole interaction between water and the MoS$_2$ nanopore is responsible to append a constraint in the water angular orientation possibilities to travel through the nanopore, but this effect also depends on the nanopore size.

1 Introduction

A key challenge in the desalination process is creating a membrane where water is able to flow through and rejects salt ions. The most common process to separate salt from water is reverse osmosis, which consists of employing pressure to filter salt water. This process has two key parts: overcome the osmotic pressure and produce an efficient selective membrane. While the energy of overcoming the osmotic pressure has little space for improvement, the trade-off between selectivity and permeability represents the desalination process frontier. The difficulty is that, in traditional polymeric membranes, a large enhancement in water permeability through increased pore size and permeability also implies an increase in salt permeability, which spoils selectivity. Therefore, a new physical phenomenon to increase water flow for small-sized pores was required. This new phenomenon was the enhancement water flow inside nanoscale materials. A number of studies have shown that sub-nanometer pores act as a highly selective and permeable filtration membrane with greater efficiency than current state-of-the-art polymer-based filtration membranes. The first system in which this property was observed was in carbon nanotubes (CNT). For diameters under 2nm, water molecules exhibit a flow five orders of magnitude larger than those observed in polymer-made membranes. The physical mechanism behind this enhanced mobility is the smooth inner hydrophobic surface of CNTs, which lubricates and speeds up a near-frictionless water transport. The drawback is that hydrophobic carbon surfaces, even though not as frictionless for salt as it is for water, fail to repeal salt. Therefore, only CNTs with sub-0.9nm diameters are able to exhibit acceptable rejection rates. In order to circumvent this problem, charged groups were added to the nanotube. The electrostatic forces added through the hydrophilic groups increased salt rejection, but decreased water velocity as well. Surface roughness produced by the hydrophilic groups also led to a reduction in water mobility. Also, the hydrophilic substrate changes the behavior of water at least in layers very close to it. Even though the physical mechanism behind the fast flow of water in CNTs is well understood, membranes based on it have been limited by low salt rejection rates and the difficulty of producing highly aligned and high-density CNT arrays. The observations that the flux through membranes scales inversely with membrane thickness led to the idea of employing monolayer membranes as a new strategy for desalination. Posteriorly, several emerging classes of single-layer membranes have been proposed. Initially, exfoliated graphene as a single atomic layer membrane was proposed, followed by functionalized nanoporous graphene sheets, with several active groups and inorganic nanoparticles. The first attempt to investigate functionalized graphene for desalination demonstrated that functionalized nanoporous graphene membranes could perform more than 99% salt rejection and provide water permeance up to 2 or 3 orders of magnitude higher than that of current commercially available reverse osmosis membranes and nanofiltration membranes. In addition, fast water flow through graphene nanocapillaries were also studied and the results indicate that the interaction with the hydrophobic confining walls induces structuring in water which significantly enhances the viscosity. Since in the case of CNTs the frictionless flow in 2nm diameter pores explain the high permeability of water and the hydrophilic
that observed in a hydrophobic pore with the same pressure. The electrostatics of the system seem to play two competing roles: one to attract water to the pore, and another to repel. These competing factors are enhanced in the case of the MoS<sub>2</sub> membrane. This system has a higher water permeability than its equivalent graphene, mainly due to its lower water density near the membrane’s surface, lower energy barrier to pass it and higher average water density and velocity inside the pore of MoS<sub>2</sub>. The surprising effect is that this MoS<sub>2</sub> pore permeability is larger if the exposed atom at the pore is the divalent Mo when compared with the exposing monovalent S. Since pore sizes and shapes in both cases (Mo or S exposed) are slightly different, it is unclear if a larger exposed charge would enhance water velocity inside the pore, or if this larger velocity would be solely the result of its size and shape. Besides that, electrically controlled water permeation through graphene oxide membranes were experimentally studied and leads to the understanding that the ionization of water molecules inside graphene capillaries plays a crucial role in water transport, varying from fast flow to complete blocking.

2 Materials and Methods

In order to clarify these questions, we performed nonequilibrium molecular dynamic (NEMD) simulations for an MoS<sub>2</sub> membrane. In earlier attempts to answer to this question, the comparison was between graphene pores with charge-altering functionalization. The issue with this procedure was that, in order to alter the charge, the functionalization also changed the available pore area and shape. We created a simulation box full of interagent particles, as described in Figure 1(a), where two reservoirs of water molecules were separated by a MoS<sub>2</sub> nanoporous membrane. Through applying a pressure gradient in the box, the pressure-driven transport along the membrane initiates, as illustrated in Figure 1(b). This type of process helps us to get insights toward designing new membrane materials and to better understand the water-nanopore relationship.

<table>
<thead>
<tr>
<th>( \sigma_{LJ} ) [Å]</th>
<th>( \epsilon_{LJ} ) [kcal/mol]</th>
<th>Charge (e)</th>
</tr>
</thead>
<tbody>
<tr>
<td>O&lt;sup&gt;29&lt;/sup&gt;</td>
<td>3.165</td>
<td>-1.054</td>
</tr>
<tr>
<td>H&lt;sup&gt;29&lt;/sup&gt;</td>
<td>0.0</td>
<td>0.5270</td>
</tr>
<tr>
<td>Mo</td>
<td>4.20</td>
<td>0.0135</td>
</tr>
<tr>
<td>S</td>
<td>3.13</td>
<td>0.0</td>
</tr>
<tr>
<td>C&lt;sup&gt;6&lt;/sup&gt;</td>
<td>3.40</td>
<td>0.0860</td>
</tr>
</tbody>
</table>

Table 1 The Lennard-Jones parameters and atoms charges employed in the simulations. The \( q_0 \) and \( q_2 \) charge parameters are fictitious.

To simply illustrate the complexity of tracking this problem, here we present the water permeability of an MoS<sub>2</sub> membrane under three conditions: a pore with no charge distribution (named \( q_0 \)), a pore with Mo and S atoms with its normal charges (named \( q_1 \)), and a pore with double the charge of Mo and S (named \( q_2 \)). The first and last configurations are not physical, but they help...
us to understand the role played by the charges in water mobility without changing pore size and shape, while also keeping intact the spacial distribution of the charge in the membrane.

In addition, three nanopore sizes were studied: 0.74nm, 0.97nm, and 1.33nm nanopore diameters (considering the center-to-center distance of atoms), as described in Figure 1(c). The NEMD simulations were performed using the Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) package. We utilized the TIP4P/ε water model and the parametrization of a reactive many-body potential as standard LJ parameters and charges values for Mo and S, as summarized in Table 1. The Lorentz-Berthelot mixing rules were used for non-bonded interactions. Long-range electrostatic interactions were calculated by the particle-particle-particle mesh method. We created a simulation box with 4nm x 4nm x 7nm, as illustrated in Figure 1-(a), with 3000 rigid water molecules. First, the particles were balanced during 2ns in an NPT ensemble in order to reach its ≈ 1 g/cm³ equilibrium density at 300K and 1atm (Figure 1-(b)-top). Graphene pistons were used to control applied pressures. Afterwards, a 500 bar of pressure was imposed in the feed reservoir and the 18ns of non-equilibrium molecular dynamics (NEMD) running starts (Figure 1-(b)-bottom). Transported water molecules were collected on the other side of the membrane. The results were averaged over 3 different set of simulations.

3 Results

The water flowrate along MoS₂ illustrated in Figures 2(a)-(c) is affected by two competing factors: charge and size. In general, the uncharged system presents the fastest flow. We discussed the water mobility in terms of filtered water molecules because it is more useful to discuss the fluid transport for this size scale (< 2 nm of channel diameter) rather than viscosity or slip length, for example. Graphene pistons were used to control applied pressures. Afterwards, a 500 bar of pressure was imposed in the feed reservoir and the 18ns of non-equilibrium molecular dynamics (NEMD) running starts (Figure 1-(b)-bottom). Transported water molecules were collected on the other side of the membrane. The results were averaged over 3 different set of simulations.

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The charged pores, $q_1$ and $q_2$, form water clusters around Mo atoms, as shown in the color maps in Figure 3. In fact, the higher average water density around these sites were mentioned
Fig. 3 Water flow density map (oxygen shown) for three different nanopore diameters and three different nanopore charge values. The illustration of
the MoS$_2$ atoms doesn't represent the exact atoms positions.

\[ PMF(z) = -k_B T \ln \left( \frac{\rho(z)}{\rho_0} \right). \]  

during the system equilibration procedure, illustrated in Figures 2(d)-(f) shows that for the $q_2$ case PMF has minima in Mo and near S sites. A small charge decrease from $q_2$ to $q_1$ flattens the PMF, which can only be understood if another force overcomes the electrostatic interactions and if water molecules move away from Mo and S as shown in the Figures 2(g)-(i). Also, from the PMFs shown in Figures 2(d)-(f) we can see the implications of tuning the nanopore charge are local with short range.

The PMFs in Figure 2(d)-(f) shows another interesting aspect of tuning the MoS$_2$ dipole strength without leaving it positive/negative charged: the effects are localized inside and near the nanopore. The implications are screened in the membrane interface and are not observed as registered by the PMF around
Fig. 4 (a-c) The water molecule orientation respect to the z axis as function of the membrane center distance. The colored shadow means one standard deviation attributed to each bin of analysis. The standard deviation was calculated taking into account different water molecules averaged in different simulations. (d-f) the $\alpha$ angle distribution inside the nanopore.

$\approx 4$ Å in the z-direction from the membrane center.

The differences between the water mobility through the 0.74nm and 0.97nm pore are intriguing. First it is interesting to note that the water flow map in the 0.74nm-$q_0$ is characterized by a single-file water molecules as observed in the radial water density map (Figure 2(g)), although the presence of charges split the single-file into three regions moving towards the Mo atoms. Besides that, as we can see from Figure 2(a), the presence of a charge distribution when the nanopore is too small, practically independent of its strength, is enough to slow down the water mobility but it is not enough to trap the water molecules there, in contrast with what happens in the Figure 2(b). The same phenomena can be seen from the density maps (Figure 3).

To clarify what happens with the water flux in the 0.74nm and 0.97nm pore, we conducted a series of angular analysis to better understand the entrance and exit effects of enhanced dipole interaction between water molecules and the tuned membrane. Figures 4(a)-(b) highlight the molecular rotation around and inside the nanopore. From that, it is clear the effects of $q_2$ and $q_1$ compared to the $q_0$ case: the charge distribution implies in dipole-dipole interaction which is responsible for limiting the possible angular configurations to pass through the pore. In contrast, the water molecules in the $q_0$ case are not so restricted in terms of assuming some specific angular state in order to pass through the pore (Figures 4(a)-(c)).

Figures 4(d)-(e) represent the evolution of the $\alpha$ angle distribution along the z axis. As we can see from it, the $q_0$ shows a range of angular possibilities and the rotation is not mandatory to pass through the pore while the $q_2$ and $q_1$ cases forces the molecule to rotate $\approx 90^\circ$ to be able to travel through the mem-
brane. The angular constraint surely impacts the water flow-rate. Sometimes, the constraint is so limited that the water molecules get trapped inside the nanopore, as illustrated by Figure 2(b) and Figures 4(b)-(e) for the 0.97nm pore. In this case, the nanopore is large so a higher number of water molecules fits in there. Attached to it, the hydrogen bond network is enhanced by the strong dipole interaction and contribute to the structure.

It is interesting to note from previous studies that the ion selectivity is improved when the nanopore is functionalized. The functionalization procedure adds a charge distribution to the system and it improves the ion rejection by the membrane. As we can see from Figures 2(a)-(c), the addition of charges slow down the water flowrate in all nanopores sizes, but it is a well paid costs thinking in ion selectivity if the charge distribution is enough to allow practically the same water flux as observed by the comparison between $q_0$ and $q_1$ cases in Figures 2(b)-(c). In contrast, the cost is too high if the charge distribution can induce the nanopore blocking by strong water-MoS$_2$ dipole interaction, as illustrated in Figures 2(b)-(e)-(h).

The mechanism for high water mobility inside nanopores involve the competition between local electrostatic forces and the cooperation of the hydrogen bond network. The strong dipole interaction is responsible to append a constraint in the the water angular orientation possibilities to travel through the nanopore, but this implication also depends on the nanopore size. As it was observed for the 0.97nm case, if the water-MoS$_2$ dipole interaction is strong enough and the nanopore has the right geometry, the water molecules don't participate in the hydrogen bond network and get trapped inside the nanopore. This is the new trade-off in thinking about design the next-generation of nanoporous membrane materials. The pore size and charge surely impacts membrane permeability performance by different flow mechanisms. These nanopores needs a charge distribution in order to enhance the ion rejection, but not too much charge to trap water molecules into there depending on the nanopore size.

4 Conclusions

The water-MoS$_2$ dipole interaction and hydrogen bond network competition is the bridge mechanism that links the observed data. The narrow nanopore is so small that only one molecule in averaged fits in there, as illustrated by Figure 5. Furthermore, the 0.97nm nanopore fits 2 water molecules for the $q_0$ and $q_1$ systems, and the averaged number of hydrogen bonds per molecule ($N_{HB}$) is 0.5, but this is not true for the $q_2$ system. The 0.97nm with $q_2$ produce such high water-MoS$_2$ dipole interaction that makes it possible to fits 3 water molecules in there breaking the possibilities $N_{HB}$. In this case, the water molecules assume an arrangement of position (see Figure 3) and angular orientation (see Figure 4(b)-(e)) that it gets trapped in there, with each water oxygen stuck in the nanopore edge (Mo sites) and with each hydrogen oriented to the center of the nanopore, producing zero $N_{HB}$. In this case, even high-pressure levels (2000bar) are not enough to push the water molecules through the 0.97nm pore (see Figure 2(b)). This competition explains the larger free energy barrier observed in the 0.97nm with $q_2$ system (see the PMF in Figure 2(e)). Then, comparing the 0.97nm/$q_2$ with the 0.74nm/$q_3$ case, it is possible to conclude that it is easier to push 1 molecule through the 0.74nm pore than 3 binding molecules through the 0.97nm pore. Besides, the 1.33nm nanopore has 6-8 water molecules inside and this makes it possible to maintain a hydrogen bond network strong enough to produce water flow even with $q_2$.

Acknowledgement

This work was supported by the Brazilian agencies CNPq (through INCT-Fcx) and Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES). The authors thank the computational infrastructure from CENAPAD/SP and CESUP/UFRGS.

Conflicts of interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Notes and references

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