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Effect of hourglass-shaped nanopore length on osmotic water transport

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ABSTRACT

In the present research, molecular dynamic (MD) simulations are utilized in order to examine the water transport properties through hourglass-shaped pore structures with various lengths. The length elongates in a range of 100–200 Å, while the size of the narrowest diameter remains constant at 3 Å. The results show that the defect effect can be substantially diminished as the length increases, so that the fluctuations of the energy barrier reaches zero inside 200 Å pore structure, which is an indication of rapid increase of water transport rate. The flux increases with length, suggesting a reduction in hydrodynamic resistance, that water molecules are able to easily enter the pore. The axial diffusivity and permeability are increased once the length increments, which indicate a fast water transport. It is concluded that the thermal fluctuations of water molecules inside reservoir affect the motion of water molecules inside the pore as length decreases.

1. Introduction

Synthetic membrane has been introduced by Reid and Breton [1], about 50 years ago, with discovering of cellulose acetate membranes for desalination. Thin synthetic membrane with nanometer sized pores have shown [2–6] that they could be used for nanoscale mass transport phenomena, such as drug delivery, isolation of individual macromolecule, efficient desalination, etc.

Due to the nanofluidic applications and realizing biological transferring phenomena, the scattering properties of fluids in a confined space gained attention such as molecular-level fluid or drug transport through the thin channel or pore such as carbon nanotubes, nanoporous materials, and biological pores [7–19].

The Molecular dynamics (MD) simulations and experimental observations have shown that water molecules transport through carbon nanotubes with high flow rates [20–26]. The results have shown that the selectivity and permeability are the main keys to estimate the fluid transport capability in such confined spaces. It is strongly postulated to design membranes with highly selectivity and permeability. To develop such membranes which transport with better selectivity and higher permeability, the biological membranes [27] could be the promising candidates. Experimentally, the idea of combination of aquaporin characteristics for desalination membranes [28] showed that water permeates remarkably through aquaporins. Aquaporins are membrane proteins that enable fast water transport and water selectivity [27–29], suggesting an hourglass shape approximately 20 Å in length and 3 Å in the narrowest diameter at the center of the pore. The structure of aquaporins provides size restriction, and ions which are larger than water molecules are impeded from passing through the aquaporins [29].

By selecting optimum values for the diameter and length of the pore, water flow rates can be increased by several orders of magnitude inside the cylindrical nanotubes which are primarily considered in the previous studies. Recently, a molecular dynamic (MD) simulation [30] summarized that a power law can be envisioned to make a link between water flow and CNT diameter, and also it showed that CNT length can influence the motion of water inside the CNT and the thermal fluctuations of water molecules outside the CNT.

Unlike the previous studies, recently, a large scale molecular dynamics simulation of micrometer-thick CNT membranes revealed that the superfast water transport does not associate with interactions between water molecules [31]. The findings showed that the transport enhancement rates were length-dependent due to entrance and exit losses in short CNTs, whereas flow rate enhancement was attributed to the slip length for long CNTs. Many studies, in both experiment [20,21] and theory [32,33] on water diffusion through nanochannels have been done in most of which the cylindrical channels are considered. Some other studies attempted to analyze the transport properties through non-cylindrical channels (e.g., Aquaporin-like nanopores). Recently, an experimental study using transmission electron microscope

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(TEM) tomography [34] showed that the solid-state nanopores suggest an hourglass-shape than a cylindrical structure.

Also, some important physical characteristics of aquaporin such as single-file water structure, dipole reorientation, and osmotic permeability have been investigated by other researchers [35–39], which showed that a minimal departure from optimized cone angle significantly increased the osmotic permeability; and that there was a non-linear relationship between permeability and the cone angle. The observation of hydrophobicity effect on pore surface showed that the maximum water flux through an hourglass-shaped nanopore was at the hydrophobic state of $\theta_{pore} = 101^{\circ}$.

Although the pore diameter robustly influences the transport properties of water molecules [40–44], little efforts have considered the effect of nanochannel length on the water transport mechanisms [45]. As experimentally reported [20,21], the length scales to utilize CNTs for water transport are mostly limited to an order of micrometer. Hence, the necessity of understanding of length effect on water permeation dynamics through confinement environments is theoretically highly appreciable.

Up to now, the hydrodynamic resistance, angle variation and hydrophobicity effects on water transport mechanisms in hourglass-shaped nanopore structures were successfully investigated. In this study, the classical molecular dynamics (MD) simulation is used to investigate the length effect on water transport properties through aquaporin-like nanpore structure.

2. Simulation details

The computational system is composed of a symmetric hourglass-shaped pore structure and a reservoir made by carbon atom, as shown in Fig. 1. The size of the reservoir is $30 \times 30 \times 30$ Å^3. The box size along the z direction is taken sufficiently large (10 times the narrowest radius of the pore [46]). The two ends of the hourglass shape pore has circular shape with a diameter of 6 Å and a small cylindrical pore section with the diameter of 3 Å is located at the center of the pore which connects the two conical sections on each side. The simulations are performed for different pore lengths while the size of the narrowest diameter is kept fixed at 3 Å. Five different lengths of 100, 130, 150, 170 and 200 Å for the hourglass-shaped nanochannels are studied. The 1500 SPC/E model of water molecules are randomly disposed into the membrane at the initial configuration.

Non-equilibrium MD simulations are implemented using LAMMPS package [47]. A constant external force f on all water molecules inside the reservoir along $+z$ direction is applied aiming at modeling a pressure driven flow. Using $\Delta p = nf/A$, the pressure difference between the two sides of a membrane can be estimated [48], where n and A are the number of water molecules and a membrane area, respectively. The interactions between water-water and water-carbon are described by the Lennard-Jones potential interactions between oxygen and carbon atoms, with parameters as $\varepsilon_{O-O} = 0.1555$ kcal/mol, $\sigma_{O-O} = 3.169$ Å, $\varepsilon_{O-C} = 0.0956$ kcal/mol, and $\sigma_{O-C} = 3.190$ Å. The long range columbic interactions are handled using Ewald method [49]. The water molecules are held rigid by applying SHAKE algorithm [50]. All non-equilibrium simulations in this work are done in NVE ensemble (in which is appropriate for the non-equilibrium quantities) with dissipative particle dynamics (DPD) thermostat [51] to keep the temperature constant at 300 K. A DPD thermostat adds pairwise interactions between atoms, with a dissipative force depending on the relative velocity between each pair and a random force with a Gaussian statistics. This method has the advantage of preserving hydrodynamics [46]. Periodic boundary conditions are applied in three directions and the van der Waals cutoff radius is set as 10°A. The simulations are composed of three steps. The first step is performed for 0.6 ns and aims at getting equilibration state for the water molecules inside the reservoir without external force (the equilibrated state can be checked through the time dependent phenomena such as temperature and pressure). The second step is carried out for 1 ns non-equilibrium simulation with applying an external force to get steady state (in which the pore is completely filled with the water molecules). The last step is carried out until the results are fully converged (which occurs after 7 ns), and the results are extracted and analyses after this time. In fact, such a simulation time is taken conservatively enough, solely to let us investigate the precise diffusion mechanism for water transport in narrow nanotubes [44]. All above steps are separately conducted for every five cases implementing

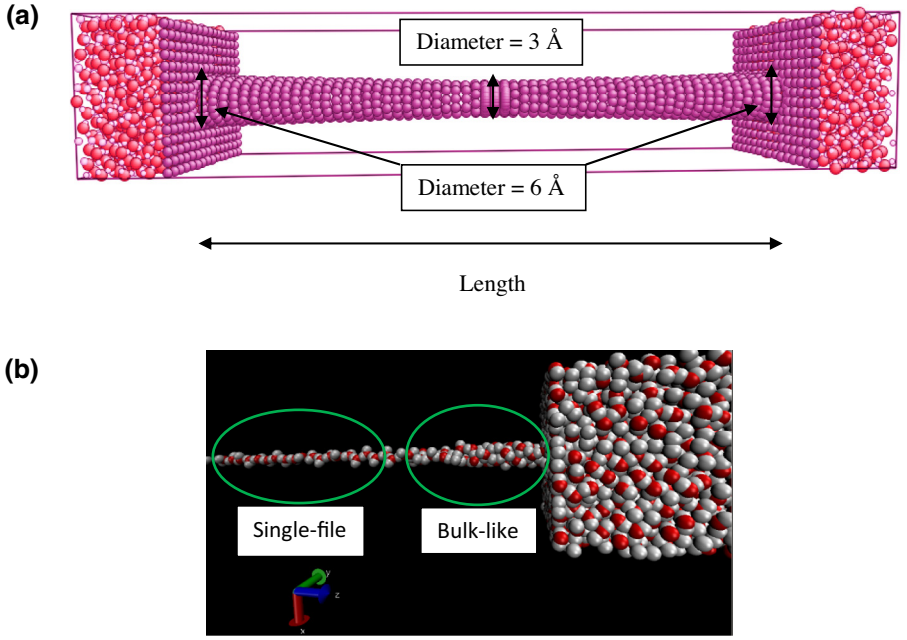

Fig. 1. (a) Schematic diagram of the hourglass-shaped pore model (b) Images of Bulk-like and Single-file water configurations inside pore.