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Molecular dynamics simulation of transport characteristics of water molecules through high aspect ratio hourglass-shaped pore

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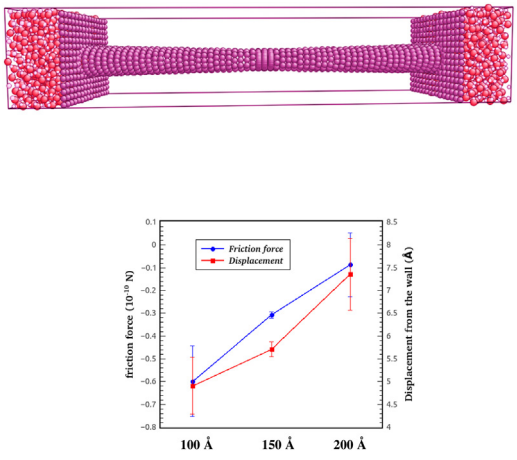
HIGHLIGHTS

- The non-equilibrium MD simulations were implemented to mimic osmosis-driven flow inside the hourglass-shaped pores.
- We analyze single file water transport through high aspect ratio hourglass-shaped nanopores.
- We observe that the aspect ratio may significantly influence on energy barrier inside the hourglass-shaped nanopores.
- We show that that diffusion can be shifted from Fickian to single-file mechanism by increasing the length.
- We describe that more of the total length covered by frictionless surface while increasing the length.

GRAPHICAL ABSTRACT



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ABSTRACT

This research utilizes molecular dynamics (MD) simulations in order to study the effect of the length on water transport properties through the pore with an hourglass shape structure. While the narrowest section of the pore is kept constant, the length of the pore is increased in the range of 100–200 Å. The narrowest section allows water molecules to cross just in single-file configuration. It observed that flow decreases as the length increases unlike the water flux which increases with length, which attributes to the frictionless surface of the pore. In comparable with flux, the efficiency increases as the length increases. The increase of the diffusion coefficient and permeability together suggest that the entrance effect can be negligible as the length increases. It revealed that the friction force decreases with increasing the length. On the other hand, the displacement of water molecules from wall increases with length. These results together suggest that as the length increases the wall surface becomes frictionless.

1. Introduction

Water molecules confined in nano-environment treat very differently toward their bulk complement. Structurally, water confined in pores can form ice or solid-like ordering [1–4] and in that shows abnormal transport or diffusion behavior [5–7]. The

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formation of 1D wires by water in narrow pores are a key point to the function of many bio-molecules, present new capabilities for industrial applications, and contribute models for studying the exceptional properties of confined fluids [8]. Recently, a carbon nanotube (CNT) is considered as a biomimetic channel because of providing closely an ideal system to study water transport in confined environment. Hummer et al. have shown that water molecules can freely enter into small cylindrical CNTs while forming a single-file arrangement [9]. The experiment and theory studies [9–12] were presented that CNT permits fast water transport with remarkably high rate in various diameter and length conditions. As reported in experiment studies [10,11] CNTs are seemingly longer ($\sim\mu m$) and wider ($\sim nm$) than that those in theory works. This issue occasionally leads to an evident divergence, e.g. flow rate enhancement in experiments versus simulations [10].

A molecular dynamics (MD) simulation has proposed a power law relation between water flow enhancement and CNT diameters and lengths, and also has shown that the channel dimension effect is related to the thermal fluctuations in the bulk water outside the CNT [13]. An effective characteristic on transport properties of CNTs is their length. CNT membranes can be manufactured as thin as 2–5 μm [14,15], however MD simulations enable to accomplish considering CNTs in which are a few nanometers in length. The length of the CNTs is the elementary identifier of the nature of the flow as Mattia and Gogotsi [16] were reported. Kalra et al. [17] have shown that the stochastic flow in very short CNT comes from the thermal fluctuations of water molecules outside the pore. Through infinitely long CNTs [18] no evidence of single-file diffusion was observed in spite of the confined CNTs structure. Generally, understanding the length effects on the fluids flow is of central importance to conceiving the nature of CNT flows.

Aquaporins and Gramicidin A mediate the transport of water, ions and protons through biological membranes [19,20]. Narrow water-filled pores, inspired by biological pores, have gained a great attention for high selectivity and fast transport rate in molecular separation devices [14,17]. Aquaporins are membrane proteins that enable fast water transport and water selectivity [21,22]. The shape of these pores suggests 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 [23].

Surprisingly, an experimental study using transmission electron microscope (TEM) tomography [24] revealed that the solid-state pores suggest an hourglass shape than a cylindrical structure. Hence, understanding the fluid transport mechanisms through nanotubes with an hourglass shape would be necessary in the view point of biological and industrial applications.

Some important physical characteristics of aquaporin such as single-file water structure, dipole reorientation, and osmotic permeability have been investigated by other researchers [25–28], 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 pore was at the hydrophobic state of $\theta_{pore} = 101^{\circ}$.

Although the pore diameter robustly influences the transport properties of water molecules [1,5,18,29,30], little efforts have considered the effect of nanochannel length on the water transport mechanisms [31]. 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 mechanism across the hourglass-shaped pore structures were successfully investigated.

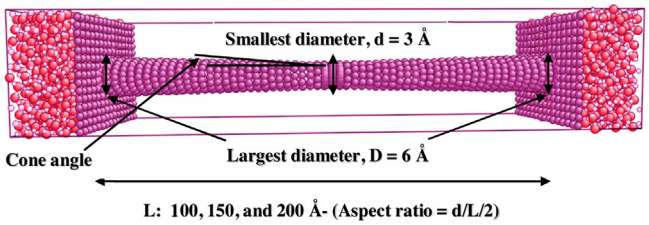

Fig. 1. Schematic diagram of the hourglass-shaped pore model.

In this study, the classical molecular dynamics (MD) simulation is used to investigate the length effect on water transport properties through aquaporin-like pore structure by showing the flow/flux, transport efficiency, hydrogen bonds distribution, probability distribution, free energy of occupancy, mean square displacement (MSD), diffusion coefficient, osmotic permeability, flow enhancement, etc.

2. Simulation details

Our computational system composed of an hourglass-shaped pore and the reservoirs made by carbon atoms, as shown in Fig. 1. The size of the reservoirs were $30 \times 30 \times 30$ Å^3. The box size along the z direction is taken sufficiently large (10 times the narrowest radius of the pore [32]). 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 constant at 3 Å. Three different lengths of 100, 150, and 200 Å for the hourglass-shaped nanochannels are studied. The 1500 SPC/E model of water molecules were randomly disposed into the reservoir at the initial configuration.

Non-equilibrium MD simulations are implemented using LAMMPS package [33]. 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 [34], 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 [35]. The water molecules are held rigid by applying SHAKE algorithm [36]. 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 [37] 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 [32]. Periodic boundary conditions are applied in three directions and the van der Waals cutoff radius is set as 10 Å. 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 was done for 7.5 ns for the analyses.

All above steps are separately conducted for every three cases implementing velocity Verlet algorithm to solve the equations of