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Molecular dynamics simulations on water permeation through hourglass-shaped nanopores with varying pore geometry

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ABSTRACT

We investigate the transport of water in hourglass-shaped nanopores using molecular dynamics (MD) simulations. We focus on the hydrodynamic effect by exploiting conical entrance/exit effects and utilizing the single-file fast water flow by limiting the cylinder diameter. We assume that the transport ability facilitated by the hourglass-shaped nanopores can be improved by varying the combination of cone angle and cylindrical pore length. The maximized results for transport properties with geometric parameters, quantified as number flux and osmotic permeability, prove that our assumption is reasonable. Further analysis for the validity of our design concerns the distribution of water inside the pore, e.g., the friction force between water molecules and the pore. Maximization of pore geometry provides a basis for improving the flux and velocity of water transport through nanoscale structural design.

1. Introduction

Thin synthetic membranes with nanometer-sized pores are used in a variety of nanoscale mass transport applications, such as in the desalination of sea water [1], isolation of individual macromolecules [2], drug delivery [3], and other applications [4,5]. The design of artificial nanopores is often inspired by cell membranes that, for example, contain aquaporin water channels, a unique channel protein that facilitates water transport while preventing protons from passing through the cell [6,7]. The high-resolution visualization of channels suggests an hourglass shape approximately 20 Å in length and 3 Å in the narrowest diameter at the center of the channel [8]. The underlying mechanism of aquaporin water channels can be mimicked to provide high water permeation through semi-permeable membranes.

Water transport through nanopores has been extensively studied, though a clear understanding has not yet been reached [9,10]. In many previous studies, nanopores were primarily considered as cylindrical nanotubes that support water flow rates exceeding the expectations of macroscopic hydrodynamics by several orders of magnitude by controlling the diameter and length of the pore. Molecular dynamics (MD) simulations are powerful tools to predicate structural and dynamic properties of nanoscale mass transport comparable to experimental data. The integrity of MD simulations has been shown in a number of studies with benefits including low computational cost and feasibility of observing molecular trajectories. For example, Hummer et al. investigated single-file water arrangement, where water molecules cross the pore one at a time, in a single-walled carbon nanotube 13.4 Å in length and 8.1 Å in diameter [11] and found that water molecules occasionally enter the carbon nanotube in unidirectional bursts without external forces [12,13]. Our previous studies showed that the pore diameter can control ion selectivity of positive charges of similar size [14–16]. Water flow rates [17–19] are significantly affected by the orientation of water and hydrogen bonding at the interface [20]. In addition, properties of fluids, such as the coefficient of friction [17] and permeability of water [21,22], are calculated from simplified theoretical models using MD simulations for comparison to experimental investigations [23,24]. In experiments, applying an external pressure is a realistic and effective method to transport water directionally, rather than applying electric fields and point charges [25–27]. However, as the entrance and exit channels are small, edge effects restrict enhanced water flow [28,29]. To mitigate size limitations, we propose an effective method using a complex structure inspired by hourglass-shaped water channels (aquaporins) by simply expanding the volume of the entrance and exit channels. The conical ends of the pore, in conjunction with the pore length, contribute to the hydrodynamic permeability. We note that an artificial nanopore model considering the effect of both cone angle and length on

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the single-file water arrangement has not been extensively studied.

In this study, we performed molecular dynamics simulations to model the pressure-driven flow of water through an hourglass-shaped pore by altering the conical entrance/exit in conjunction with the cylindrical center. We assume that the proper combination of cone angle and cylinder pore size has the potential for fast transport of a large number of water molecules. Furthermore, we investigated the influence of channel structure by the cone angle, ratio of length of the cone to length of the cylinder pore, and length of the cylindrical section of the pore. We found that the transport properties, represented by the average number of water molecules and the number flux, change significantly with the alteration of the above-mentioned geometric parameters. Specifically, the osmotic permeability and hydrodynamic resistance can be maximized with respect to the cone length and angle. Furthermore, the trajectories of a single water molecule and the number density of water distributed along the pore axis aid in understanding transport processes. We also calculated the friction force using our non-equilibrium simulations. Finally, we demonstrate that the improved properties indeed support our assumption that controlling the properties of an hourglass-shaped pore can control water transport through the pore.

2. Simulation details

Water transport through nanoscale pores is dependent on the pore diameter and length. A key problem in nanoscale mass transport is the edge effect at the entrance and exit of a pore. For example, the osmotic permeability through a biconical nanoscale pore is sensitive to the cone angle of the pore. The maximized permeability reaches a maximum at an expanded entrance volume, contrary to the behavior in cylindrical pores [22]. The estimation of an maximized permeability in respect to the cone angle and length is available by both analytical modeling and computer simulations. The water filling and flow behavior has also been observed in pores with diameters as small as 1 nm. The formation of single-file water has been confirmed by several experimental studies and molecular dynamics simulations [30–33]. This phenomenon of water in nanoscale confinement slightly accelerates the flow speed through a narrow pore.

We assumed that the combination of conical pores and narrow cylindrical pores would lead to effective water transport by taking advantage of the benefits of the two geometries. Here, the conical pores may weaken the hydrodynamic blockage and the narrow cylindrical pores may result in the single-file water arrangement. Fig. 1 shows our simulation model constructed with a cuboid pool region ($50 \times 50 \times 20$ Å^3) and an hourglass-shaped pore. A cylindrical pore section is located at the center of the hourglass-shaped pore and connects the two conical sections on each end. Here, d is the diameter of cylinder section, H is the length of cylinder section, L is the total length of pore, and α is the cone angle of the conical channel (entrance and exit).

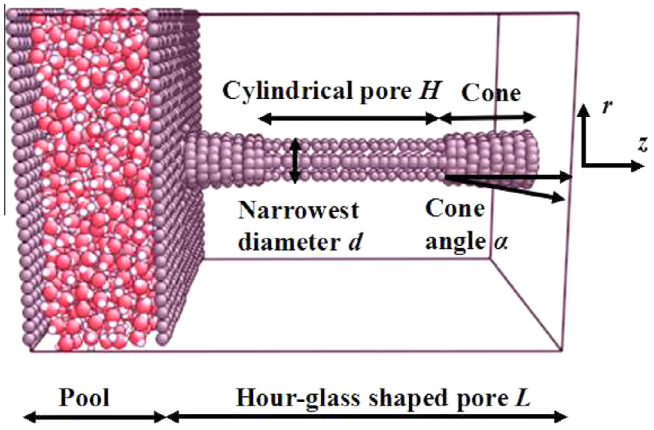

Fig. 1. Schematic of the molecular dynamics simulation model of an hourglass-shaped pore, where $d = 3$ Å (the narrowest diameter of the cylindrical pore) and $L = 60$ Å (the total length of pore). In this report, we varied the length H and cone angle α of the cylindrical pore.

In order to investigate the water permeation through this type of pore, we fixed the size of the narrowest diameter at 3 Å and the total length of the pore at 60 Å. Our previous study showed that a maximized osmotic permeability occurs when the cone angle equals 5° in a 60 Å-long hourglass-shaped pore. Thus, we tested the current model with a 5° cone angle, while also considering models with 1° and 7° cone angles. The length of the cylindrical pore varies from 10 Å to 40 Å, which generates an H/L ratio of 0.167–0.667. Because the total length of pore is fixed, the diameter of the entrance and exit of the conical region changes with the H/L ratio, as the narrow diameter of the cylindrical pore.

In this study, we employed DL_Poly 2 [34,35] to conduct the MD simulations. We used an NVT ensemble with 2 fs time steps for each simulation and constrained bond lengths and angles of the transported water molecules. A simple point charge-extended (SPC/E) water model was used. Initially the distribution of 1700 SPC/E water molecules were random in the pool region. After the system equilibrated for around 1 ns, we performed simulations by adding a uniform external force to achieve an osmotic pressure-driven flow through the hourglass-shaped pore. Each non-equilibrium simulation lasted for 2 ns on average to achieve the steady state. Then, all the data, including the coordinate, velocity, and force of particles changing with simulation time, was obtained from another 2–4 ns non-equilibrium simulation. To decrease the computational time while maintaining sufficient data statistics, we used an applied pressure of over 6 katm (the discussion on the pressure can be found in our previous paper [45] and related references cited therein). The walls of the pool region and hourglass-shaped pore were fixed to avoid undesirable vertical and horizontal aberrations. We modeled the inter-atomic interaction between the oxygen of water and the wall atoms (assumed to be carbon) by the well-known pair-wise Lennard–Jones (LJ) potential [36] with $\sigma_{o-c} = 0.319$ nm and $\varepsilon_{o-c} = 0.392$ kJ/mol. The used Lennard–Jones parameters of water–water are the default value of the SPC/E water model, $\sigma_{o-o} = 0.3169$ nm and $\varepsilon_{o-o} = 0.6498$ kJ/mol. Because the walls and the nanopore are located at fixed locations (the effect of pore flexibility can be found, e.g., in [45]), there is no need to define the potential between carbon atoms. The cutoff distance for the LJ interactions is 10 Å. And, the long-range electrostatic interactions were computed using the particle mesh Ewald method with the cutoff of 10 Å. We applied periodic boundary conditions all three dimensions, and held the temperature at constant 300 K during the simulation using a Nosé–Hoover thermostat.

3. Results and discussion

Water molecules are pushed from the pool into the cylindrical pore by a pressure that creates flux and permeability through the membrane. The average number of water molecules N versus the cone angle α and cylinder length H inside of the pore is plotted in Fig. 2a. The average number of water molecules increases linearly with increasing cone angle, but decreases with cylinder length. When H is fixed, the number of water molecules increases with the cone angle. When the cone angle is fixed, the number of water molecules decreases with H. In this case, the total pore volume also decreases with H. The entry of water molecules is