Flow resistance analysis of nanoconfined water in silt pores by molecular simulations: Effect of pore wall interfacial properties

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A B S T R A C T

The anomalous flow behavior of nanoconfined water is attracting considerable attention. This study aimed to investigate the effect of pore wall interfacial properties on the flow behavior of water confined in a slit pore. Non-equilibrium molecular dynamics simulations were performed on water molecules confined in slit pores. By moving the two pore walls to opposite directions, the confined water molecules were made in a directed flowing. The flow resistance of the water molecules was then analyzed at the nanoscale. Two Si(1 1 1) surfaces were used to construct the slit pore model. The interaction strength, ε_{Si-w}, between the pore wall atom and water's oxygen atom was adjusted to represent different pore wall interfacial properties. A higher ε_{Si-w} indicates a more hydrophilic pore wall interface. Simulation results show that for the studied cases, more hydrophilic pore walls leads to larger flow resistance of the confined water. At the molecular level, the friction between the pore wall and water molecules increases with increased hydrophilicity of pore walls and further hampers the flow of the confined water in the slit pore. Moreover, simulation results demonstrate that water molecules confined in the slits are layered. The increase in the hydrophilicity increases hydrogen bonds between water layers, thereby enhancing flow resistance arising from the water molecules themselves.

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1. Introduction

In recent years, the anomalous flow behavior of nanoconfined fluids has intensely attracted the attention of membrane scientists [1,2]. From a conventional viewpoint, increasing the flux can result in the low selectivity of a membrane. However, Fornasiero et al. developed a sub-2-nm modified carbon nanotube membrane, which exhibited significant high selectivity (ion exclusion as high as 98%) as well as high flux [3]. Moreover, the diffusion of a liquid through a pore is generally much more difficult than that of gases. However, Nair et al. observed that water permeates through the graphene-based membranes at least 10^{10} times faster than He [4].

The flow of a fluid through a pore is in essence a process in which fluid molecules overcome two types of flow resistance (i.e., the friction between the pore wall and the fluid molecules and the interactions among the fluid molecules themselves) under a certain driving force. The difference in the resistance of various fluid molecules flowing through a pore leads to different flow properties. At the nanoscale, a decrease in the number of fluid molecules confined within nanostructures enhances the influence of their interfacial properties on fluid molecule behaviors, resulting

in unique flow properties. Thus, in this study, we focus on water molecules confined in a slit pore formed by two solid walls and study the effect of interfacial properties of pore walls on the two types of flow resistance: the friction between the walls and the confined water molecules and the interactions among the water molecules themselves.

Water is one of the most important fluids used in industrial processes. Most applications involving nanoporous membrane materials are closely associated with water, such as seawater desalination and wastewater treatment [5,6]. Moreover, the behavior of the nanoconfined water is of great interest to researchers in the field of biology, which prompts the design of biomimetic nanoporous membrane materials [7]. Molecular dynamics (MD) simulation is recognized as an effective tool for investigating the behaviors of water molecules under nanoconfinements. In our previous studies, we have conducted a series of MD simulations at equilibrium conditions to evaluate the factors affecting the behavior of confined water molecules, including pore wall modification by functional groups, size, and temperature, and so on [8–11]. These systematic studies have demonstrated that the effects of pore size and surface chemistry at the nanoscale are more dominant than external effects, such as temperature and pressure [12].

To investigate the flow properties of nanoconfined water, the system should be under non-equilibrium conditions, so that water molecules are kept in a state of directed flow. Various MD
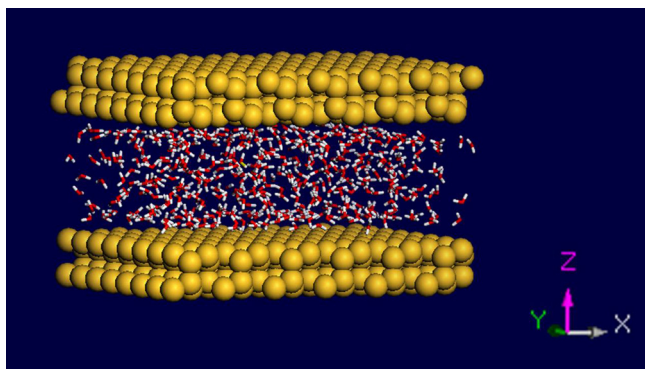
Fig. 1. Simulation model.

simulation techniques have been developed, including the external field non-equilibrium molecular dynamics (EF-NEMD) method, the dual control volume grand canonical molecular dynamics (DCV-GCMD) method, and so on. For instance, Kalra et al. investigated the osmosis of water through carbon nanotube membranes by using the concentration gradient to make water flow [13]. Zheng et al. adopted the DCV-GCMD method to transport a water and methanol mixture under a fixed concentration gradient through nanotubes [14]. Gong et al. applied a constant electric field along the nanopore to induce the flow of a charged solute and to investigate the selectivity of K^+ and Na^+ [15]. Zhao et al. applied the gravitational force field on the fluid molecules in the tube axial direction to initiate the flow, and then removed the force to allow the molecules to freely decelerate [16].

To induce the confined molecules flow into a directed flow, the aforementioned techniques apply a driving force directly on the molecules or construct a chemical potential gradient. Pore walls are fixed throughout the process. According to the principle of transport, an alternative avenue that keeps the pore walls moving can also make the confined fluid directed flow. This method is not suitable for the investigation of the transport behavior of bulk fluids, because only the molecules influenced by the pore wall can be driven [17]. However, under nanoconfinement, the confined fluid is strongly affected by the interfacial properties of nanopores. Experimentally, nanoscale force measurement apparatuses such as atomic force microscopy (AFM) are also adopted this way to study the confined fluid [18–20], which facilitates dialogs between simulation and experimental observations. Therefore, we performed the non-equilibrium molecular simulation (NEMD) simulations on confined water molecules in this study by keeping the pore walls moving and analyzed of the flow properties of the nanoconfined water.

The aim of this study is to investigate the effect of the interfacial properties of pore walls on the flow behavior of confined water. Flow resistance can be studied in its two types: (1) the friction between the pore wall and water molecules and (2) the interactions among the water molecules themselves. The question that interests us is how the hydrophilicity of pore wall affects the two types of flow resistance. Section 2 describes the simulation model and the details of the method. Section 3 discusses the simulation results. Based on the discussions, Section 4 draws the main conclusions.

2. Simulation model and method

The simulation model used in the NEMD is shown in Fig. 1. Water molecules were confined between two solid walls. The solid walls were infinite in the X and Y directions. Three-dimensional periodic boundary conditions were applied on the entire simulation box except for the confined water molecules in the Z-direction. Two

Table 1
The Lennard–Jones parameters and partial charges for Si atoms of wall, water molecules (TIP/3P).

	Site	σ (Å)	ε (K)	q (e)
Wall	Si	3.8264	202.4506	0
Water	O	3.152	78.020	−0.834
	H	0.000	0.000	0.417

Si(1 1 1) surfaces were adopted to construct the slit pore model. Each Si(1 1 1) surface consisted of four layers of silicon atoms, which were cleaved from its bulk. The total number of silicon atoms in each wall was 384. For all the simulated cases in this study, the slit width was set to 1.6 nm.

All atoms of confined water molecules and pore walls were treated as charged Lennard–Jones (L-J) sites. The TIP/3P model of water was employed. The total interaction potentials between the water molecules and the silicon atoms of the wall surfaces were calculated using the site-site interaction method:

$$U_{Si-w} = 4\varepsilon_{Si-w} \sum_{i=1}^{N_w} \sum_{j=1}^{N_{Si}} \left[\left(\frac{\sigma_{Si-w}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{Si-w}}{r_{ij}} \right)^6 \right] \qquad (1)$$

where N_w is the total number of atoms for water molecules, N_{Si} is the total number of silicon atoms of the wall, and r_{ij} is the center-to-center distance between an atom of the water molecule and a silicon atom from the wall. The subscript "w" denotes the water molecule, and "Si" denotes the silicon atom. The cross-term of energy and size parameters, ε and σ were obtained by Lorentz–Berthlot combination rules:

$$\varepsilon_{Si-w} = \sqrt{\varepsilon_w \varepsilon_{Si}} \qquad (2)$$

$$\sigma_{Si-w} = \frac{\sigma_w + \sigma_{Si}}{2} \qquad (3)$$

Table 1 summarizes all the Lennard–Jones parameters and partial charge values used in the MD simulations.

In this study, the interaction strength, ε_{Si-w} between the pore wall atom and the water's oxygen atom was adjusted to simulate various different pore wall interfacial properties. A higher ε_{Si-w} indicates a more hydrophilic pore wall [21]. Five simulation cases were set-up, denoted as Case_0.1, Case_0.5, Case_1, Case_2 and Case_5 (see Table 2). The numbers in label stand for the change factor of the ε_{Si} adopted in each case. For example, the label "Case_2" indicates that the ε_{Si} in the case is increased by a factor of 2. The change in the ε_{Si} results in different the interaction strength between the wall and the water molecules. For Case_2, the ε_{Si-w} is increased by a factor (ε_{Si-w}^*: relative change rate of interaction strength) of 1.414, accordingly.

As shown in Table 2, the number of confined water molecules in each case is different, because slits with different pore wall interfacial properties accommodate different water molecules under the equilibrium state. For this reason, we obtained the number of water molecules by the equilibrum MD method. The procedure is as follows: (i) the slit was solvated in the center of a periodic bulk water box (8 nm × 7 nm × 6.4 nm) with a density of 1.0 g cm^{-3}. The slit was

Table 2
The details of simulated systems.

Label	ε_{Si-w}^*	N_w	b (nm)	Friction coefficient
Case_0.1	0.316	408	4.00	0.15
Case_0.5	0.707	419	1.56	0.17
Case_1	1	446	0.83	0.28
Case_2	1.414	466	0.33	0.41
Case_5	2.236	493	0.02	0.53

N_w: number of water molecules inside the slits. ε_{Si-w}^*: relative change rate of interaction strength of ε_{Si-w}.