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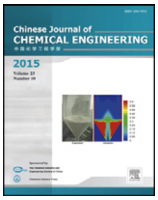

Fluid Dynamics and Transport Phenomena

Molecular dynamics simulation of water transport through graphene-based nanopores: Flow behavior and structure characteristics☆

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ABSTRACT

The flow behavior of pressure-driven water infiltration through graphene-based slit nanopores has been studied by molecular simulation. The simulated flow rate is close to the experimental values, which demonstrates the reasonability of simulation results. Water molecules can spontaneously infiltrate into the nanopores, but an external driving force is generally required to pass through the whole pores. The exit of nanopore has a large obstruction on the water effusion. The flow velocity within the graphene nanochannels does not display monotonous dependence upon the pore width, indicating that the flow is related to the microscopic structures of water confined in the nanopores. Extensive structures of confined water are characterized in order to understand the flow behavior. This simulation improves the understanding of graphene-based nanofluidics, which helps in developing a new type of membrane separation technique.

1. Introduction

Graphene-based materials, such as graphene and graphene oxide, have been considered as promising membrane materials [1–4]. Graphene layers usually self-assemble into laminate paper-like structures with interlayer distance on nanometer scales [5–7]. This specific laminate structure allows water molecules to permeate through interconnected nanochannels between graphene nanosheets. Recently, Nair *et al.* [3] have reported submicrometer-thick graphene-oxide laminate membrane with a typical ~1 nm pore width. This kind of membrane can impede the permeation of various species, including helium, but the membrane allows unhampered permeation for water. As further extension of the pioneer work, Joshi *et al.* [8] evaluated the filtration and separation performance of laminate membrane for extensive solutes, including ions and organics. In addition, ultrathin graphene nanofiltration membrane with two-dimensional nanocapillary has been fabricated by packing reduced graphene oxide structures [4]. The graphene membrane performs excellently for retention of organic dyes with high water flux.

Although carbon nanotubes (CNTs) have been reported as potential nanofiltration membranes, the CNT-based membranes suffer from the difficulty in larger-scale fabrication and preparation. On the contrary, the laminate two-dimensional graphene membranes, with superior flexibility and chemical stability, can be facilely prepared by filtration-assisted assembly method. According to a previous model [3], the interconnected nanochannels in the layered graphene membrane have two regions: functional and pristine. The former acts as spacers to keep adjacent graphene sheets apart, whereas the pristine region provides a capillary network that allows high water flux. It is also suggested that the nanoscale spacing between graphene nanosheets can be adjusted through inserting spacers [9]. Therefore, a broad spectrum of graphene membrane could be prepared, which shows extensive potential applications.

In order to develop this new-typed graphene-based laminate membrane, it is necessary to understand the flow behavior and confined structure of fluid molecules in the two-dimensional nanochannels. Molecular simulation has been extensively applied to study the transport behavior and confined structures in the nanoscale CNTs [10–12]. However, to our best knowledge, no molecular simulation has been reported for the pressure-driven infiltration transport of water molecules from bulk phase going through the slit nanochannels formed by graphene sheets. In particular, graphene pores with subnanometer size show significant molecular sieve performance, which can be used to develop new-typed membrane separation materials [3,9]. For this kind of pore size, the interfacial effect is expected to overwhelmingly control the flow behavior. It is highly required to explore the unique flow behavior through the subnanometer graphene slit pores. In this work, we use molecular dynamics (MD) simulation to study the infiltration behavior of water driven by external pressure through the graphene nanocapillary with

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typical pore widths (≤1 nm). The confined water structures are also investigated in order to understand the flow mechanisms.

2. Simulation Methods

In this work, water molecules are simulated using the SPC/E model [13]. Carbon atoms of graphene are held stationary and modeled as Lennard-Jones (LJ) spheres employing the parameters proposed by Chang and Steele [14]. The van der Waals interactions between different particles are calculated with the LJ potential using the Lorentz–Berthelot mixing rule. This water-carbon interaction has been successfully applied to represent the structural and dynamic properties of water molecules confined in carbon pores [15].

As shown in Fig. 1, the graphene-based slit nanopores consist of a pair of three-layer graphene sheets, which adopt ABA stacking configurations [16] with the natural interspacing space of 0.335 nm [17]. Each graphene sheet has the size of 2.333×5.105 nm^2. The slit pore is incorporated into the simulation cell with various separation distances ($H =$ 0.7, 0.8, 0.9, and 1 nm). The simulation box lengths in x, y, and z directions are set to be 2.48,2.40, and 17.21 nm, respectively. Water molecules are randomly placed in the right reservoir with a density of 1.0 g·m^{-3} and the left reservoir is kept empty. One additional graphene sheet is as moveable wall for creating the driven force toward the water molecules in the right reservoir. The simulated pressure of the right water reservoir is obtained around 0.1 MPa.

We perform equilibrium and non-equilibrium MD simulations in the canonical ensemble (NVT) using the LAMMPS MD package [18] with a time step of 1 fs. The Nose–Hoover thermostat [19,20] is used to keep the temperature of 298.15 K. The particle–particle particle–mesh method is used for the Coulombic interaction. The cutoff for LJ potential is set to be 1.2 nm. Periodic boundary conditions are used only in the x and y directions (the coordinate system in Fig. 1). The confined structures are mainly evaluated through the equilibrium MD simulation. In the non-equilibrium MD simulation, following the general treatment in Ref [11,12], an external force along the z direction is applied to the moveable wall in order to push water molecules to enter the nanopores. The applied pressure (P) is calculated from the moving acceleration rate (a) of moving graphene sheet, $P = Nma/A$, where N is the number of atom in the confined pore, m is the mass, and A is the area of moving graphene. In this work, we use relatively high pressure, which is common in the non-equilibrium MD simulation [12] to reduce the thermal noise and speed up the simulation process. Meanwhile, in order to simulate the water penetration in the pervaporation membrane process, the water molecules after passing the slit pore will be removed from the system.

3. Results and Discussion

Fig. 2(a) shows that the volumetric flow rate (Q, nm^3·ns^{-1}) of water through the slit nanopores increases with the applied pressure. Fig. 2(b) shows an approximate linear dependence of the number of permeating molecules on the time, from which the flow rate is obtained from slopes of these curves. Moreover, effective flow velocity is estimated to be in the range of $(1.5–27.8) \times 10^4$ nm·s^{-1} in the pore of 1 nm, which is higher than the experimentally observable flow velocity of water within the CNT pore (~0.43×10^3 nm·s^{-1}). It should be noted that under low-pressure condition, the linear dependence behavior is somewhat suppressed due to thermal noise effect. As expected, larger slit nanopore leads to higher volumetric flow rate. It is noteworthy that the volumetric flow rate does not exhibit a linear relationship with pressure. In the graphene nanopores with the pore width of 0.7-1 nm, the simulated mass flow rate varies from 1.9×10^{-11} to 6.4×10^{-10} mg·s^{-1} in the pressure ranges investigated, which are consistent with the experimentally measured permeability of water through graphene oxide membranes with the width of 0.7-1.1 nm [3]. The result suggests that this simulation system can describe the basic flow characteristics of fluid through graphene-based slit nanopores.

We further evaluate the flow enhancement factor ($\varepsilon = Q/Q^{\mathrm{HP}}$) in our graphene nanopores, in which the Hagen–Poiseuille equation [21,22] is used to describe the classical flow rate (Q^{HP}). The inset of Fig. 2(a) displays the enhancement factors, which are lower than those reported for water flow through CNTs [21,23]. The enhanced flow behavior is generally explained by small friction between water molecules and carbon surfaces, corresponding to the so-called boundary slip behavior [24–26]. However, different carbon-based nanopores often exhibit variant flow features. The simple boundary slip concept cannot give a full explanation to the microscopic characteristics of fluid flow through the graphene-based slit nanopores. Especially, in our system, there exist capillary suction and discharge between bulk phase and micropore phase, which might affect the flow velocity.

The simulation results indicate that water molecules could spontaneously permeate into the microscopic nanopores, because the capillary pressure generated at the pore entrance would drive water into the nanopores. Without the applied pressure as the driven force, water could not permeate the nanopores with the pore width below 10 Å. Moreover, Fig. 2(b) shows that at the initial stage water molecules could not enter the nanopores under lower pressure. The reason is that certain external force is required to overcome the permeation resistance from micropore surface interaction [3,27,28]. In our simulation system, the interaction between graphene surface and water molecules exhibits somewhat hydrophilic characteristics [29], as a result, the capillary permeation pressure at the exit of nanopore would block or suppress fluid permeation.

Fig. 3(a) shows the variation in the number of water molecules entering the nanopore ($H = 0.8$ nm) *versus* time. Higher pressure results in larger driving force, increasing the transportation rate. Similar phenomena are also observed in other size nanopores. The permeation and flow behavior of water molecules in the graphene-based slit nanopores involve three steps: (1) permeate into nanopores; (2) move along nanopores; and (3) flow out of nanopores (exit effect). Fig. 3(b) shows the axial (z-direction) trajectories of several typical water molecules through the 0.7 nm pore under the pressure of 108 MPa. In the graphene slit nanopores, the axial movement of water molecules demonstrates a typical pulse-like behavior to some extent, which is in agreement with the behavior of water molecules in single-walled carbon nanotubes [30]. However, as compared to the moving behavior along the direction parallel to the surface, the movement in the lateral direction does not show significant fluctuation, demonstrating the restriction effect of solid surface. Moreover, Fig. 3(b) shows that the dwelling time of water molecules near the nanopore end is obviously long, indicating that the permeation of water molecules is largely hindered by the exit effect. Generally, this exit effect can be quantitatively characterized by the free energy profile for a molecule passing through the exit [31], which reflects the degree of diffusivity for molecule passage. However, in this work, this computation is not conducted.

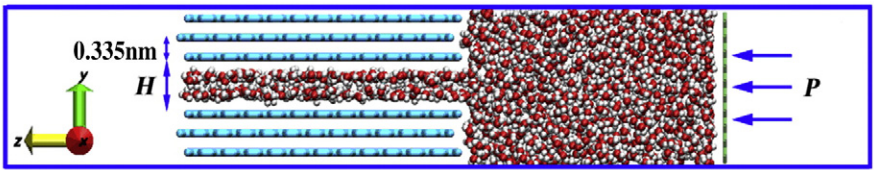

Fig. 1. Snapshot of system schematic in the non-equilibrium MD simulation.