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Transport behavior of water molecules through two-dimensional nanopores

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Water transport through a two-dimensional nanoporous membrane has attracted increasing attention in recent years thanks to great demands in water purification and desalination applications. However, few studies have been reported on the microscopic mechanisms of water transport through structured nanopores, especially at the atomistic scale. Here we investigate the microstructure of water flow through two-dimensional model graphene membrane containing a variety of nanopores of different size by using molecular dynamics simulations. Our results clearly indicate that the continuum flow transits to discrete molecular flow patterns with decreasing pore sizes. While for pores with a diameter ≥ 15 Å water flux exhibits a linear dependence on the pore area, a nonlinear relationship between water flux and pore area has been identified for smaller pores. We attribute this deviation from linear behavior to the presence of discrete water flow, which is strongly influenced by the watermembrane interaction and hydrogen bonding between water molecules. © 2014 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4898075]

I. INTRODUCTION

There have been numerous studies in recent years showing that the properties of water fluid at the nanoscale are different from those predicted by continuum approaches.¹⁻⁶ For example, using molecular dynamics (MD) simulations Hummer et al. found water can flow very fast through hydrophobic single-walled carbon nanotubes due to the existence of ordered hydrogen bonds between the water molecules inside the nanotube.^{1,3} Shortly afterwards, experimental results showed that the flow rate of water through carbon nanotubes with a diameter around 7 nm is about 10/ns/MPa (the number of water molecules across the nanotube under 1 MPa per nano second), which is four to five orders of magnitude faster than the conventional fluid theory would predict.⁴ Single-file motion of water is believed to exist in the water channel of aquaporin proteins, where water flux through the cell membrane embedding aquaporin-1 is around 0.02/ns/MPa per aquaporin molecule.² The reported fast water transport at the nanoscale has received a lot of attention because of its great potential in real world applications, including molecular sieves, membranes, sensors, nanofluidic devices.4,5,7,8

Besides nanotube-based membranes, two-dimensional (2D) materials have also been proposed for molecular sieving or water filtration, due to their ultrathin nature.^{9–11} For example, MD simulations indicate that nanoporous graphene membranes provide even higher water flux (about 28/ns/MPa) compared to carbon nanotube membranes (about 25/ns/MPa) with almost the same pore diameter (2.75 nm).⁹ By using MD simulations, we found that water flux is around 0.02/ns/MPa for a perfectly two-dimensional graphyne-3 membrane with the nanopore diameter of 0.4 nm.¹¹ More importantly, we found that although the nanopore size has a drastic increase going from graphyne-4 to graphyne-5 (effective pore area increasing by 70%), the water flux exhibits little change. This counter-intuitive behavior is different from what continuum approaches of water flow could predict and was assigned to the quantized nature of water flow at the nanoscale.¹¹ Then a question arises on what the critical pore size is for the transition from quantized flow to continuum flow. Since the step size in graphyne-n's nanopore is too large, no true transition in water flow rate from discrete to continuum water flow had been observed, and no quantitatively relationship was established between water flux and the pore size for large twodimensional nanopores in general. Also, few efforts have been made to investigate the microscopic mechanisms of water transport through two-dimensional nanopores at the atomistic level.

As a prototype two-dimensional membrane, graphene films are readily available experimentally in large scales and nanopores can be easily introduced into graphene's structure by ion lithography and oxidative etching.¹² Although nanoporous graphene membrane has been used for water treatment,^{9,10,12} there is no systematic study on the atomistic mechanisms and the optimal pore size for water transport through graphene nanopores. Therefore, taking well-defined rectangular pores in single layer graphene membrane, we attempt to explore the transport behavior of water molecules through atomically thin two-dimensional nanopores by using molecular dynamics simulations, and compare the results to predictions from continuum approaches. Here, we show first evidences in water flux for a transition from discrete water flow to continuum flow when the size of a nanopore reaches a critical value. For pores with a diameter >15 Å water flux exhibits a linear dependence on the pore area, while a nonlinear relationship between water flux and pore area has been identified for smaller pores. In particular, we present a quantitative relationship between macroscopic water flux and the pore area for large nanopores in general. According to

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this empirical relationship, the water flux for some smaller nanopores should be zero, while our MD simulations show water molecules can pass through these nanopores. Our analysis show this is because of the interaction between the water molecules and the membrane. Since our simulations are based on nanopores in graphene membrane, these effects can be directly examined by experiments. We anticipate that this study will help the design of efficient two-dimensional membranes for water filtration and desalination. In particular, understanding the microscopic mechanisms of water transport through two-dimensional nanopores at the atomistic level is of fundamental significance to the advancement of basic science of water.

II. MODEL AND SIMULATION DETAILS

A graphene membrane with a nanopore was modeled with the atomic structure shown in Fig. 1(a). Since there are dangling bonds in the edge of nanopore and they are chemically very active, we use hydrogen atoms to passivate the edge carbon atoms. For simplicity and for understanding the general trends, we adopt ideal rectangular pore shapes with two sides along the armchair direction and the other two along the zigzag direction of the graphene lattice. The pore size can be



FIG. 1. (a) Atomic structure of model two-dimensional nanopore with edges saturated by hydrogen in the graphene membrane. We use (N_a, N_b) to describe the nanopore size, where N_a is the number of hydrogen atoms in the pore edge along the armchair direction and N_b is the number of hydrogen atoms in the pore edge along the zigzag direction. (b) Side view of the simulation system used in this work.

described by two length indexes as (N_a, N_b) , where N_a is the number of hydrogen atoms in the armchair edge of the pore while N_b is the number of hydrogen atoms in the zigzag edge of the nanopore. Obviously, the effective area *S* of this kind of nanopores can be expressed as

$$S = k_0(N_a + k_a)(N_b + k_b) = k_1 N_a N_b + k_2 N_a + k_3 N_b + k_4,$$
(1)

where k_1, k_2, k_3 , and k_4 are constant parameters. Various pore sizes were tested in our simulations.

The rigid SPC/E water model is employed to account for the interactions between water molecules.¹³ The carbon-water interaction potential is described by the Lennard-Jones potential, $V(r) = 4\varepsilon((\frac{\sigma}{r})^{12} - (\frac{\sigma}{r})^6)$, where r is the distance between a pair of atoms, ε is the depth of the potential well, and the parameter σ is related to the equilibrium distance of the atomic contact. The Lennard-Jones potential depth for carbon (ε_{CC}) and hydrogen (ε_{HH}) in the nanopore membrane are 0.2327 kJ/mol and 0.1255 kJ/mol, while σ_{CC} and σ_{HH} are kept at 3.40 Å and 2.42 Å, respectively.^{10,14} The parameter values for the interactions between carbon, oxygen, and hydrogen were obtained by using carbon and hydrogen atoms' parameters in the membrane and oxygen atoms' parameters in SPC/E water model via the Lorentz-Berthelot mixing rules: $\varepsilon_{AB} = \sqrt{\varepsilon_{AA} \varepsilon_{BB}}$. This means that the values of ε_{CO} , ε_{HO} , σ_{CO} , and σ_{HO} for water-membrane interaction potential are 0.3980 kJ/mol, 0.2923 kJ/mol, 3.28 Å, and 2.79 Å, respectively. For simplicity, no atomic charges were assigned to the membrane. In order to justify this simplication, we performed a MD simulation for (6, 8) nanopore with atomic charges assigned to the membranes in the same way as that in Ref. 10 (0.115 e for hydrogen atoms, and -0.115 e for the neighboring carbon atoms). The result shows that the water flux is almost the same as that through the nanopore with no atomic charges.

All simulations were performed using the Gromacs package.¹⁵ The carbon and hydrogen atoms in the membrane were held fixed during all simulations. Our system contains 3875 water molecules. The initial system consists of a box measuring 200 Å in the z-direction and a unit cell size of 39.352×42.6 Å² periodically in the x-y plane. The nanopore membrane is fixed at z = 100 Å, with all water molecules initially placed on one side of the membrane. A rigid piston initially placed at z = 10 Å slowly pushes the solution toward the membrane under 500 MPa. Since previous studies show that the water flux is proportional to applied pressure,^{10,11} our simulation results can be extrapolated to other pressure values.

In our simulations, the short-range van der Waals interactions were cut off at 1.0 nm. The long-range electrostatic interactions were computed with particle mesh Ewald summation method.¹⁶ The water molecules are constrained to be rigid using the LINCS algorithm.¹⁷ The simulation systems are first equilibrated in a constant-volume and constanttemperature (NVT) ensemble for 200 ps at 300 K using Nose-Hoover thermostat¹⁸ with the external piston pressure kept at P = 0. Each system is then simulated for another 10 ns by maintaining a constant pressure normal to the piston with a time step of 2 fs. Totally five parallel MD trajectories are

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collected for each system. Configurations were stored every 0.2 ps for analysis.

III. RESULTS AND DISCUSSION

A. Water flux

When the nanopore size is too small ($N_a < 2 \text{ or } N_b < 4$), no water molecule across the membrane was observed during 10 ns MD simulations. Water molecules start to pass through the nanopore when $N_a \ge 2$ and $N_b \ge 4$. Figure 2 shows the number of filtered water molecules flowing across different nanopores as a function of time. The slope of each curve corresponds to water flux, defined as the number of filtered water molecules per unit time. Obviously, water flux through the nanopores is constant in time and increases with the pore size under the same constant pressure. When water flow is fast enough, the entire reservoir of water molecules on the feed side becomes depleted before the end of the simulation. This is why in some cases, such as that for the (4, 6) or (4, 8) nanopore, a plateau in water flow develops, where the curves eventually reach a saturation.

From Fig. 2 we observe that water flux is dependent on the pore size (N_a, N_b) . We plot water flux V_s across the nanopores as a function of N_a for different N_b , as shown in Fig. 3. According to the Hagen-Poiseuille equation for classical fluid dynamics flowing through a cylindrical pore,¹⁹ the water flux scales linearly with pore area at a given pressure. This means the water flow rate V_s could be written as

$$V_{s} = K \cdot S = Kk_{1}N_{a}N_{b} + Kk_{2}N_{a} + Kk_{3}N_{b} + Kk_{4}$$

= $K_{1}N_{a}N_{b} + K_{2}N_{a} + K_{3}N_{b} + K_{4}.$ (2)

When N_b is fixed, V_s should show a linear relation with N_a . However, a nonlinear relationship between V_s and N_a is observed in Fig. 3. We found when the nanopore is big enough $(N_a \ge 6 \text{ and } N_b \ge 8)$, the water flow rate V_s does increases linearly with the area of nanopore. By fitting the simulation data, V_s under the pressure of 500 MPa can be obtained,

$$V_s = K \cdot S = 0.4829 N_a N_b - 2.779 N_a - 2.126 N_b + 14.1886.$$
(3)



FIG. 2. Number of filtered water molecules as a function of simulation time for different two-dimensional nanopores.



FIG. 3. Water flux through the (N_a, N_b) nanopores. When the pore size is big enough $(N_a \ge 6 \text{ and } N_b \ge 8)$, water flux shows a linear dependence on the pore area. For comparison, when the pore size is small, nonlinear relationship between the pore area and water flux is observed.

We found that this linear equation is independent of the detailed parameters (size, shape, etc.) of the nanopore, implying it is a universal behavior for water transport through 2D membranes. However, when the nanopore is small ($N_a < 6$ or N_b < 8), the water flux V_s obtained from our simulations is different from that predicted by this universal equation (3).

In particular, Eq. (3) predicts that water flux would be zero for the nanopores with $N_b = 4$. However, nonzero water flux is observed for the $N_b = 4$ nanopores, see Fig. 3. The finite water flux is related to the water-membrane interactions (more discussion below).

B. Microstructure of water flow in the 2D nanopores

As previously reported, the microstructure of water flow in the vicinity of the nanopores plays a key role in determining water flux.^{10,11} Water flow structure is dramatically affected by the structure parameters of the nanopore such as its sizes and shapes. To further understand the abnormal water flux at the nanoscale, we have investigated the 2D density distribution map of oxygen atoms in water molecules, shown in Fig. 4, and the angular distribution function (ADF) of water molecules inside the nanopores, shown in Fig. 5.

Taking the quasi one-dimensional (1D) nano slits ($N_a = 2$; $N_b = 4$, 6, 8, 10, ...) as an example, the density map for oxygen atoms of water molecules in Fig. 4(a) shows a considerable ordered structure during water molecules passing across the nanopore membrane. For comparison, water flowing through a narrow carbon nanotube forms an ordered structure along the direction of water flow, instead of the normal direction to the water flow here.^{1,6} This difference implies that the behavior of water transport through atomically thin 2D membrane is different from that through finite-thickness nanotube membranes. The ordered structure along the normal direction to the water flow can be further observed via snapshots in Fig. 6. It is found that water molecules indeed form an ordered structure when passing through these pores.

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FIG. 4. (a) Oxygen density distribution and (b) the potential energy of a water molecule inside the slit-like nanopores with $N_a = 2$. (c) Projected oxygen density and potential energy of a water molecule inside the nano silt as a function of the distance between the water and the center of nanopore (d_{oc}) .

The same phenomenon can be extrapolated to other 2D membranes with small nanopores. For instance, four maxima in oxygen density distribution are observed inside the (3, 4) nanopore, as shown in Fig. 7. Non-uniform oxygen density distribution indicates that the structural pattern of water molecules in the nanoscale flow cannot be neglected, and the notion that a representative infinitesimal volumetric element successfully applied to describe continuum liquids is invalid for such cases. For these reasons, the applicability of uniform, structureless, continuum-based analysis for nanoscale water transport is questionable.²⁰ For these cases, the movement of individual water molecules must be considered because water flow has the microstructure features at the atomistic scale.

Different from water transport through small nanopores, a uniform density distribution of oxygen atoms is observed in the central region of the (6, 8) nanopore (Fig. 7(c)). This suggests the discrete water flow transits to a continuous flow for large pores.



FIG. 5. Distribution of the orientation of OH groups in water molecules during passing through the nanopores.

This effect is further demonstrated by the observation on the orientation distributions of water OH groups inside the nanopores (Fig. 5). The angular distribution shows two major peaks at $\theta = 120^{\circ}$ and 20° between the OH group in the water molecule in the vicinity of a nanopore and the normal axis z of the nanopore, for the (2, 4) and (2, 10) nanopores, implying water molecules adopt a non-flat (or quasi-vertical) orientation with respective to the nanopore plane during water filtering. For the (3, 4) nanopore, the two peaks are shifted to $\theta = 30^{\circ}$ and 90°, meaning both vertical and parallel orientations are observed in the angular distribution profile. This observation suggests water molecules can also adopt the flat configuration inside larger two-dimensional nanopore during passing. We attribute the parallel orientation to the hydrogen bonds between water molecules inside the nanopore. However, consistent with the oxygen density map, there is no obvious peak in water angular distributions for water passing through the central region of the (6, 8) nanopore, implying no special orientation is required in that case, and there exists a discrete-to-continuum transition for water transport through 2D nanopores when increasing the nanopore size.

C. Potential energy of water in the nanopores

For macroscale pores, the interaction between water and the edge of the pore can be neglected, thanks to the great distance between most of the water molecules and the pore edges. Water in the edge regions only makes a tiny fraction of total water molecules in the bulk. In a system where the size of the nanopore is comparable to the size of water molecule, however, the interactions between water molecules and the membrane play a key role for water transport. Discrete oxygen density distributions shown in Fig. 4(a) are related to the potential energy of a water molecule inside the nanopore, as shown in Fig. 4(b). Two major minima are observed in the water potential map for the $((2,N_b), N_b = 4-10)$ nanopores, suggesting two major spots for water molecule

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FIG. 6. Snapshots for water molecules passing through the nanopores of membrane. (a) Top views and (b) side views.

transport, which produce two major maxima in O-density map shown in Fig. 4(a). Obviously, the existence of van der Waals interactions between water molecules and the atoms in the membrane can partly recover the energy lost during water transport. That is the exact reason for the non-zero water flux obtained for $N_b = 4$, contrasting the zero water flux predicted by Eq. (3). Moreover, the water flux increases linearly with N_a for $N_b = 4$ and $N_b = 6$ as shown in Fig. 2. This linear relationship is the result of the linear dependence of the number of effective water pathways, namely the maxima in oxygen density maps, on N_a . Similar phenomena have been observed for water transport through graphyne membranes.¹¹



FIG. 7. (a) The oxygen density map and (b) the potential energy distribution of a water molecule inside the (3, 4) nanopore. (c) The oxygen density map and (d) the potential energy of a water molecule inside the (6, 8) nanopore.

Besides these two major spots, other subtle local maxima have been also observed in the oxygen density map. However, there is no one-to-one correspondence existing between these subtle local maxima and the local minima in the potential map. For clarity, we project the oxygen density distribution and the water potential energy to the center line of the nanopore going parallel to the one-dimensional nano silt, which is shown in Fig. 4(c). Two maxima in the probability profile are observed for the (2, 4) nanopore, while there is only one minimum in the potential energy for water inside the nanopore. This observation can be explained by the fact that the hydrogen bond strength between water molecules $(\sim 21 \text{ kJ/mol})$ is much greater than the potential energy differences at difference places of the nanopore (~6 kJ/mol), therefore the two passing water molecules favor the formation of a hydrogen bond in between. Similar discrepancies between the potential energy distribution of water inside the nanopore and the oxygen density distribution are also observed for the other nanopores ((2, N_h), $N_h = 4-10$). As a consequence, the microstructure of water flow in the nanopore is also strongly affected by hydrogen bonding besides the water-membrane interactions. This effect can also be found for the square-like nanopores, such as (3, 4) nanopore (Fig. 7(a)).

When the pore size is large enough (for example the (6, 8) nanopore), the van der waals interactions between water in the center of the nanopore and the membrane are found to be negligible as shown in Fig. 7(d). This is the reason why the uniform featureless distribution of water density is observed in the center region of the (6, 8) nanopore (Fig. 7(c)). Although water density analysis insides the pore shows discrete density distributions near the edge of the nanopore, the effective area of the edge region is small, at a small fraction (20%) of that for the central region. Moreover, this edge-to-area ratio would decrease rapidly as the pore size increases. This indicates that the discrete water flow transits to a continuum flow

Fhis article is copyrighted as indicated in the article. Reuse of AIP content is subject to the terms at: http://scitation.aip.org/termsconditions. Downloaded to IP 159.226.35.16 On: Fri. 14 Nov 2014 01:49:32 for large pores ($N_a \ge 6$ and $N_b \ge 8$). The size of the nanopore, ~ 15 Å in each side, corresponds to the critical length where the discrete-to-continuum flow transition takes place. The different behavior of water molecules transporting through small and big nanopores offers a physical explanation of the nonlinear dependence of water flux under pressure on the pore size, as presented in Fig. 3.

IV. CONCLUSION

The transport behavior of water molecules through the model two-dimensional nanopores in the atomically thin graphene membrane has been investigated by using molecular dynamics simulations. The results show that water flux depends linearly on the pore area when the pore size is big enough. However, for smaller nanopore, nonlinear relationship between water flow rate and the pore area is observed. This phenomenon cannot be explained by conventional theoretical models based on continuum water fluid, implying a transition from the continuous to discrete flow occurs for nanopore sizes around 15-17 Å. We attribute this phenomenon to the size effect of nanopores and the watermembrane interaction. When the size of nanopore is comparable to that of a water molecule, water flow rate is strongly affected by the microstructure of water flow passing through the pore, which is dependent on both the water-membrane interaction and the hydrogen bond structure between water molecules. The structured water flow patterns increase the rate of water flow and introduce additional water molecules to pass through inside the smallest nanopores, because of the potential drops induced by the nanopore edges. Therefore non-zero water flux and the nonlinear dependence on the pore area are observed for water filtering by small nanopores. While for macroscale pores, interactions between the water molecules and the membrane only account for a small fraction of the total water flow at the edge region, which can be

neglected. Consequently, water flow is disordered and featureless when passing through the large pores, as shown in our simulations.

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