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Molecular Simulation on Transport Properties of Confined Water

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Abstract: The diffusivity and viscosity of water confined in micropores were studied by molecular dynamics simulations. The effects of pore width and density were analyzed at pore widths from 0.9 to 2.6 nm. The diffusivity in micropores is lower than that of the bulk, and it decreases as pore width decreases and as density increases. But the viscosity in micropores is much larger than that of the bulk, and it increases as pore width decreases and as density increases. The diffusivity in channel parallel direction is obviously larger than that in channel perpendicular directions.

Keywords: Micropore, transport property, molecular dynamics simulation.

Quantitative prediction of diffusivity and viscosity in porous media is very important in guiding experiments and improving engineering designs in diversified applications [1]. But it is quite difficult to obtain the experimental data under the normal conditions. Computer simulations are able to simulate the real systems under real conditions and give satisfying results, especially by molecular dynamics (MD). Dynamics of nano-confined water in particular have received considerable attention, due in no small part to the importance of confined water in the structure and function of biomolecules [2]. Bitsanis *et al.* [3~4] studied the flow of fluids confined in slit pore and found that the diffusivity decreases as the pore width decreases and viscosity increases at vary small pore width. But they only concentrated on one state point that has only one temperature and density in slit pores. The transport properties of fluids in channel-type micropores are still not clear. In this work, a channel pore model was employed to replace the slit pore model, and the effects of pore size and density on diffusivity and viscosity of water were studied. The SPC model [5] of water was employed in the MD simulation. Firstly, the diffusivity and viscosity of bulk water was simulated at 298K by *NVT* ensemble. As a result, diffusivity $D = 3.1\times10^{-9}\ \mathrm{m^2 \cdot s^{-1}}$, it agrees with Jorgensen's simulation data [6], $(3.85\pm0.09)\times10^{-9}\ \mathrm{m^2 \cdot s^{-1}}$. And viscosity $\eta = 1.0$ cp, which agrees with the experimental data [7], 0.8904 cp. Bitsanis' [4] slit pore model was improved in this work, the periodic boundary conditions were only applied in the *x*-direction. The channel pore model used in this work is illustrated in **Figure 1**. The Beeman algorithm [8] for integration of the equations of motion was employed in the MD steps. The cut-off distance of potential

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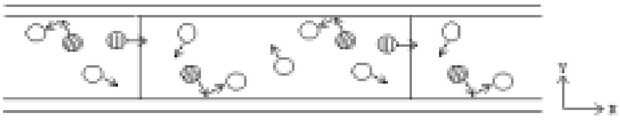
function was taken to be 0.9 nm. The time step was set to be 1 fs. Runs of 6×10^5 time steps (0.6 ns) were performed to relax and equilibrate the systems. Then runs of 1.2×10^6 time steps (1.2 ns) were used to analyze the statistical properties.

Figure 1 A schematic drawing of the channel pore model



The diffusivity (D) and its components in x-, y-, z-direction were calculated by using the Einstein relation [9].

$$\lim_{t\to\infty}\left\langle \left| r(t+\Delta t)-r(t)\right|^2 \right\rangle = 6D\Delta t$$

Figure 2 shows the diffusivity in micropores is lower than that of the bulk and it decreases as the pore width decreases at 298 K and density of 1.10 g · cm^{-3}. Roughly, it is hindered diffusion, which can be explained in part by the fact that the constrained space of a pore causes the collision frequency to exceed its value for bulk water. **Figure 3** shows diffusivity decreases as density increases. Usually, we can observe that the diffusivity is isotropic in bulk fluids, but it is anisotropic in channel-type micropores. The diffusivity in channel parallel (x-) direction (D_x) is obviously larger than that in channel perpendicular (y- and z-) direction (D_y , D_z) and the overall diffusivity in micropores. The mean square displacement (MSD) becomes smaller in micropores, which leads to the decreasing of the diffusivity. **Figures 4-6** show that the MSD and its components within the same time interval (*e.g.* 1000-1200 ps) vary with the time in bulk and in micropores at 298 K and density of 1.10 g · cm^{-3}. The MSD is nearly equipotent and isotropic in bulk water, as shown in **Figure 4.** But it is anisotropic in micropores. Owing to the confinement of channel walls, the motion of molecules is depressed. As to the micropores with small pore width, *e.g.*, 0.9 nm, it is too difficult for a molecule to move in y- and z-direction in such a small space. Therefore, the MSD in y- and z-direction is changed as the time very gentle, as shown in **Figure 5**. But as pore width is increased, the difference between parallel and perpendicular direction tends to be reduced, as shown in **Figure 6**. Obviously, MSD_x is larger than overall MSD, MSD_y and MSD_z within the same time interval, so D_x is markedly larger than overall diffusivity, D_y and D_z . It can be concluded that the diffusivity in channel parallel direction controls the overall diffusivity in channel-type micropores.

The viscosity was calculated by using Green-Kubo equation [10, 11],

$$\eta = \frac{1}{k_B T V}\int_0^\infty \left\langle J_v(0) J_v(t) \right\rangle dt$$

where k_B is the Boltzmann constant, and J_v is the momentum flux. **Figure 7** shows that the viscosity of water varies with pore width at 298 K and at two different densities. The viscosity in micropores is much larger than that of the bulk water, and it increases as the pore width decreases and as density increases. In particular, the viscosity dramatically increases in very narrow micropores. This phenomenon is essentially an excluded volume effect on the glide of molecular layers required in a shearing flow. Although the viscosity increases sharply with pore width decreasing, the diffusivity, by contrast, decreases slowly, as shown in **Figure 2**. It is originated that the diffusive motion depends only on fluidity to individual molecular movement, not glide of an entire layer. This demonstrates the nature of flow in micropores is quite different from the bulk fluids, and two aspects of transport property, diffusivity and viscosity, behave profoundly different. It can be concluded that the transport properties of water confined in micropores are greatly affected by the pore width and it behaves some particularities in micropores.

Figure 2 The diffusivity as a function of pore width at 298 K, 1.10 g · cm^{-3}

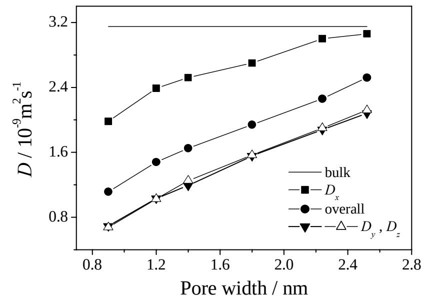


Figure 3 The diffusivity as a function of pore width at 298 K and at different densities

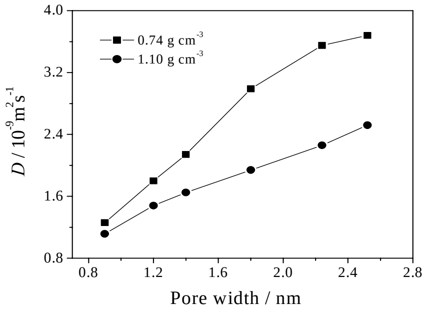


Figure 4 MSD *vs*. time for bulk water at 298 K and at 1.10 g · cm^{-3}

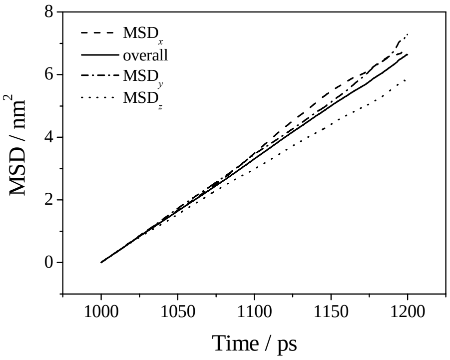


Figure 5 MSD *vs*. time in micropore with pore width of 0.9 nm at 298 K, 1.10 g · cm^{-3}

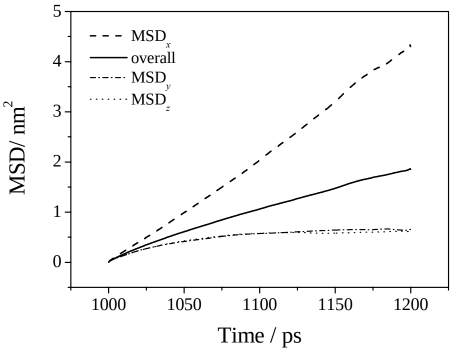


Figure 6 MSD *vs*. time in micropore with pore width of 1.4 nm at 298 K, 1.10g ·cm^{-3}

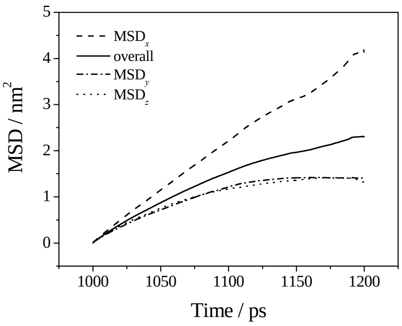
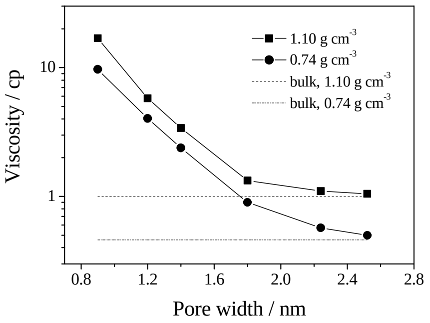


Figure 7 The viscosity as a function of pore width at 298 K and at different densities



In conclusion, the diffusivity in micropores is lower than that of the bulk, and it decreases as the pore width decreases and the density increases. But the viscosity in micropores is much larger than that of the bulk, and it increases as the pore width decreases and the density increases. In particular, the viscosity sharply increases in very narrow micropores. The diffusivity in channel parallel direction is obviously larger than that in channel perpendicular directions.

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