Transport Properties of Fluids in Micropores by Molecular Dynamics Simulation

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The transport properties of fluid argon in micropores, *i.e.* diffusivity and viscosity, were studied by molecular dynamics simulations. The effects of pore width, temperature and density on diffusivity and viscosity were analyzed in micropores with pore widths from 0.8 to 4.0 nm. The results show that the diffusivity in micropores is much lower than the bulk diffusivity, and it decreases as the pore width decreases; but the viscosity in micropores is significantly larger than the bulk one, and it increases sharply in narrow micropores. The diffusivity in channel parallel direction is obviously larger than that in channel perpendicular direction. The temperature and density are important factors that obviously affect diffusivity and viscosity in micropores.

Keywords   micropore, transport property, molecular dynamics simulation

Introduction

In the last two decades molecular dynamics (MD) simulations have been employed successfully for the study of transport properties of fluids, *i.e.* diffusion coefficients and viscosities. Quantitative predictions of diffusivity and viscosity are of great importance in guiding experiments and improving engineering designs, such as molecular sieve operations, catalytic processing of heavy liquid petroleum fractions, gel permeation chromatography and membrane separation technologies.[1] But it is quite difficult to obtain the experimental data under the normal conditions because of the complexity of the systems and the extreme conditions. Computer simulations are able to simulate the real systems and real conditions and give reasonable results, especially by MD simulation. The behavior of fluids confined in micropores can change radically upon confinement in regions with dimensions in the order of a few molecular diameters.[2,3] An important phenomenon of a fluid confined in porous media is the hindered diffusion.[4,5] Bitsanis and co-workers[6,7] studied the flow of fluids confined in molecularly narrow pores by MD simulation. They found that the self-diffusion coefficient decreases as the pore width decreases and the viscosity increases at very small pore width. But they only concentrated on one state point that has one specified temperature and density. Diestler *et al.*[8] and Somers and Davis[9] simulated the self-diffusion of Lennard-Jones fluids constrained between two plane-parallel hard walls and the microscopic dynamics of fluids confined between smooth and structured walls, respectively. Zhou *et al.*[3] simulated the adsorption and diffusion behavior of supercritical CO_2 in slit pores. But most of these re-ported works were concerned with slit pores, and only a few simulation data of several states for fluid argon were reported in the literature. The transport properties in channel pores are still not clear. The main purpose of this work is focused on the investigation of diffusivity and viscosity properties in micropores. In this work, a channel pore model was employed to replace the slit pore model that is frequently used in simulations for micropores. The effects of micropore size, temperature and density on diffusivity and viscosity were investigated for the pore widths from one or two molecular diameters up to 4.0 nm.

Simulation

Molecular dynamics simulations were performed in the NVT ensemble. The weak coupling method was used to regulate the temperature[10] with a relaxation time of 0.1 ps. The orientation was initialized from random orientation, and the initial *x*-, *y*-, *z*-velocity components were randomly chosen from the Maxwell distribution. The velocity was then corrected afresh to keep the total momentum at zero. The time step was set to be 1 fs. The cut-off distance of the potential function was taken to be 0.8 nm. The equilibration was judged primarily by whether the temperature fluctuation was maintained within 0.2%. Generally, 0.5×10^6 time steps (0.5 ns) were enough for the full development of the equilibrium system. Therefore, runs of 0.6×10^6 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 statistical properties. Configurations were stored every 0.1 ps for analysis. The density was kept to be a constant during the entire simulations. In this work,

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the molecular interaction potentials were calculated with the Optimized Potentials for Liquid Simulations-All Atom (OPLS-AA) force field developed by Jorgensen *et al.*[11] The expression is

$$u(r)=4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12}-\left(\frac{\sigma}{r}\right)^{6}\right] \qquad r< R_{c}$$

$$u(r)=0 \qquad r\geqslant R_{c}$$

where r is the intermolecular distance, R_c is the cut-off distance of the potential function. Two parameters are of the values of $\sigma=3.405$ Å, and $\varepsilon/k_B=119.8$ K, where k_B is the Boltzmann constant.

In order to verify the simulation programs used in this work, the self-diffusion coefficients and viscosity of argon in bulk system were firstly simulated before working on the properties in micropores. The OPLS-AA force field and the periodic boundary conditions were used in the simulations. As the result, the self-diffusion coefficients and viscosity were calculated and compared with experimental data,[12] which is presented in Table 1. The simulated results are in good agreement with the experimental data.

Table 1 Experimental and simulated results at different states

T/K	ρ/(g $\cdot$ cm^{-3})	$D/(10^{-9}$ m$^2 \cdot$ s^{-1})		η/cp	
		Exptl.	Simul.	Exptl.	Simul.
90	1.374	2.43	2.20	0.232	0.25
100	1.309	3.54	3.48	0.170	0.20
110	1.238	4.80	5.00	0.140	0.18
120	1.160	6.06	5.85	0.114	0.16

Bitsanis' slit pore model,[7] which has two flat, semi-infinite, structureless pore-walls separated by a distance h in the z-direction, *i.e.*, the periodic boundary conditions were applied in x- and y-direction, but not in z-direction, was improved. In this work, the periodic boundary conditions were only applied in the x-direction. A schematic drawing of two types of pore model is illustrated in Figure 1. The major difference between the two models is in the y-direction, but both models have two structureless pore-walls separated by a distance h in the z-direction. The Beeman algorithm[13] for integration of the equations of motion was employed in the MD simulation. The particle-wall collisions were dealt with as follows: the equations of motion are solved, as if the walls were not there, resulting in the prediction of a new set of x, y and z coordinates for each particle. If this coordinate lies outside the constraining walls of y- (or z-) direction for a certain particle, this particle is kept at its current position and velocity, but its y- (or z-) displacement and velocity during the current time interval change signs. This is equivalent to the assumption

that the above particle had undergone an elastic impulsive collision with a wall located in the mean y- (or z-) distance between its old and new rejected position.
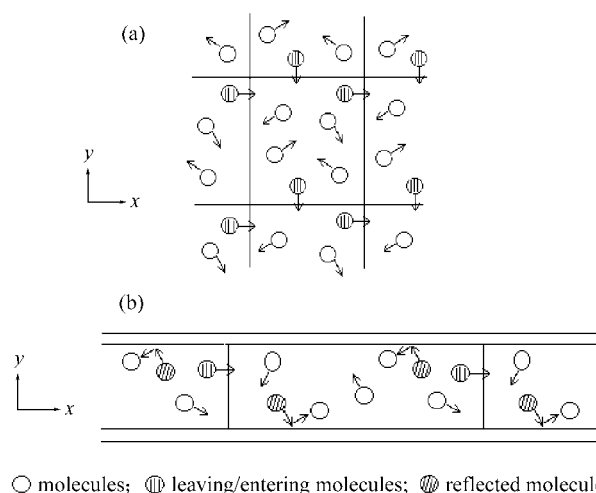

○ molecules; ⦶ leaving/entering molecules; ⦸ reflected molecules

Figure 1 A schematic drawing of two types of pore model. Both models have two structureless pore-walls separated by a distance h in the z-direction. (a) slit pore; (b) channel pore.

Results and discussion

Diffusivity

The diffusivity (D) was calculated from the mean square displacement (MSD) of molecule by using the Einstein relation.[14]

$$\lim_{t\to\infty}\left\langle\left|r(t'+t)-r(t')\right|^{2}\right\rangle=6Dt$$

Where $r(t)$ is the position of molecule at time t, D is the self-diffusion coefficient, and the brackets denote averaging over all molecules and time origins t. The corresponding diffusion coefficients can be related to the limit of the long time derivating of MSD. The time step was set to be 1 fs and the D-values were calculated in a period of 1.2×10^{6} time steps (1.2 ns) after equilibration. The MSD were averaged in every 0.2×10^{6} time steps (0.2 ns) for 101 different time origins in an increment of 0.01×10^{6} time steps equally, and then the diffusivity was averaged again from 101 values in the period of 1.2×10^{6} steps.[15] Furthermore, the diffusivity components in x-, y-, and z-direction can be calculated by

$$\lim_{t\to\infty}\left\langle\left|r_{i}(t'+t)-r_{i}(t')\right|^{2}\right\rangle=2D_{i}t \qquad (i=x, y, z)$$

which is decomposed from the Einstein relation above. Here D_i are the diffusivity components in x-, y-, and z-direction, $r_i(t)$ is the position of molecule at time t.

The diffusivity as a function of pore width at 120 K and $\rho=1.160$ g $\cdot$ cm^{-3} is shown in Figure 2. The diffusivity in micropores is much lower than the bulk diffusivity and it decreases with the pore width decreasing. Roughly, it is a hindered diffusion, which can be ex-
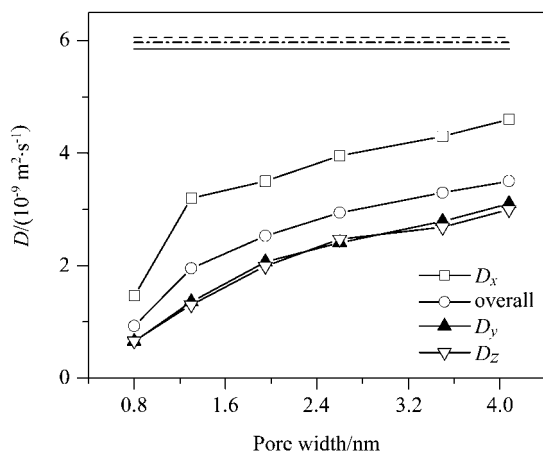
Figure 2   Diffusivity as a function of pore width at $T=120$ K and $\rho=1.160$ g · cm^{-3}. ------, from Ref. 12; -----, from Ref. 7; ——— simulated results.

plained in part by the fact that the constrained space of a pore causes the collision frequency to exceed the value in bulk fluid. Here we can see that the diffusion 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 space of motion of molecules in micropores might be the major nature to discourage molecule from diffusing. The MSD gets smaller in micropores, leading to the decrease of the diffusivity. Figure 3 and Figure 4 show that the MSD and its components in x-, y-, and z-direction within the same time interval (*i.e.* 1000—1200 ps) vary with the time in bulk and in micropores with different pore
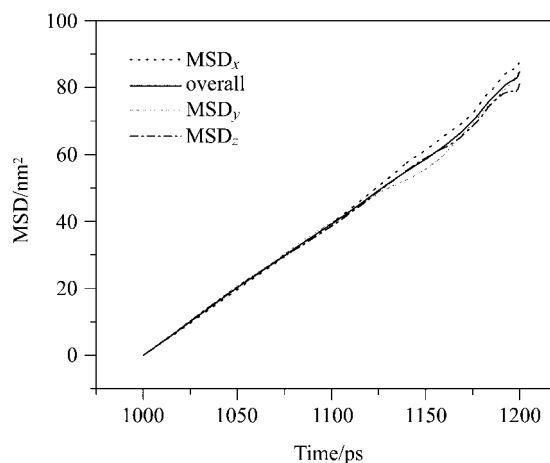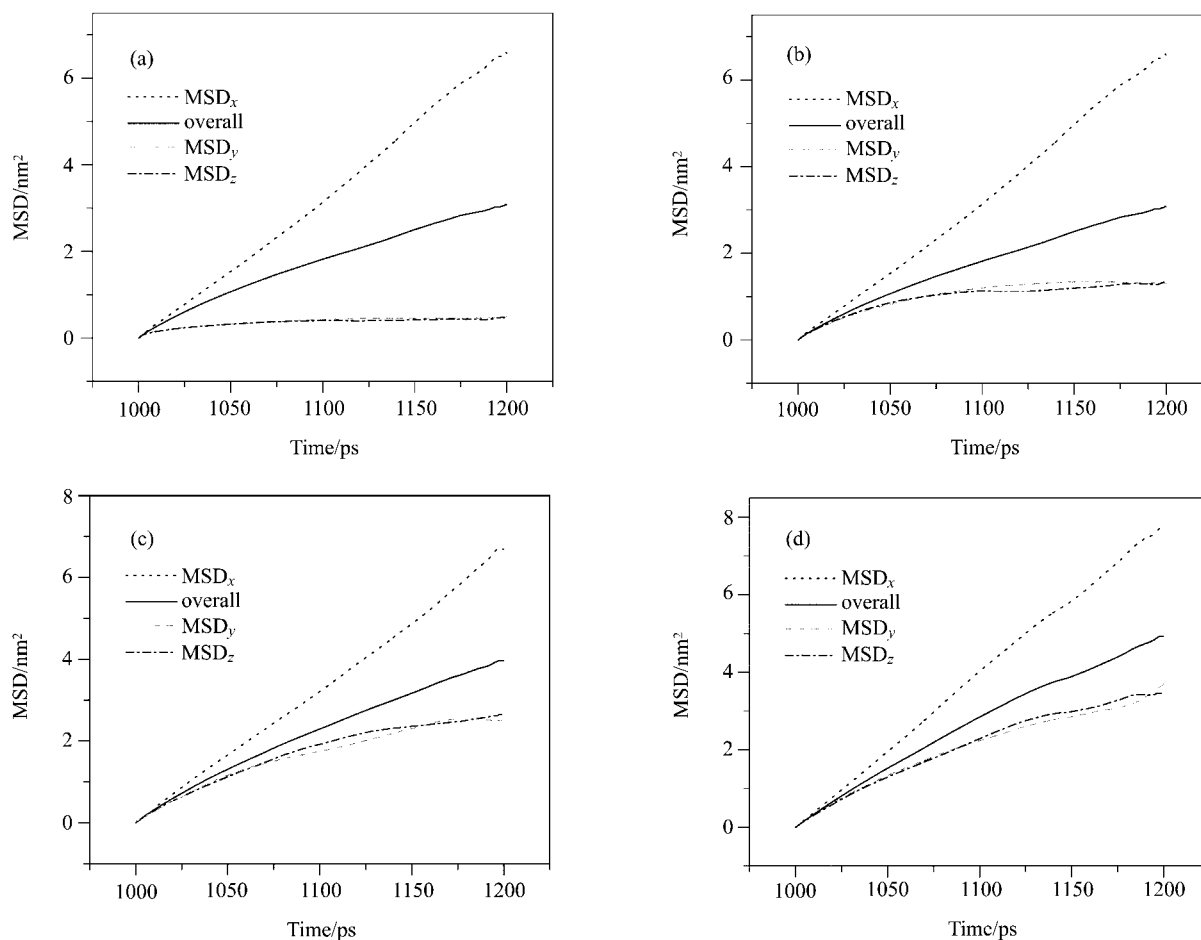

Figure 3   MSD vs. time for bulk fluid argon.

Figure 4   MSD vs. time for fluid argon in channel pore at different pore widths. (a) 0.8 nm; (b) 1.3 nm; (c) 1.9 nm; (d) 2.6 nm.

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widths at 120 K and $\rho = 1.160$ g·cm^{-3}. The MSD is nearly equipotent and isotropic in bulk fluids (see Figure 3). But in channel-type micropores, the MSD in channel parallel direction (MSD_x) is obviously larger than that of the overall and that in channel perpendicular direction (MSD_y, MSD_z), and as the pore width decreases, the difference tends to be enhanced. Owing to the confinement of channel walls, the motion of molecules is depressed. As to the micropores with small pore width, *e.g.*, 0.8 nm and 1.3 nm, only 2 or 3 layers of molecules, it is too difficult for a molecule to move in *y*- and *z*-direction in such a small space. Therefore, the MSD changes in *y*- and/or *z*-direction with time are very small, as shown in Figure 4(a) and (b). But as pore width increases, the space in *y*- and *z*-direction increases, and the slope of MSD *vs.* the time increases gradually. The difference between parallel and perpendicular direction tends to be reduced, as shown in Figure 4(c) and (d). Obviously, MSD_x is larger than the overall MSD, MSD_y and MSD_z within the same time interval, so D_x is markedly larger than the overall diffusivity, D_y and D_z, which is similar to the result of Wolf *et al.*[16] on two-dimensional diffusion. It can be concluded that the diffusivity in channel parallel direction (D_x) controls the overall diffusivity in channel-type micropores.

The dependences of the diffusivity in channel pores on temperature and density are plotted in Figure 5 and Figure 6, respectively. As expected, the overall averaged diffusivity was enhanced with the temperature increasing but weakened with the density increasing. From these figures, it can be observed that the diffusivity as a function of pore width changes more obviously at higher temperature and in lower density.
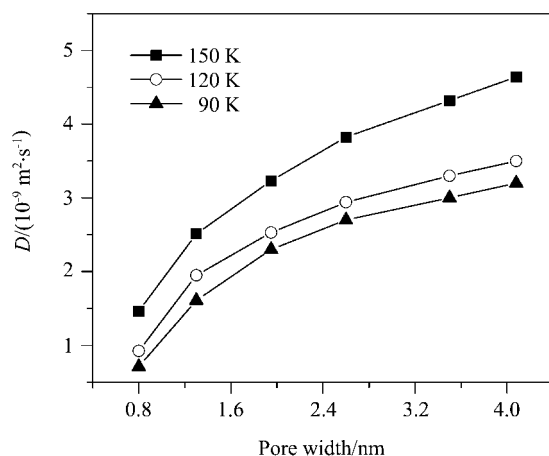
Figure 5 Diffusivity as a function of pore width at different temperatures.

Viscosity

The viscosity is calculated by the Green-Kubo equation[17,18]

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

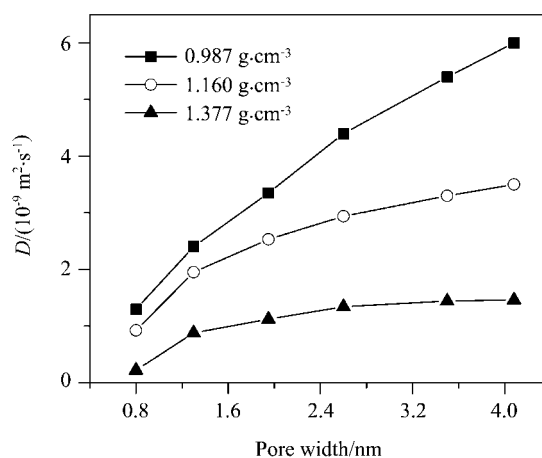where k_B is the Boltzmann constant, and J_v is the momentum flux.

Figure 6 Diffusivity as a function of pore width at different densities.

Figures 7 and 8 show that viscosity varies with pore width at different temperatures and with different densities. The viscosity in micropores is significantly larger than the bulk one, and it increases as pore width decreases and as density increases, but it changes with temperatures not as obviously as with density. Particularly, the viscosity dramatically increases at very narrow pores. This phenomenon essentially results from an excluded volume effect on the glide of molecular layers required in a shearing flow. Although the viscosity increases sharply with decreasing pore width, the self-diffusion coefficient, by contrast, decreases slowly (Figure 2). Diffusive motion depends only on fluidity to individual molecular movement, not on the glide of an entire layer. In this case the same result was gotten as that of Bitsanis *et al.*,[6] but only one temperature and one density were examined in their work. This phenomenon demonstrates that the nature of flow in micropores is quite different from in the bulk fluids, and two aspects of transport property (diffusivity and viscosity) also
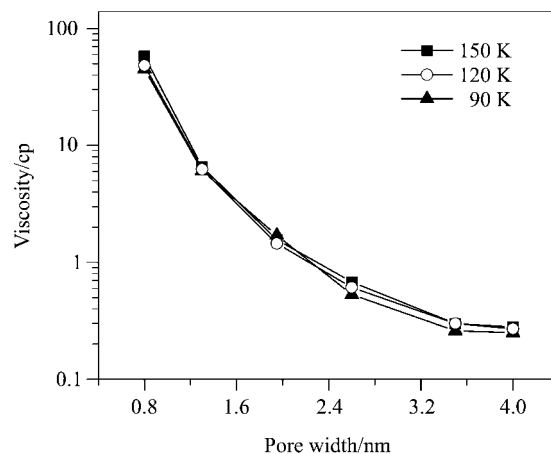
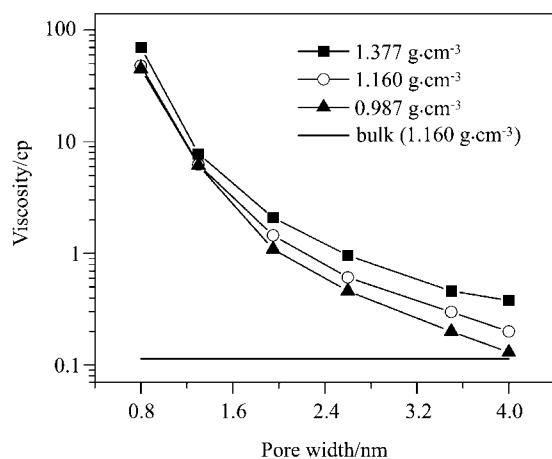**Figure 7** Viscosity as a function of pore width at different temperatures and at 1.160 g·cm^{-3}.

Figure 8   Viscosity as a function of pore width at different densities and at 120 K. ——, for bulk fluid argon at 1.160 g · cm^{-3}, from Ref. 7.

behave profoundly differently. It can be concluded that transport properties of simple fluid are greatly affected by pore width.

Conclusions

A channel pore model was employed to replace the slit-pore one for MD simulations of micropores. The transport properties of fluid argon in micropores were studied. The diffusivity in micropores is much lower than the bulk one, and it decreases as pore width decreases. The diffusion is anisotropic in channel-type micropores, rather than isotropic in the bulk. The diffusivity in channel parallel direction is obviously larger than that in channel perpendicular direction, and larger than the overall diffusivity in micropores. The viscosity in micropores is significantly larger than the bulk one, and it increases as pore width decreases and as density increases. In particular, the viscosity dramatically increases in the small size micropores. It can be concluded that the transport properties of simple fluid are greatly affected by the pore width and it behaves particularly in micropores.

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