DYNAMICS OF SIMPLE FLUIDS CONFINED IN CYLINDRICAL PORE: EFFECT OF PORE SIZE

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We study the thermodynamic and dynamical properties of Weeks–Chandler–Anderson (WCA) fluids confined in a cylindrical pore by means of a canonical molecular dynamics simulation method. The pore model is an infinitely long cylinder consisted of a thermal wall and mimics a typical carbon nanotube. The thermodynamic properties are obtained for relatively high density fluids over a wide range of pore diameters at a given temperature. The size dependence of the self-diffusion coefficients in the cylindrical pore is also investigated. It is found that, as the pore diameter decreases, the potential energy and axial component of the pressure exhibit a sharp rise and the self-diffusion coefficient decreases. The observed behaviors can be understood in terms of the geometrical confinement and attenuation of transport induced by dispersive fluid-wall interaction. In addition, anomalous diffusion is observed at the pore size corresponding to twice the particle diameter.

Keywords: Molecular dynamics; cylindrical pore; thermal wall.

1. Introduction

Studies on the thermodynamic and the transport properties of fluids confined in a microscopic size of pores has been an interesting subject in recent years. Theoretical and experimental researches on this subject have potential applications including gas separations, lubrication, adhesion and heterogeneous catalysis in porous media.\(^1\)

It is well known that the confined fluids have quite different structural and dynamical characteristics compared to the homogeneous bulk fluids whose transport is isotropic in all directions.\(^2\)–\(^19\)

Most numerical simulation studies on this subject have been carried out to investigate the behavior of fluids in single pores with idealized geometry such as slit-like pores\(^2\)–\(^10,20\) or cylindrical pores\(^11\)–\(^15,22\)–\(^24\). These pore models are considered as the most commonly used ones to study the transport properties of fluids through very narrow pores. In addition, the cylindrical pore model can mimic the carbon nanotubes\(^15,24\)–\(^26\) and the theoretical studies on such model system may provide
useful information on the mechanism of spreading, melting, lubrication, and friction of microporous media.\textsuperscript{21,22,26–30} In addition, the fluids confined in cylindrical pores can imitate blood in vessels or ions in biological channels.\textsuperscript{31–33} The selective ion transport phenomenon in channels through biological membranes has been a long-standing interest in the research field of specific ion channels.\textsuperscript{32,33} One possible way to study these complicated biological systems is to employ the molecular dynamics (MD) technique, which is a powerful tool for understanding the structure and dynamics of the confined fluids at the atomistic level and offers information that is difficult to obtain by experiments.

In order to perform a numerical simulation of fluids confined in pores, the description of pore walls or surfaces in contact with fluids has to be realistic. The wall models can be classified into either structured wall\textsuperscript{8,10,15,24} or structureless wall,\textsuperscript{3–7,16,21,34} depending on its lattice structure. The structured wall takes into account of the wall-wall interaction and the fluid-wall interaction at atomistic level. This type of wall model fixes the temperature of the wall by using Gauss’ principle of least constraint.\textsuperscript{35} On the other hand, the structureless wall has no wall-wall interaction and controls the temperature in a stochastic manner. Hence, the structureless wall is easier to be implemented in MD simulation code, so can be more efficient in reducing computing time in comparison with the structured wall.

In this paper, our principal focus is to examine equilibrium thermodynamic properties of the simple, one component fluids confined in a cylindrical pore. The wall model employed in this study is a structureless thermal wall.\textsuperscript{3,4,20,34} This type of wall controls temperature through a stochastic boundary condition.\textsuperscript{36} When a particle passes across a thermal wall, it is reentered inside of the cylinder by applying the thermalization mechanism designed by Tennenbaum \textit{et al.}\textsuperscript{34} We have conducted a series of constant temperature equilibrium molecular dynamics (TEMD) simulations with this wall model, and calculated characteristic thermodynamic properties for various pore diameters. For the TEMD simulations, no external acceleration needs to be applied on the particles, and a collective transport coefficient can be obtained either from axial velocity autocorrelation via the Green–Kubo relation or from mean square displacement via the Einstein–Enskog relation.\textsuperscript{11,37} First, we present and discuss characteristic features of several thermodynamic and dynamical properties of fluids confined in a cylindrical pore with varying the pore width until it is reduced to twice as large as the diameter of the particles. Second, we investigate the effect of the pore width on the self-diffusion coefficients.

The present article is organized as follows. The next section describes the cylindrical pore model and the MD method in brief. In Sec. 3, the results of MD simulations and discussions are presented. Concluding remarks follow in the last section.

2. Model and Simulation Details
We consider a system of $N$ spherical particles confined in a cylindrical pore whose radius is $R$ and longitudinal length is $h$. Inner surface of the cylinder is designed
as a perfectly smooth surface, so the volume inside of the cylinder is \( V = \pi R^2 h \).

We assume that the pore wall is infinitely heavy and the periodic boundary condition (PBC) is applied along the z direction to represent the longitudinal direction of pore of infinite extent while the x and y directions are bounded by the thermal wall.

We consider a system of fluid particles interacting via Weeks–Chandler–Anderson (WCA) potential

\[
u(r) = 4\epsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^{6} \right] + \epsilon, \quad r < 2^{1/6} \sigma, \tag{1}\]

where \( \sigma \) and \( \epsilon \) represent the characteristic length and energy scales of the fluid, respectively, and \( r \) denotes the distance between two spheres. The trajectories of particles confined in a cylindrical pore are described by following equation of motion,

\[
f_i = m\ddot{r}_i = -\sum_{j \neq i} \nabla_i u(r_{ij}) + f_w(r_i), \tag{2}\]

where \( m \) is the mass of particle, \( f_i \) is the force acting on the \( i \)th particle due to the other particles, and \( f_w(r_i) \) represents stochastic force due to the interaction \( i \)th particle and the thermal wall, which is given by an impulsive momentum to be discussed below. The equations of motion have been integrated using the Störmer–Verlet algorithm which computes the position and velocity of a particle with time step, \( \Delta t \) as follows:

\[
r_i(t + \Delta t) = 2r_i(t) - r_i(t - \Delta t) + \frac{\ddot{r}_i(t)}{m} \Delta t^2 \tag{3}\]

\[
v_i(t) = \frac{r_i(t + \Delta t) - r_i(t - \Delta t)}{2\Delta t}. \tag{4}\]

In the above equations, \( r_i \) and \( v_i \) are the position and velocity of \( i \)th particle, respectively.

If a particle located at the position \( A \) (see Fig. 1) passes across the thermal wall and moves to the position \( B \), it will re-enter inside of the cylinder with stochastic impulsive momentum determined by temperature of the wall. Once the center of mass position of the particle is located within \( 0.5\sigma \) from the wall (see Fig. 1), we assume that the particle was in collision with the thermal wall. Parallel component, \( v_{||} \) of the velocity of the particle along the wall is chosen by random sampling from the Gaussian distribution of Eq. (5), and its normal components, \( v_\bot \) are sampled from the distribution of Eq. (6).

\[
\phi(v_{||}) = \sqrt{\frac{m}{2\pi k_B T_w}} \exp\left[-\frac{m v_{||}^2}{2k_B T_w}\right], \tag{5}\]

\[
\phi(v_\bot) = \frac{m}{k_B T_w}|v_\bot| \exp\left[-\frac{m v_\bot^2}{2k_B T_w}\right], \tag{6}\]

where \( T_w \) is a specified wall temperature.
Following the Tenenbaum’s reentry mechanism, the particle in position $A$ at time $t$ moves to position $C$ after $\Delta t$. If the position $C$ is still outside of the cylinder as shown in Fig. 1, it moves along the direction perpendicular to the wall surface until it is allowed inside of the cylinder (position $C'$). In this case, the position at time $t$, which was originally at $A$, is modified to $B'$ before computation of the position of the particle at time $t + 2\Delta t$.

The MD simulation starts with a random initial configuration of particles inside of the pore, with initial velocity distribution following the Maxwell distribution. The system is then allowed to evolve into its equilibrium configuration, which takes about $100,000 \sim 500,000$ time steps. Then $2,000,000$ subsequent time steps were used to evaluate the equilibrium averages with $\Delta t^* = 0.001$. In our numerical calculations, all physical quantities are given with dimensionless units by setting the $\epsilon$, $\sigma$, and $m$ to unity. The number of particles and pore diameters $d^*$, with which MD simulations have been performed are listed in Table 1.

We have calculated the structural and thermodynamic properties such as density profile inside of the pore, internal potential energy, axial component of the pressure and self-diffusion coefficients at a given temperature for various pore diameters. The internal potential energy was computed using the pair-wise interaction potential function given in Eq. (1). We also evaluated the axial component

<table>
<thead>
<tr>
<th>$\rho^*$</th>
<th>0.5</th>
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<tr>
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</tr>
<tr>
<td></td>
<td>7.0014</td>
<td>7.0014</td>
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<tr>
<td></td>
<td>9.9987</td>
<td>9.9975</td>
</tr>
<tr>
<td></td>
<td>14.9994</td>
<td>14.9980</td>
</tr>
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</table>

Table 1. Number of particle and pore diameters where the simulations were performed with fixed longitudinal length $h^* = 20$. $N$ and $d^*$ were chosen so that the number densities can be fixed either $\rho^* = 0.5$ or $\rho^* = 0.6$. 
of self-diffusion coefficient $D_z$ as a function of pore diameter. The diffusion coefficient $D_z$ was evaluated both from the velocity autocorrelation function using the Green–Kubo relation shown in Eq. (7), and from the mean square displacement using Einstein–Enskog relation shown in Eq. (8).

$$D_z = \int_0^\infty dt \langle v_{iz}(t) \cdot v_{iz}(0) \rangle$$

$$D_z = \frac{1}{2t} \langle [r_{iz}(t) - r_{iz}(0)]^2 \rangle$$

3. Results and Discussion

We calculated equilibrium density profiles at number densities $\rho^* = 0.5$ and $\rho^* = 0.6$ for the pore diameter $d^* = 4σ$ (see Fig. 2). In addition, density profiles for several pore diameters at number density $\rho^* = 0.6$ are shown in Fig. 3. In these figures, the

![Fig. 2](image1)

Fig. 2. Radial density profiles for the pore diameter $d^* = 4$ at densities $\rho^* = 0.5$ (solid line), and $\rho^* = 0.6$ (dotted line).

![Fig. 3](image2)

Fig. 3. Radial density profiles for the pore diameters $d^* = 2$ (solid line), $d^* = 3$ (dotted line), and $d^* = 4$ (dashed line) at density $\rho^* = 0.6$. 
radial position \( r = 0 \) denotes the center of a cylindrical pore. Since no particle is allowed to be located within 0.5\( \sigma \) from the wall, the location of the wall surface is at \( r = 1\sigma \) for \( d = 2\sigma \), \( r = 1.5\sigma \) for \( d = 3\sigma \), and \( r = 2\sigma \) for \( d = 4\sigma \), etc. As shown in Fig. 2, the density profiles form layered structures having a maximum located at 0.5\( \sigma \) from the wall. This layering tendency becomes more pronounced at higher density. In Fig. 3, the local density at the wall rises sharply as the pore diameter becomes smaller. Such density profiles are characteristic feature of fluid systems having impulsive fluid-wall interaction.\(^5\),\(^7\),\(^10\),\(^13\)

Next, the thermodynamic properties of fluids in the cylindrical pore system were calculated as a function of the pore diameter. Since the thermal wall acting as a thermostated reservoir maintains temperature constant during the simulation, temperature of the fluids is fixed constant at any instantaneous time. Therefore, we can consider this system as a canonical ensemble. The kinetic energy of the fluid system is fixed constant regardless of pore sizes, so change of the internal energy wholly depends on the internal potential energy. In Fig. 4, the sharp increase of the potential energy is observed as the pore size becomes smaller. Similar behavior is also observed in axial component of the pressure as shown in Fig. 5. Such trends are due to the fact that average collision frequency increases as the pore diameter decreases (see Fig. 6). It is confirmed that in the limit of large pore size, \( P_{zz} \) and the potential energy of the fluids approach to the values of the bulk fluids.

The dependence of self-diffusion coefficients on the pore size was examined at two different number densities. We first confirmed that diffusion in a cylindrical pore obeys Fick’s law for the pore size ranging from 3\( \sigma \) to 15\( \sigma \) as shown in Fig. 7. Next we computed the self-diffusion coefficients \( D_z \), both from Green–Kubo relation of Eq. (7) as well as Einstein–Enskog relation of Eq. (8), and confirmed that these two results are essentially identical. \( D_z \) as a function of the pore diameter is shown in Fig. 8 for two different values of number density. The behavior of \( D_z \) shows...
Fig. 5. Axial pressures $P_{zz}$ as a function of pore diameter for two different densities. $P_{zz}$ for bulk system are 1.28 at $\rho^* = 0.5$ and 2.08 at $\rho^* = 0.6$.

Fig. 6. Average particle-particle collision frequencies per particle and per unit time as a function of pore diameter for two different densities.

Fig. 7. Mean square displacements at $\rho^* = 6$ for four different diameters.
Fig. 8. Self diffusion coefficients $D_z$ as a function of pore diameter for two different densities. $D_z$ for bulk system are 0.210 at $\rho^* = 0.5$ and 0.145 at $\rho^* = 0.6$.

a tendency to decrease with decreasing the pore diameters from $15\sigma$ to $3\sigma$, indicating that dispersive fluid-wall interactions considerably attenuate transport. Analogous behavior has been reported in the theoretical and simulation work of Jepps, Bhatia and Searles, where they have used LJ fluids in low density regime.

The variation of potential energy, axial pressure, and self-diffusion coefficient on the pore diameter is due to the geometrical hindrance effect, which becomes more pronounced as the pore size becomes small. Such dependence seems to be related partly with reduction of the free volume available for motion of each particle as the pore size decreases.

The diffusion coefficient $D_z$ calculated from the cylindrical model system is strongly influenced not only by the effect of the geometrical hindrance as mentioned in the above, but also by the dispersive fluid-wall interaction. After a collision with the thermal wall, the momentum of the particle becomes random satisfying the distribution laws given in Eqs. (5) and (6), which means that, after the collision, the particle loses the net momentum. The number of wall-particle collisions per unit wall area and per unit time is presented in Fig. 9. The rate of wall-particle collisions increases with decreasing the pore diameters. Therefore the average number of particles in the system which loses net momentum increase as the pore size decreases, and the resulting diffusion coefficient diminishes.

For the pore diameters greater than $3\sigma$, the mean square displacement (MSD) of fluids in the cylindrical pore system is linearly proportional to time, and then the self-diffusion coefficient can be calculated from Eq. (8). However, for the case of smaller pore diameter such as $d = 2\sigma$, there is a significant deviation from Fickian behavior as shown in Fig. 10, thus yielding anomalous diffusion. It is found that anomalous diffusion in this study is slower than normal diffusion. At this pore diameter, the behavior of MSD is somewhat close to that of a single file fluid, even though not exactly same. The single-file diffusion under the influence of random
Fig. 9. Average wall-particle collision frequencies per unit wall area and per unit time as a function of pore diameter for two different densities.

Fig. 10. Mean square displacements at the $d = 2\sigma$ for two different densities.

background forces has been studied for one dimensional hard rods system. An analytical study by Levitt has shown that MSD is proportional to the square root of time,

$$\langle |r_i(t) - r_i(0)|^2 \rangle = 2D_s\sqrt{t},$$

where $D_s$ denotes a single-file diffusion constant. Recently, Mon and Percus performed molecular dynamics simulations of hard sphere fluids confined in a cylindrical pore composed of a hard wall. They introduced the fluid-wall interaction with a longitudinal momentum reversal and observed anomalous diffusion in single file fluids. From Fig. 10, we calculated the exponents $\alpha$ by fitting MSD into $t^{\alpha}$ for each density. In our system, the exponent $\alpha$ is 0.54 at $\rho^* = 0.5$ and 0.62 at $\rho^* = 0.6$, having a range from $\alpha = 0.5$ (single-file diffusion) to $\alpha = 1$ (normal diffusion). Such a transition mode of the self-diffusion has been also observed from the MD study conducted by Keffer, McCormick and Davis.
4. Conclusion

We conducted equilibrium molecular dynamics simulation of WCA fluids confined in a cylindrical pore. Internal potential energy, axial pressure and self-diffusion coefficient have been evaluated for a wide range of the pore diameters. The trends of the thermodynamic quantities with respect to the pore diameter are due to the increase of the average particle-particle collision frequency. Furthermore, transport property is influenced not only by the average particle-particle collision frequency, but also by the dispersive wall-fluid interaction. Also, we were able to observe the transition mode of the self-diffusion phenomena for the pore size less than $2\sigma$.

Systematic studies of these thermodynamic and transport properties will provide a good guide to understand the behavior of fluids confined in carbon nanotubes, or blood in very narrow vessel.

Acknowledgments

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References

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