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Nonpolar and polar fluid flow through flat nanochannels with amorphous and crystalline walls

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ABSTRACT

The flow of nonpolar and polar fluids through flat nanochannels with amorphous and crystalline boundary walls is investigated by means of molecular dynamics (MD) simulations. It is shown that the fluid polarity and structure of the boundary walls have very strong influences on both the average fluid flow rate and the shape of the fluid velocity profiles. For channels with amorphous boundary walls, the nonpolar fluid flow appears to be faster than the flow of the polar fluid, whereas for channels with crystalline boundary walls, one has the reversed trend. This feature is discussed under the light of the larger self-diffusivity of bulk polar fluids, contrasting with their smaller slip velocities near crystalline walls.

1. Introduction

During the last two decades, the transport of fluids through nanochannels and carbon nanotubes became a subject of intensive experimental and theoretical investigations. The interest to this phenomenon is mainly caused by its fundamental and technological importance for chemistry, biology, material science, and nanosciences [1–7]. From the fundamental point of view, understanding the behavior of liquids confined to nanoscale channels is of prime importance because such liquids demonstrate unusual properties different from those of the bulk liquid phase. In addition, nanochannel–liquid systems can have a wide scope of applications in nanofluidics, including sensors, filters, and gating devices. As molecular transporters, carbon nanotubes can shuttle various cargoes across cellular membranes that could give rise to a new route for drug delivery and, hence, to a novel mechanism for cancer therapy [8].

Experimental investigations and computer simulations of the behavior of water and other fluids confined to nanochannels revealed considerable differences between the confined behavior and that in the corresponding bulk phase [9–16]. For example, a pressure drop driven fluid flow through carbon nanotubes and sheets was found to be much faster than the predictions of classic hydrodynamics [9,10,17–21]. In addition, in recent studies carried out in [22], the axial and radial diffusion coefficients of water molecules indicate a significant enhancement of the diffusion rate near the boundary wall. However, there is a very strong variation in experimental data on flow rates obtained from different experiments on the fluid flows through nanochannels. Usually, data of such experiments are interpreted on the basis of the slip-modified Hagen–Poiseuille equation [23], and values of slip lengths obtained from different papers vary from several nanometers [24] to 54 μm [10]. This fact suggests that there are many factors determining the fluid flow through nanochannels which are not completely understood by now. One of this factors is a structure of boundary walls. It is clear that interactions between fluid atoms (molecules) and boundary wall atoms should depend on positions of latter in the space. The randomly distributed boundary wall atoms should give a contribution to the total interaction with fluid atoms (molecules) different from that given by those located in the sites of a regular crystalline lattice. Thus, the behavior of the fluid in nanochannels with amorphous boundary walls should differ from that of the fluid in nanochannels with crystalline boundary walls. Another factor that should influence the behavior of fluids in nanochannels is their polarity. Really, for polar fluids composed of molecules possessing permanent dipole moments, in addition to short-range intermolecular interactions such as van der Waals ones, the long-range dipole–dipole interaction should be considered. Since the strength of these long-range interactions may be comparable or even stronger than those of the short-range interactions, the behavior of polar fluids in nanochannels can be significantly different from the behavior of nonpolar ones.

The present paper is devoted to a theoretical investigation of the factors discussed above. Using molecular dynamics (MD) simulations, we investigated flows of both nonpolar and polar fluids

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through flat nanochannels with amorphous and crystalline boundary walls. It will be shown that the boundary wall structure and the fluid polarity have very strong influences not only on the average fluid flow rate but also on the shape of the fluid velocity profiles. In particular, it will be unveiled that for channels with amorphous boundary walls, the nonpolar fluid flow is faster than the flow of the polar fluid. However, for channels with crystalline boundary walls, the above trend is reversed.

2. Simulation details

We performed MD simulations of fluid flows through flat nanochannels with both amorphous and crystalline boundary walls. For nanochannels with amorphous boundary walls, the wall atoms are randomly distributed in space with a density equal to that of the confined fluid, whereas for nanochannels with crystalline boundary walls, the wall atoms are placed in the sites of a face-centered cubic (fcc) lattice. In both cases, the wall atoms are assumed to be fixed in space. We considered two types of model fluids, namely, nonpolar and polar ones. As a polar model fluid we used a very simple model in which molecules are assumed to be point-like particles possessing a permanent dipole moment. These particles interact with each other via the short-range Lennard-Jones (LJ) pairwise inter-particle potential

$$U_{LJ}(r_{ij}) = 4\epsilon_{ij}\lceil(\sigma_{ij}/r_{ij})^{12} - (\sigma_{ij}/r_{ij})^{6}\rceil, \tag{1}$$

where ϵ_{ij} and σ_{ij} are the strength and characteristic length, respectively, for the LJ interaction between i-th and j-th particles, r_{ij} is the distance between these particles, and the dipole–dipole interaction potential

$$U_{dd}(r_{ij}) = (\vec{d}_i \cdot \vec{d}_j)/r_{ij}^3 - 3(\vec{d}_i \cdot \vec{r}_{ij})(\vec{d}_j \cdot \vec{r}_{ij})/r_{ij}^5, \tag{2}$$

where $\vec{d}_i$ is the dipole of the i-th particle. Further, the polar molecules will be considered as the water ones. Then, the LJ interaction constants ϵ_{ij} and σ_{ij} in Eq. (1) should be similar to those for the LJ interactions between oxygen atoms of the i-th and j-th water molecules. These constants, namely, ϵ_{OO} and σ_{OO}, can be taken from the well known SPC model for water molecules [25,26], and they are equal to $\epsilon_{OO} = 1.083 \times 10^{-14}$ erg and $\sigma_{OO} = 3.166$ Å, respectively. According to this model, the oxygen atom in the water molecule is connected with two hydrogen atoms with the intramolecular hydrogen–oxygen bonds with equilibrium lengths $r_w = 1$ Å, and the angle between these bonds has an equilibrium value $\theta_w = 109.47°$. Furthermore, effective charges of oxygen and hydrogen atoms are equal to $-0.82e$ and $0.41e$, respectively, where e is the elementary charge. From these data, one can easily obtain an effective dipole moment of the water molecule $d_w = 1.89 \times 10^{-18}\ \mathrm{g}^{1/2}\,\mathrm{cm}^{5/2}\,\mathrm{s}^{-1}$.

The total force $\vec{F}_i$ and the total torque $\vec{\tau}_i$ acting on the i-th molecule due to the other molecules are given by $\vec{F}_i = \sum_{j \neq i} \vec{f}_{ij}$ and $\vec{\tau}_i = \sum_{j \neq i} \vec{\tau}_{ij}$, where $\vec{f}_{ij}$ and $\vec{\tau}_{ij}$ are the force and the torque, respectively, exerted by the j-th molecule over the i-th one. The force $\vec{f}_{ij}$ and the torque $\vec{\tau}_{ij}$ are determined by the following expressions:

$$\vec{f}_{ij} = -(\partial(U_{LJ} + U_{dd})/\partial r_{ij})\hat{r}_{ij}; \qquad \hat{r}_{ij} = \vec{r}_{ij}/r_{ij}, \tag{3}$$

$$\vec{\tau}_{ij} = \vec{d}_i \times \vec{E}_{ij}, \tag{4}$$

where the electric field $\vec{E}_{ij}$ acting on the dipole $\vec{d}_i$ from the dipole $\vec{d}_j$ is given by

$$\vec{E}_{ij} = 3(\vec{d}_j \cdot \vec{r}_{ij})\vec{r}_{ij}/r_{ij}^5 - \vec{d}_j/r_{ij}^3. \tag{5}$$

The motion of particles of polar fluids is governed by the following equations:

$$\frac{\partial^2 \vec{r}_i}{\partial t^2} = \frac{\vec{F}_i}{m}, \tag{6}$$

$$\frac{\partial \vec{e}_i}{\partial t} = \vec{\omega}_i \times \vec{e}_i, \tag{7}$$

$$\frac{\partial \vec{\omega}_i}{\partial t} = \frac{\vec{\tau}_i}{I}, \tag{8}$$

where $\vec{e}_i = \vec{d}_i / \mid \vec{d}_i \mid$ is the unit vector which defines the orientation of the dipole moment of the i-th particle, $\vec{\omega}_i$ is the rotation rate of the vector $\vec{e}_i$, m and I are the mass and the moment of inertia of the particle, respectively.

The systems under investigation were placed in a simulation cubic box of $20\sigma_{OO} \times 20\sigma_{OO} \times 20\sigma_{OO}$ in size. In simulations of the bulk properties of the fluids, the periodic boundary conditions [27] were imposed on the system in x, y, and z directions, whereas, in simulations of the fluid flows, we used the periodic boundary conditions only in x and y directions (z direction is perpendicular to the bounding walls of the channels). The total number of particles in the channel is kept fix by reinjecting a new particle whenever a particle leaves the channel. All simulations were performed in the *NVT* ensemble and they were started from random distributions of fluid molecules' centers of mass. These simulations were run for a number of time steps (one time step was equal to 0.0017 ps) necessary to reach a statistically stationary state of the system (equilibrium structure for the motionless fluid inside the nanochannel or stationary fluid flow through this nanochannel under an external pressure drop). The external pressure drop was mimiced by a constant force acting on each fluid molecule inside the nanochannel along the x direction parallel to the boundary walls. At each time step, the equations of motion of fluid molecules were solved numerically by the standard method described in [27]. The temperature of the system was kept constant ($T = 300$ K) by employment of the Berendsen thermostat [28]. This temperature corresponds to the reduced temperature $T^* = k_B T/\epsilon_{OO} \approx 4$, where k_B is the Boltzmann constant.

3. Simulation results and discussion

First of all, we checked the suitability of our very simple model to describe nonpolar and polar fluid flows through nanochannels. For this purpose, we simulated the equilibrium behavior of nonpolar and polar fluids in the bulk phase and calculated certain equilibrium characteristics of these fluids. We start by computing

$$D(t) = \frac{<\mid \vec{r}_i(t) - \vec{r}_i(0) \mid^2>}{6t}, \tag{9}$$

where $< \ldots >$ means an average over all fluid molecules. The time dependences of $D(t)$ (in dimensionless MD units [27]) for nonpolar and polar fluids obtained from the MD simulations of an ensemble of 8788 molecules are reported in Fig. 1. For a nonpolar fluid, the constant ϵ_{OO} is assumed to be the same as for the polar one, whereas the dipole moments are equal to zero.

One can see that, for both nonpolar and polar fluids, the time dependences $D(t)$ sufficiently fast achieve a saturated levels which can be considered as the equilibrium self-diffusion constant D_s. It should be noted that these equilibrium values are achieved in ~ 5 MD time units that, for the above mentioned values of ϵ_{OO} and σ_{OO} is equal to ~8–9 ps. For comparison, equilibrium values of the self-diffusivity constant for water can be obtained from MD simulations based on well known models for water [25] only after running over ~6.5 ns. As expected, for a nonpolar fluid, the self-diffusivity constant D_s is slightly larger than that for the polar one because in the latter intermolecular interactions are stronger due to the dipole–dipole interaction. Similar result was obtained from simulations of the self-diffusivity of the water and methane in carbon nanotubes [21]. As for the absolute value of D_s for the polar