Multi- and Single- Atoms Liquid Flow Systems for Nano-sized channels

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ABSTRACT

In this paper, molecular dynamic (MD) simulations are employed to characterize the liquid flow systems consisting of single- or multi-atoms as argon, water or ethane. These molecular flows are driven by various pressure gradients in nano-sized channels of different heights. The simulations find the existence of layer structures near the wall and the compressibility effect across the nano-sized channel for argon molecules. Slip velocity is obtained and the associated accommodation factor and laminar friction factor are varied with channel size in nano-scale. Furthermore, the flow characteristic in terms of velocity distribution inside nano-channels for different liquid molecules with multi-atoms exhibits very different transport phenomena. In conclusion, the inter-atomic interaction models between liquid atoms or liquid-solid atoms play important roles near interfaces in fluid transport of nano-sized channel flow.

Keywords: Molecular dynamics simulation, nano-sized channel flow, liquid flow characterization, inter-atomic interaction models, slip velocity.

1 INTRODUCTION

Flow based assays use continuous forward flow in micro/nano-fluidic systems to deliver and transport biomedical sample to destined spots for biomedical diagnosis. Accurate dose control, less drag force from contact surface, and simpler flow system directing and dispending the bio-fluids are the aims of flow system designs. Numerous studies have been performed using Molecular Dynamic simulation for simple flow, such as Couette, Poiseuille and channel flows, but mostly with Argon molecules. A limited number of studies are performed using multi-atoms systems, for example, n-hexadecane [1]. Present work studies the liquid flows for argon, water or ethane molecules in nanosized channels. Water and ethane molecules are multi-atoms systems ar fluid-wall interactions between these clustered atoms and platinum atom will make the flow different.

2 SIMULATION METHOD

The detailed flow characteristics are investigated using molecular dynamic simulations with different pressure gradients for three different height nano channels. The solid wall is made of platinum, which acts as flowing boundaries of molecule systems with constituents: argon, water and ethane. The potentials employed for the simulation include Lennard-Jones function [2], SPC/E [3], and Amber [4] models. Molecular models are briefly described as follows

The simulated liquids made of Argon, water or ethane molecules are sandwiched by floor and ceiling wall molecules made of platinum (Fig. 1). The motion of liquid molecules are governed by Newton's second law:

$$\dot{r}_i = \frac{\wp_i}{m}, \quad \dot{\wp}_i = \sum_{j \neq i} f_{ij} + F_e \tag{1}$$

Where m, $\dot{r}_i$ and $\wp_i$ are the mass, velocity and momentum of molecule i, f_{ij} is the intermolecular force on molecule i by j, and $F_e = (F_{e_L} - F_{e_R})\ (l_i / L)$, is the applied external force, where L is the length of the channel and l_i is the distance along the channel for molecule i. The force difference experienced by the fluid molecules between two boundaries $(F_{e_L} - F_{e_R})$ mimic the pressure gradient

2.1 Liquid Composed of Argon Atoms

Well-known Lennard-Jones function [2] with a cutoff distance $r_c = 2.5\sigma$ is employed as the potential $\phi(r_{ij})$ between argon molecules and argon-wall molecules:

$$\phi(r_{ij}) = 4\varepsilon[(\frac{\sigma}{r_{ij}})^{12} - (\frac{\sigma}{r_{ij}})^{6}] \tag{2}$$

Where r_{ij} is the distance between two molecules, ε represents the interaction strength, and σ is an inter-atomic length scale.

The Lennard-Jones parameters between argon molecules are $\sigma = 0.34$ nm and $\varepsilon = 1.67 \times 10^{-21} J$, and the mass of argon molecule $m = 6.63 \times 10^{-26} kg$. The parameters between argon and wall molecules are $\sigma_{fw} / \sigma = 0.907$ and $\varepsilon_{fw} / \varepsilon = 0.412$.

2.2 Liquid Composed of Water Molecules

SPC/E [3] model is employed for interactions between water and platinum molecules. Assuming the water molecule is structured as Fig. 2. The distance between OH is 0.1 nm and the tetrahedral angle HOH is fixed as $\theta = 2\cos^{-1}(1/\sqrt{3}) \cong 109.47°$. Charges on oxygen and hydrogen equal to –0.8476 and +0.4238 e, respectively. The expression of SPC/E model [3] is as follows:

$$\phi(r_1, r_2) = 4\varepsilon_{oo}[(\frac{\sigma_{00}}{r_{12}})^{12} - (\frac{\sigma_{00}}{r_{12}})^{6}] + \sum_i \sum_j \frac{q_i q_j}{4\pi\varepsilon_o r_{ij}} \quad (3)$$

Where r_{12} represents the distance between oxygen atoms, σ_{oo}, ε_{oo} are LJ parameters between oxygen molecules and the corresponding values (0.316 nm and 1.08×10^{-21} J, respectively), q_i, q_j are the charges on atoms i & j, and ε_o represents the dielectric constant.

The analytical form of the water-platinum pair potential is given by [5]

$$\phi_{H_2O-Pt} = \phi_{O-Pt}(r_{O-Pt}, \rho_{O-Pt}) + \phi_{H-Pt}(r_{H_1-Pt}) + \phi_{H-pt}(r_{H_2-Pt}) \quad (4)$$

2.3 Liquid Composed of Ethane Molecules

For ethane flow, AMBER [4] potential model is chosen as the potential model which combines the Van Der Walls (VDW) interaction model represented by a 6-12 L-J potential, with and an electrostatic interaction model by a Columbic interactions of atom-centered point charges, dihedral, bond and angle energies. This potential is represented as follows:

$$\phi_{total} = \sum_{bonds} K_{r_b}(r_b - r_{b_0})^2 + \sum_{angles} K_{\theta_b}(\theta_b - \theta_{b_0})^2 + \sum_{dihedrals} \frac{V_n}{2}[1 + \cos(n\varphi - \varphi_0)] + \sum_{i<j}[\frac{A_{ij}}{r_{ij}^2} - \frac{B_{ij}}{r_{ij}^2} + \frac{q_i q_j}{\varepsilon_0 r_{ij}}] \quad (5)$$

The four terms on the right hand side of Eq. (5) denotes the bond energy between two atoms in a molecule, the bond angle energy in a molecule, the dihedral energy in a molecule and electrostatic and VDW interaction.

3 SIMULATION SYSTEM

The liquid fluid is sandwiched by top and bottom wall plates that are represented by one layer of platinum molecules in <111> face-centered cubic lattice. The heat dissipation by the external force is adjusted by phantom molecules [6] so that wall boundary temperature is kept as a constant. The potential between wall molecules and wall phantom molecules is assumed as a simple harmonic potential.

$$\phi(r_{ij}) = \frac{1}{2}k(r_{ij} - r_{ij_0})^2 \quad (6)$$

Where k is the spring stiffness, r_{ij} is the distance between two molecules, and r_{ij_0} is the equilibrium distance between two wall molecules in solid crystal. In present work, these constants for the platinum molecule are set as k = 4.68 N/m, and r_{ij_0} = 0.277 nm.

The flowing systems consist of 2744, 5488, and 8232 Argon molecules inside channels with heights of ~40Å, 80Å, and 120Å respectively, and the liquid Argon is enclosed by solid wall with one layer of fcc <111> surface of 510 platinum molecules. (The initial positions of argon, water, and ethane are initially assigned at the sites of a face-centered lattice, face centered lattice with half the tetrahedral holes filled and face-centered lattice.) The initial velocities of liquid molecules are set as a Gaussian distribution with temperature controlled at 0.71, 2.51 and $0.75\varepsilon/k_B$ where k_B is Boltzmann's Constant. During the computation, the Verlet neighbor list method [7] is applied in force calculation. In order to integrate the local flow properties, the flow area is divided into matrices in x, y z directions with each cell of about 0.59σ in length.

4 RESULTS & DISCUSSION

Different magnitudes of forces are applied on the left and right boundaries of the flow channel in x direction to mimic the pressure gradient in flow directions. The pressure gradient is obtained by dF/A, where dF is the force gradient, A is the cross section area in x direction,

$$dF = \frac{F_{e_L} - F_{e_R}}{n_x - 1} \quad (7)$$

Fe_L & Fe_R are the applied forces on the left and right boundaries in x direction and n_x is the number of grids in x direction. Figure 3 indicates that the normalized velocity

profiles are parabolic curves with large jumps at wall for argon liquid flow. The density (Fig.4) and pressure profiles across the channel indicate the obvious layer structure near the wall. Table 1 tabulates the slip velocity and corresponding accommodation coefficient, which indicates that higher the pressure gradient gives larger slip velocity and higher accommodation coefficient. Furthermore, these values may imply that the effect of channel size on accommodation coefficient is more pronounced than the pressure gradient does for the calculated range. Table 2 indicates that the constants are very small compared to 96 (laminar constant for macro-scale-channel) and the applied pressure gradient varies the laminar friction constant a little for the same size nano-channel (11.7σ). The laminar friction constant increases significantly as the channel size increases if the same pressure gradient is applied.

Figure 5 shows the normalized scattered velocity profile with non-slip velocity at wall for water flowing in an 11.76σ height channel, which follows the trend of classical laminar result. However, there is still one layer existing near the wall as shown in density profile (Fig.6). Figure 7 compares the normalized velocity profiles of argon, water and ethane fluid and reports that slip velocity at wall for ethane flow does exist and more irregular distribution is observed due to the much longer chain of clustered atoms for one ethane molecule.

5 CONCLUSION

MD simulations of fluids of argon, water, and ethane molecules in a nano channel are performed and indicate the existence of layer structure near the wall and the compressibility effect across the nano-sized channel. The integrated local properties of accommodation factor, laminar friction factor are largely changed due to the change of channel size in nano-scale, which implies the tremendous reduction of the friction of the liquid flow due to the slip velocity. It implies the inter-atomic interaction model between liquid atoms or liquid-solid atoms plays important roles in fluid transport, therefore, very different transport phenomena can be observed for different fluids flowing inside the same size channel in nano-scale.

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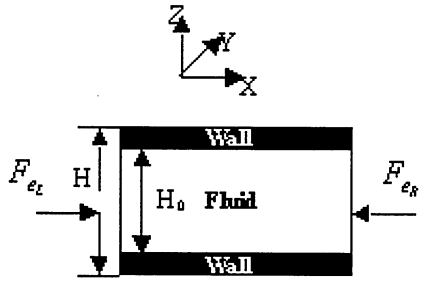

Figure 1: Schematic diagram of the force driven channel flow

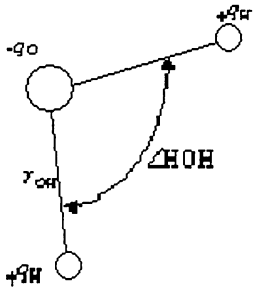

Figure 2: SPC/E Structure of Water Molecule

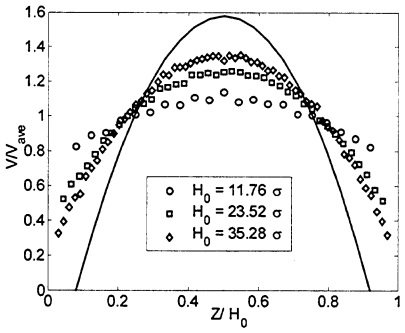

Figure 3: The velocity profiles of the same pressure gradient ($dp/dx = 4.82 \times 10^{-5}\ \varepsilon\sigma^{-4}$.) for three height channels, solid line is the analytical solution from continuous theory (Argon)

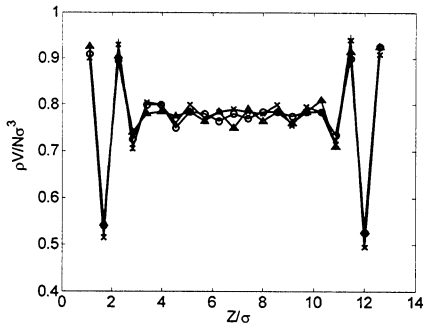

Figure 4: The density profiles by three different pressure gradients (x, o, Δ : dp/dx= 2.41 x 10^{-5}, 4.82 x 10^{-5} and 7.23 x 10^{-5} $\varepsilon\sigma^{-4}$) in 11.76 σ argon height channel.

Table 1: Slip velocity and accommodation coefficient for various height of channels and pressure conditions (Argon)

H (σ)	dp/dx ($\varepsilon\sigma^{-4}$)	$V_{slip}(\sqrt{\varepsilon/m})$	σ_V
11.7	2.41e-5	0.91	0.28
	4.82e-5	1.51	0.33
	7.23e-5	1.91	0.38
23.5	4.82e-5	2.29	0.56
35.3	4.82e-5	2.34	0.74

Table 2: Product of Reynolds number and friction factor for various heights of channels and pressure conditions.

H (σ)	dp/dx ($\varepsilon\sigma^{-4}$)	Re	τ_{ave} (N/m^2)	f=8*τ_{ave}/(0.5ρu^2)	C=f*Re
11.7	2.41e-5	4.25	6.72e+5	0.27	1.13
	4.82e-5	7.19	1.02e+6	0.14	1.01
	7.23e-5	9.30	1.84e+6	0.15	1.41
23.5	4.82e-5	23.4	6.58e+6	0.16	3.73
35.3	4.82e-5	46.6	1.91e+7	0.17	7.96

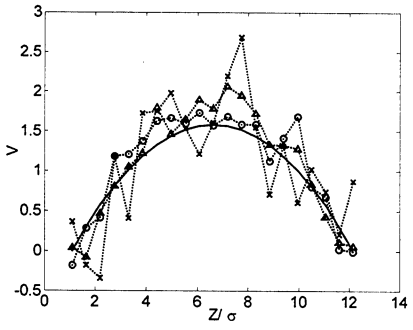

Figure 5 Normalized velocity profiles of three different pressure gradients (x, o, Δ ⇒ dp/dx= 2.41 x 10^{-5}, 4.82 x 10^{-5} and 7.23 x 10^{-5} $\varepsilon\sigma^{-4}$) in 11.76σ height channel for water fluid, solid line is the classical laminar result, for water flow.

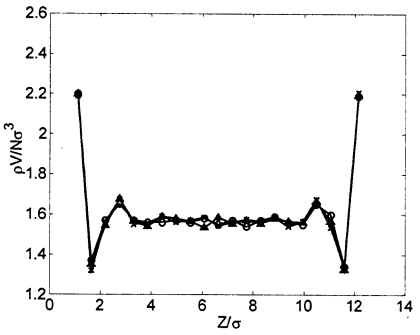

Figure 6: The density profiles by three different pressure gradients (x, o, Δ : dp/dx= 2.41 x 10^{-5}, 4.82 x 10^{-5} and 7.23 x 10^{-5} $\varepsilon\sigma^{-4}$) in 11.76 σ height water channel.

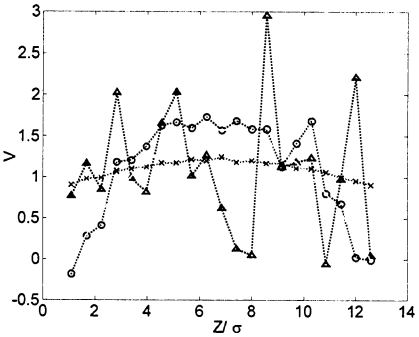

Figure 7: Normalized velocity profiles of argon (×), water (o) and ethane (Δ) and the Laminar theory (solid line) for channel size of 12.2, 12.7 and 13.2σ in x, y z directions.