Molecular dynamics simulation for flow characteristics in nanochannels and single walled carbon nanotubes

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Abstract. Flows in graphite-, diamond- and silicon-walled nanochannels are discussed by performing molecular dynamics simulations. Flows in carbon nanotubes (CNTs) and graphene-walled nanochannels are also investigated. It is found that the flow rate in the graphite-walled channel tends to be the largest because of its slippery wall structure by the short bond length and the high molecular density of the CNTs. The flow rate in the single walled CNT at a very narrow diameter tends to increase although such a tendency is not seen in the graphene-walled channel.

1. Introduction
Carbon nanotubes (CNTs) and nanochannels attract much attention because these nano-structures are expected for expanding the applications of the membrane engineering. Recently, it was reported that hydrocarbons or water molecules flowed through a CNT much faster than in the other materials [1]. After this sensational report, many research studies have been reported on flows in CNTs [2-4]. However, the mechanism of the fast transport in a CNT has not been clearly understood. Also, understanding the detailed flow physics in nano-structures is still underway. Therefore, in this study, molecular dynamics (MD) simulations of flows in nanochannels and CNTs are performed to understand the flow characteristics in nano-structures and the fast transport mechanism in a CNT.

2. Molecular dynamics method

2.1. Lennard-Jones fluid
The presently applied classical molecular dynamics simulation consists of the numerical solution of classical equations of motions of N molecules interacting via model potentials. The well-known model potential is the 6-12 Lennard-Jones (L-J) potential \( \phi \) which is defined as

\[
\phi(r_{ij}) = 4\epsilon \left[ \left( \frac{\sigma}{r_{ij}} \right)^{12} - \left( \frac{\sigma}{r_{ij}} \right)^{6} \right] - \left[ \left( \frac{\sigma}{r_c} \right)^{12} - \left( \frac{\sigma}{r_c} \right)^{6} \right],
\]

where \( r_{ij} \) is the intermolecular distance between \( i \) and \( j \) molecules, \( r_c \) is the cut-off radius, \( \epsilon \) and \( \sigma \) are the well depth and the diameter of the molecules. From this potential, intermolecular force \( \mathbf{F} \) is written as
This model has been used in the classical MD simulation by argon (Ar) molecules. In the system which is modeled by the Lennard-Jones molecules, the classical equation of motion can be written as

\[ \frac{d^2 r^*}{dt^2} = -\frac{\varepsilon^*}{m^*} \frac{\partial \phi^*}{\partial r^*}, \]

where \( m^* = r^*/\sigma \), \( t^* = t/\tau = t/\sqrt{m \sigma^3/\varepsilon} \) and \( \phi^* = \phi/\varepsilon \) are the mass, the nondimensional length, time and energy, respectively. However, to make a physical interpretation, it is sometimes expressed as dimensional values in terms of Ar. In addition, the nondimensional number density \( N^* = N\sigma^3 \) and temperature \( T^* = k_b T/\varepsilon \) are used in the Lennard-Jones fluid. Here \( k_b \) is the Boltzmann constant. In actual calculations, to hold down the calculation effort of the interactions, the potential effects are truncated over cut off distance \( \sigma_c \) which is defined as \( r_c \). In the present study, \( r_c = 3\sigma \) is employed.

### 2.2. Brenner and Tersoff potentials

To describe the covalent bond, the Brenner and Tersoff potentials [5, 6] are applied to carbon and silicon walls. The covalent bond energy is written as

\[ E_b = \sum_i \sum_{j>i} f_c(r_{ij}) \left[ f_B(r_{ij}) - \overline{b}_{ij} f_A(r_{ij}) \right]. \]

For the Brenner potential, \( f_B(r_{ij}) \) and \( f_A(r_{ij}) \) are written as

\[ f_B(r_{ij}) = \frac{D_{ij}^{(e)}}{S-1} \exp \left( -\sqrt{2/S} \beta (r - R_c) \right), \]

\[ f_A(r_{ij}) = \frac{D_{ij}^{(e)} S}{S-1} \exp \left( -\sqrt{2/S} \beta (r - R_c) \right), \]

where \( D_{ij} \), \( S \) and \( R_c \) are determined by the physical properties of carbon. For the Tersoff potential, \( f_\text{T}(r_{ij}) \) and \( f_A(r_{ij}) \) are written as

\[ f_B(r_{ij}) = A \exp \left( -\lambda_1 r_{ij} \right), \]

\[ f_A(r_{ij}) = B \exp \left( -\lambda_2 r_{ij} \right), \]

where \( A, B, \lambda_1 \) and \( \lambda_2 \) are physical properties of silicon. The cut off function \( f_c \) is written as

\[ f_c(r_{ij}) = \begin{cases} 1, & r < R - D \\ 1 - \frac{1}{2} \sin \left( \frac{\pi}{2} \frac{r_{ij} - R}{D} \right), & R - D < r < R + D \\ 0, & r > R + D \end{cases} \]

The bond order term is described as

\[ \overline{b}_{ij} = \frac{b_{ij} + b_{ji}}{2}. \]
The function $b_{ij}$ is written as

$$b_{ij} = \left[ 1 + (\beta \zeta_{ij})^{n_0} \right]^{-\delta},$$

(11)

where $\zeta_{ij}$ is

$$\zeta_{ij} = \sum_{k=i,j} f_{ij}(r_{ik}) g_{ij}(\theta_{ik}) \exp\left[ \lambda_{ij}^3 (r_{ij} - r_{ik})^3 \right],$$

(12)

and $g_c(\theta)$ is described as

$$g_c(\theta_{ik}) = 1 + \frac{c^2}{d^2} - \frac{c^2}{d^2 + (h - \cos \theta_{ik})^2},$$

(13)

where $\theta_{ik}$ is the angle between bonds $ij$ and $ik$. The parameters of the Brenner and Tersoff potentials are tabulated in table 1.

### Table 1. The parameter of the Brenner and Tersoff potentials.

| Parameter | Brenner value | Tersoff value |
|-----------|---------------|---------------|
| $D_e$ (eV) | 6.325         | 3264.7        |
| $S$       | 1.29          | 95.373        |
| $\lambda$ ($\text{Å}^{-1}$) | 1.5          | 3.2394        |
| $R_e$ (Å) | 1.315         | 1.3528        |
| $\beta$   | 1.0           | 0.33675       |
| $n_0$     | 1.0           | 22.956        |
| $\delta$  | 0.80469       | 11.478        |
| $\lambda_3$ ($\text{Å}^{-1}$) | 0           | 1.3258        |
| $a$       | 0.011304      | 1             |
| $c$       | 19            | 4.8381        |
| $d$       | 2.5           | 2.0417        |
| $h$       | -1.0          | 0             |
| $R$ (Å)   | 1.85          | 3.0           |
| $D$ (Å)   | 0.15          | 0.2           |

3. Wall structures

In this study, five types of wall structures: diamond, silicon, graphite, graphene and CNT wall structures are discussed. These five structures can be categorized into two kinds of structures which are the diamond and six membered ring structures. Figure 1 shows the diamond structure. The diamond and silicon walls have this structure. The lattice constants of the diamond and silicon crystals are 0.356 and 0.543nm, respectively. The six membered ring structure for the graphene and graphite is
shown in figure 2. Their bond length is 0.1421nm. The distance between the graphite layers is 0.3354 nm. The armchair CNT is considered in the present study.

![Figure 1. Diamond structure.](image1)

![Figure 2. Six membered ring structure.](image2)

4. Results and discussions

4.1. Nanochannel flows of three types of wall structures

Firstly, flows in diamond-, silicon- and graphite-walled nanochannels are discussed. Argon molecules are applied for the fluid molecules. Figure 3 illustrates calculation domains for the nanochannels and CNTs. For the nanochannels, the calculation domain whose length $L=3.4$ nm, width $W=3.4$nm and height $H=6.8$nm are applied. Periodic boundary conditions are applied for the $x$ and $z$ directions. The external force $F = 2.45(\times10^{-14}$ N) acts on the fluid molecules to the $x$ direction. The numbers of fluid and wall molecules are tabulated in table 2. In these cases, the Langevin method [7] is applied to the calculation domain to keep the temperature at 298K and thus the pressure of calculation domain is 5.9Pa. For taking the statistical average, the computations are performed for about 100 million time steps.

| Fluid     | Wall    |
|-----------|---------|
| Ar-Graphite | 114  | 4480  |
| Ar-Diamond  | 120  | 6272  |
| Ar-Silicon  | 112  | 1800  |

Table 2. Number of fluid and wall molecules of nanochannel flows.
Figure 4 shows the number density profiles of the three wall cases. It is seen that the fluid molecules are densely distributed near the walls. This is because the channel walls strongly attract the fluid molecules. Figure 5 shows velocity profiles across the channels. In this figure, the flow in the graphite-walled channel has the largest velocity profile and the silicon-walled channel has the smallest one. One of the reasons why the velocity profiles have such tendencies is considered to be the roughness effect of the wall structure. In the three types of wall structures, the graphite wall has the largest atomic packing factor on the wall surface $P_f = 0.956$ and the silicon wall has smallest atomic packing factor $P_f = 0.811$ while the diamond wall has $P_f = 0.922$. It is considered that the velocity profiles correspond to these atomic packing factors.

![Figure 3](image-url) **Figure 3.** Calculation domains for nanochannel and CNT; (a) nanochannel, (b) CNT.

![Figure 4](image-url) **Figure 4.** Number density profiles of fluid molecules in nanochannels.

![Figure 5](image-url) **Figure 5.** Velocity profile in nanochannels.

### 4.2. Flows in CNT and graphene-walled channel cases

Under a constant temperature and a pressure, the channel height $H$ and the diameter $D$ of calculation domains are varied in the range of 0.91 - 7.83nm. The domain length $L$ of the CNTs and the graphene-walled channels are $L = 1.23 - 9.84$ nm. The width $W$ of the graphene-walled channel is $W = 3.84 - 24.60$ nm. For the CNTs, periodic boundary conditions are applied for the $x$ direction. The external force $F = 7.36\times10^{-14}$ N acts on the fluid molecules to the $x$ direction. The Nose-Hoover thermostat [8, 9] is applied to the calculation domain to keep the temperature at 121 K. The pressure of the domain is 34.3 MPa. The numbers of fluid and wall molecules are tabulated in table 3. For taking the statistical average, the computations are performed for about 100 million time steps are performed as before.
Table 3. Number of fluid and wall molecules of CNT and graphene channel flows.

| $H, D$ [nm] | Fluid | Wall  | Fluid | Wall  |
|------------|-------|-------|-------|-------|
| 0.91       | 132   | 1440  | 708   | 2880  |
| 1.32       | 207   | 1440  | 1024  | 2880  |
| 2.95       | 690   | 1920  | 3048  | 3840  |
| 4.58       | 831   | 1440  | 3548  | 2880  |
| 6.21       | 764   | 960   | 3207  | 1920  |
| 7.83       | 1217  | 1200  | 5060  | 2400  |

Figure 6 shows centerline and slippage velocities normalized by the bulk velocities. In all channel heights or diameters, centerline and slippage velocities are nearly the same corresponding to flat velocity profiles.

Next, the tendency of flow rate depending on the tube diameter and the channel height is compared. The normalized flow rate is defined as

$$ Q = \frac{\int 2\pi \rho U(r)dr}{\rho a D^3/8Cs} \quad \text{for the CNT,} \quad (14) $$

$$ Q = \frac{\int \rho U(y)dy}{\rho a H^3/Cs} \quad \text{for the graphene channel,} \quad (15) $$

where $\rho$ and $a$ are the number density and the acceleration. The sound speed $Cs$ of argon is defined as

$$ Cs = \sqrt{\gamma RT}, \quad (16) $$

where $\gamma = 1.67$ and $R = 208 \text{ m}^2/(\text{s}^2\cdot\text{K})$ are the specific heat ratio and the gas constant. Figure 7 shows the distribution of the normalized flow rates.

Figure 6. Normalized centerline and slippage velocities in CNTs and graphene-walled channels.

Figure 7. Normalized flow rates in CNTs and graphene-walled channels.
As shown in figure 7, the normalized flow rates $Q$ of the two cases against $H$ or $D$ show a similar tendency where $H$ or $D$ are larger than 2.9 nm. However, the flow rate in the CNT at very narrow diameter (smaller than 2.9 nm) tends to be increase as the diameter decreases unlike in the graphene channel. This is because the attractive forces from the surrounding wall molecules are almost canceled each other. Moreover, the motions of fluid molecules in the narrow CNT are almost limited to the streamwise direction although those in the graphene-walled channel are allowed also in the spanwise direction. Thus the loss of the kinetic energy by collisions between fluid molecules in the CNT is less than that in the graphene-walled channel.

5. Conclusions

Nano-flows in several nano-structures are discussed by performing molecular dynamics simulations. Under a constant temperature and a pressure, three types of structures: diamond-, silicon- and graphite-walled nanochannel cases are calculated. The flow tendencies in the CNTs and the graphene-walled channels are also discussed. The number density profiles of the fluid molecules have peaks near the walls because the walls strongly attract the fluid molecules. Amongst the three types of wall structures, the flow in the graphite-walled channel has the largest velocity profile and that in the silicon-walled channel has the smallest velocity because of the roughness effect of the wall structure. In the case of the flows in the CNTs and the graphene-walled channels, flat velocity profiles across the tubes or channels are seen regardless of their diameters or heights. The flow rates of the CNT have a different tendency when the tube diameter is less than 2.9 nm due to the effects of the surrounding wall molecules.

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