Molecular dynamics study of Ar flow and He flow inside carbon nanotube junction as a molecular nozzle and diffuser

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Abstract

A carbon nanotube junction consists of two connected nanotubes with different diameters. It has been extensively investigated as a molecular electronic device since carbon nanotubes can be metallic and semiconductive, depending on their structure. However, a carbon nanotube junction can also be viewed as a nanoscale nozzle and diffuser. Here, we focus on the nanotube junction from the perspective of an intersection between machine, material and device. We have conducted a molecular dynamics simulation of the molecular flow inside a modeled (12,12)–(8,8) nanotube junction. A strong gravitational field and a periodic boundary condition are applied in the flow direction. We investigated dense-Ar flows and dense-He flows while controlling the temperature of the nanotube junction. The results show that Ar atoms tend to be near to the wall and the density of the Ar is higher in the wide (12,12) nanotube than in the narrow (8,8) nanotube, while it is lower in the wide tube when no flow occurs. The streaming velocities of both the Ar and the He are higher in the narrow nanotube than in the wide nanotube, but the velocity of the Ar is higher than the velocity of the He and the temperature of the flowing Ar is higher than the temperature of the He when the same magnitude of gravitational field is applied.

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1. Introduction

A carbon nanotube [1,2] consists of a rolled-up hexagonal lattice of carbon atoms with a diameter of a few nanometres. Carbon nanotubes have been extensively investigated for their outstanding mechanical and electronic properties, and there are numerous possible applications. Expected applications, other than those that take advantage of their mechanical or electronic properties, involve interactions with fluid molecules (fluid in a broad sense). For example, carbon nanotubes are expected to be used as molecular sieves or membranes for the separation of molecules [3], molecular shape selective catalysts, nano test-tubes or nano-reactors [4], channels for the transportation of molecules with an accuracy on the molecular level in terms of position and quantity, hydraulic actuators, nanopumps, sensors [5] and so on. Recently, the field of ‘nanofluidics’ has emerged and has started to be developed [4,6–8].

There have been extensive studies of the insertion of material into carbon nanotubes, and there are already not only theoretical calculations [9] but also many experiments on the subject [10–15] (See also Ref. [16] for review). If we focus on interactions between carbon nanotubes and ‘fluid’ molecules, there are reports on the simulations of molecular dynamics [3,6–8,17–21] and experiments relating to their ‘wetability’ and so on [4,22–24].

However, there have been few experimental reports so far that make use of the dynamical behaviour of fluid inside carbon nanotubes [5,25], and the nanoscale behaviour of fluid molecules is not well understood as yet. Carbon nanotubes can naturally behave as nanoscale channels, so investigating the differences in flow inside nanotubes compared to the flow in macroscopic tubes is important from the viewpoint of controlling the behaviour of molecules on the nanoscale. Furthermore, the differences in the properties of nanoscale ‘machines’ from the properties of macroscopic ones could be the source of a new
functionality, and an understanding of these differences could have great biophysical importance [26].

In this work, we focus on carbon nanotube junctions. A carbon nanotube junction, where two carbon nanotubes with different diameters are connected [27], is expected to act as a molecular electronic device, since it can exhibit metallic and semiconductive character, depending on its structure. However, when controlling the dynamics of molecules (handling not only the statically stable position of molecules but also their kinetics) and using nano-carbon as a molecular machine, the interactions between the carbon nanotube and the fluid molecules are important as well as the mechanical and electronic properties of the nanotube itself. From this point of view, carbon nanotube junctions can be regarded as a nanoscale nozzle and diffuser. There has been no previous consideration of carbon nanotube junctions as nanoscale nozzles or diffusers, though there have been extensive investigations into the electronic properties of carbon nanotube junctions [28]. In this study, we have conducted a molecular dynamics simulation of the Ar flow and the He flow inside carbon nanotube junctions.

2. Computational details

2.1. Computation model

We use a molecular dynamics method in this study [29]. In a molecular dynamics simulation, the dynamics of the system are obtained in a deterministic way by numerically solving the equations of motion for the atoms (or molecules) that it is composed of. The forces acting on each molecule are derived from the potential energy function that describes the interaction energy of the atomic system.

A carbon nanotube consists of a rolled-up hexagonal lattice of carbon atoms, and its structure is uniquely defined by a chiral vector [30]. The structure of a carbon nanotube junction can be determined by the two chiral vectors of the nanotubes that it is composed of [28]. Two nanotubes with different diameters can be connected by introducing a pentagon and a heptagon ring into the region of the junction [28] (Fig. 1). Such a junction structure was experimentally observed by Iijima et al. [27].

The initial configuration of the carbon atoms is determined based on the considerations described by Saito et al. [28]. In this study, we deal with a (12,12)–(8,8) nanotube junction comprising of a (12,12) nanotube and a (8,8) nanotube with their tube axes parallel to each other. The diameter of the (12,12) nanotube is $16.2 \times 10^{-10}$ m and that of the (8,8) nanotube is $10.8 \times 10^{-10}$ m.

A schematic view of the (12,12)–(8,8) nanotube junction model is shown (with coordinates) in Fig. 2. The structure of this model comprises of two connected nanotube junctions, and a periodic boundary condition is applied in the $z$ direction. The four nanotubes that this model incorporates each have a length of $49.12 \times 10^{-10}$ m, which corresponds to 40 atomic rings. The lengths of the two junction regions are $14.74 \times 10^{-10}$ m, respectively. Hence the total length of this model in the $z$ direction is $226.0 \times 10^{-10}$ m, and the total number of carbon atoms is 3680.

We compare the flow of Ar atoms with that of He atoms. The Ar or He atoms are placed in a form of cubic lattice with a lattice constant of $4 \times 10^{-10}$ m inside the (12,12)–(8,8) nanotube junction model. The total number of fluid atoms is 158. (The densities of liquid Ar and liquid He correspond to 1010 m and 3.76 $10^{-10}$ m, respectively [6].)

We use the interatomic potential energy function ascribed to Guo et al. [31], which was subsequently used by Tuzun et al. [6,32] to describe the interactions between carbon atoms. The potential function consists of a Morse-type functional form of bonding interaction (Eq. (1)), a harmonic cosine form of bending interaction (Eq. (2)) and 4-body term for the torsional interaction (Eq. (3)), where $\sigma^{\alpha\beta}$ is the distance between atoms $\alpha$ and $\beta$, $\theta^{\alpha\beta\gamma}$ is the bending angle subtended by atoms $\alpha$, $\beta$ and $\gamma$ and $\tau^{\alpha\beta\gamma\delta}$ is the dihedral angle comprising of atoms $\alpha$, $\beta$, $\gamma$ and $\delta$. The values of these parameters are listed in Table 1. The potential from Guo et al. is used in calculating the energetics, the structure, the mechanical and vibrational properties of single-walled carbon nanotubes [28].

![Fig. 1. Schematic view of the pentagon–heptagon pair in the nanotube junction.](image)

![Fig. 2. Initial structure of the (12,12)–(8,8) nanotube junction model.](image)

| Parameter | Value | Unit |
|-----------|-------|------|
| $D_e$     | $7.947168 \times 10^{-19}$ | J    |
| $\alpha_e$| $2.1867 \times 10^{-10}$  | m    |
| $r_e$     | $1.418 \times 10^{-10}$   | m    |
| $E_e$     | $4.664894 \times 10^{-19}$| J    |
| $\theta_0$| $120$                        | deg  |
| $C_e$     | $7.395968 \times 10^{-20}$ | J    |
carbon nanotubes and so on [33–35]. Later on, this type of potential is also used in other investigations [7, 8]. The nanotube junction does not undergo plastic deformation in the system we investigate here, so this type of potential is appropriate.

\[
\phi_{\text{bond}}(r_{\text{ab}}) = D_1(1 - \exp[-\alpha_c(r_{\text{ab}} - r_c)])^2
\]

(1)

\[
\phi_{\text{bond}}(\cos \theta_{\text{ab}}) = E_6(\cos \theta_{\text{ab}} - \cos \theta_0)^2
\]

(2)

\[
\phi_{\text{tension}}(r_{\text{ab}}) = C_e(1 - \cos 2\theta_{\text{ab}})
\]

(3)

The interactions between carbon and fluid atoms and between fluid atoms are modeled by the Lennard-Jones potential (Eq. (4)) [6]. The parameters are listed in Table 2. The cut-off distance of the Lennard-Jones potential is taken to be \(20 \times 10^{-10}\) m.

\[
\phi_{\text{LJ}}(r_{\text{ab}}) = 4\epsilon\left(\frac{\sigma}{r_{\text{ab}}}\right)^{12} - \left(\frac{\sigma}{r_{\text{ab}}}\right)^{6}
\]

(4)

2.2. Conditions

2.2.1. Relaxation calculation

Before starting the flow simulation, a stable atomic configuration for the system is obtained. The carbon atoms are clamped in four rings at each end and in the centre of the model (shown in Fig. 2 as the light colour) from the beginning of the simulation in order to fix the position of the model. The rest of the carbon and fluid atoms are given the initial velocities of the Maxwell–Boltzmann distribution at 300 K. The equation of motion is solved using the velocity Verlet method with a time step of 1 fs. Velocity scaling with a goal temperature of 300 K is applied for the initial 200,000 steps and is computed for the 100,000 subsequent steps with no temperature control.

2.3. Flow calculation

Using the atomic positions and velocities from the relaxation result, a flow simulation is then conducted. No initial streaming velocity is assigned to the Ar atoms but a driving force is applied to the whole system in order to induce a flow. A uniform gravitational field with a magnitude of \(1.5 \times 10^{12} \times 9.80665 \text{ m/s}^2\) is applied to the whole system in the cases of Ar flow and He flow (denoted as Case 1 and Case 2, respectively) and a driving force with the same magnitude \((3 \times 10^{-13} \text{ N/atom})\) is applied in Case 3 and Case 4. Case 5 and Case 6 are the calculation without the use of a driving force for comparison. The patterns of the analysis are summarized in Table 3. The nature of the driving force for the flow is fundamentally the same in Cases 1 and 2 and in Cases 3 and 4, but the viewpoints of comparison are different. A gravity-fed flow has been used in the molecular dynamics simulation of the fluid dynamics [36–38]. It is more realistic to induce a flow by a density gradient, but this gravity-fed flow is more computationally inexpensive, since there is no particle reservoir and a comparison with the same gravitational field can clarify any differences in the friction drag.

The equation of motion is solved using the 5-value Gear predictor-corrector method, with a time step of 0.5 fs. The flow calculation is conducted for 2,000,000 steps, and the data are sampled for the last 1,000,000 steps. Only the temperature of the carbon nanotube junction is controlled with a Nosé–Hoover thermostat with a goal temperature of 300 K.

### Table 2

| Pair of atoms | \(\sigma\) (m) | \(\epsilon\) (J) |
|---------------|----------------|----------------|
| C–Ar          | \(3.573 \times 10^{-10}\) | \(1.9643 \times 10^{-21}\) |
| Ar–Ar         | \(3.350 \times 10^{-10}\) | \(1.9886 \times 10^{-21}\) |
| C–He          | \(3.191 \times 10^{-10}\) | \(2.6646 \times 10^{-22}\) |
| He–He         | \(2.633 \times 10^{-10}\) | \(1.5008 \times 10^{-22}\) |

### Table 3

| Case | Fluid | Driving force |
|------|-------|---------------|
| 1    | Ar    | \(1.5 \times 10^{12} \times 9.80665 \text{ m/s}^2\) |
| 2    | He    | \(1.5 \times 10^{12} \times 9.80665 \text{ m/s}^2\) |
| 3    | Ar    | \(3 \times 10^{-13} \text{ N/atom}\) |
| 4    | He    | \(3 \times 10^{-13} \text{ N/atom}\) |
| 5    | Ar    | No driving force |
| 6    | He    | No driving force |

3. Results and discussion

The number density distribution of the fluid atoms in each case is shown in Fig. 3. The number density of the Ar

![Number density distribution of fluid atoms.](image-url)

Fig. 3. Number density distribution of fluid atoms. The density in the cylindrical region is plotted. By dividing the system into 10 bins in the \(z\) direction, the density can be calculated by using the volume estimated from the initial positions of the centre of the carbon atoms for simplicity, and the plotted data is the time average from 500 ps to 1 ns after the flow calculation started.
atoms is larger in the narrow tube than in the wide nanotube in Case 5, although the distribution of the He atoms is different (Case 6) when there is no driving force for the flow. This can be seen also in the snapshots of the flow (Fig. 4(e) and (f)). This difference is caused by the potential parameter $\varepsilon$. The attractive interaction is stronger between Ar and carbon atoms than it is between He and carbon atoms. This causes a difference in the density distribution at equilibrium. In other words, Ar atoms tend to be near to the wall of carbon atoms, while that is not the case for He. This is understood from the trajectory of a fluid atom shown in Fig. 5. The number density is estimated using a definition of volume derived from the initial position of the centre of the carbon atoms, hence the density distribution in Case 6 will be roughly uniform when using the volume derived at the position where the repulsive force from the carbon atoms vanishes.

When a strong gravitational field is applied in the $z$ direction, the density distribution of the Ar becomes different from the equilibrium state, while that of the He is about the same as the equilibrium state (see also Fig. 4(a) and (b)). In Case 1 the number density of the Ar atoms is larger in the wide nanotube than in the narrow nanotube, and the number density gets larger as the Ar atoms get nearer to the narrowing junction region within the wide nanotube. This is caused by the concentration of the Ar atoms at the entrance of the narrow channel. This does not seem to occur in Case 2. This difference is mainly due to the difference in the driving force itself. The gravitational field is the same but the difference in the atomic mass leads to a driving force.

Fig. 4. Snapshots of (a) Case 1, (b) Case 2, (c) Case 3, (d) Case 4, (e) Case 5, (f) Case 6, at 1ns. Carbon atoms with $y$-coordinates of less than 0 and all fluid atoms are displayed in a dark colour and a light colour, respectively.

Fig. 5. Trajectory of a fluid atom in (a) Case 1, (b) Case 2, (c) Case 3, (d) Case 4, (e) Case 5, (f) Case 6. The trajectory of the average value is plotted at several positions, each representing 500 steps of a fluid atom after 500 ps since the flow calculation started.
of $9.76 \times 10^{-13}$ N per one Ar atom and $9.78 \times 10^{-14}$ N per one He atom. Consequently, the average streaming velocity (which is the time-averaged $z$ velocity over all of the fluid atoms in the last 500 ps) of the Ar in Case 1 is 405 m/s, and that of the He in Case 2 is 150 m/s.

However, the characteristics of the density distributions of the Ar and He are clearly different when the same magnitude of driving force is applied to the system (see also Fig. 4(c) and (d)). The Number density of the Ar atoms is larger in the narrow nanotube than in the wide nanotube in Case 3, and this is about the same as for the equilibrium state in Case 5. On the other hand, the number density of the He atoms in Case 4 is even larger in the wide tube in the vicinity of the narrowing junction and is smaller in the narrow tube as compared to equilibrium state in Case 6, due to the effect of congestion of the He atoms at the narrowing junction region of the nanotube. The Average streaming velocity of the Ar in Case 3 is 66 m/s and that of the He in Case 4 is 417 m/s.

The atomic mass of Ar is about 10 times larger than that of He, so the force that is necessary to accelerate the Ar atoms is larger than in the case of the He atoms. However, the same gravitational field does not lead to the same average streaming velocity. This is due to the friction drag of the Ar in the nanotube junction being larger than that of the He, which originates from the interactions between the atoms. The tendency for an Ar atom to get near to the wall can also be seen when Ar atoms are flowing in Case 1 and Case 3, as well as in the equilibrium state in Case 5, while this is not the case for He (Fig. 5).

Fig. 6 shows that the streaming velocity, i.e. the velocity in the $z$ direction, is larger in the narrow nanotube than in the wide nanotube in each case. Although the $y$ velocity is uniformly 0 m/s in all cases (Fig. 7), the characteristic distribution of the $x$ velocity can be seen in Fig. 8. This is caused by the form of the junction regions. The centre of the cross section of the tube translates in the minus $x$ direction in the narrowing junction region and in the plus $x$ direction in the widening junction region. The former leads to the collision of Ar atoms with the wall and a negative $x$ velocity in the narrowing junction region. The latter leads to a positive $x$ velocity in the widening junction region. It can be seen from Figs. 6 and 8 that the absolute value of the $x$ velocity becomes larger as the $z$ velocity becomes larger for the cases of both Ar and He.

Fig. 9 shows the temperature distribution of the fluid in each case. By dividing the system into 10 bins in the $z$ direction, the temperature of fluid in each bin can be calculated by Eq. (5)–(8) [39], where $T$ is the temperature of the fluid, $T_x$, $T_y$, $T_z$ are the $x$, $y$ and $z$ components of the temperature of the fluid respectively, $v_x$, $v_y$, $v_z$ are the $x$, $y$ and $z$ components of the velocity of each fluid atom respectively, $m$ is the mass of a fluid atom, $N$ is the number of fluid atoms in a bin, and $E$ is the internal energy of the fluid.
of a fluid atom in a bin and $k_B$ is the Boltzmann constant. The time average of the temperature and the velocity can now be calculated, excluding the steps when there are no fluid atoms in a bin.

$$T_x = \frac{m}{k_B N} \sum v_x^2 \tag{5}$$

$$T_y = \frac{m}{k_B N} \sum v_y^2 \tag{6}$$

$$T_z = m \left[ \frac{1}{N} \sum v_z^2 - \left( \frac{1}{N} \sum v_z \right)^2 \right] \tag{7}$$

$$T = \frac{1}{3} (T_x + T_y + T_z) \tag{8}$$

The temperature distribution of the Ar in Case 1 is much higher than 300 K, i.e. the temperature of the nanotube junction as a whole. The temperature of the Ar is markedly higher in both junction regions and lower in the narrow nanotube. The temperature is higher in the high Ar-density region because colliding interactions between atoms increase. The collision of Ar atoms with the wall causes the higher temperature in the vicinity of the narrowing junction. Ar atoms with a large streaming velocity enter the high Ar-density region from the low Ar-density region in the region of the widening junction, which causes the higher temperature that is noted there. The temperature of the He in Case 2 is about 300 K except in the region of the narrowing junction. The temperature of the Ar in Case 3 is higher in this region. The mechanism that causes the higher temperature in this region is the same as that in Case 1. The temperature of the Ar in Case 3 becomes lower than 300 K just downstream from the narrow nanotube because the density of the Ar is low and the streaming velocity is small, which leads to weak colliding interactions and a small variance in the $z$ velocity. The temperature of the He in Case 4 is higher at the narrowing junction region and lower in the narrow nanotube, but it is lower than in Case 1 throughout the system. The temperature of the Ar becomes higher as the streaming velocity becomes larger (compare Case 1 with Case 3) as is the case in He (compare Case 2 with Case 4), but the temperature of the Ar in Case 1 is much higher than that of the He in Case 4. This is mainly because the temperature of the Ar that corresponds to the same thermal velocity is higher than that of the He with its different atomic mass, and partly because the smaller diameter of a He atom than an Ar atom leads to a weaker interaction between He atoms.

4. Concluding remarks

In this paper, we reported on a molecular dynamics simulation of the flow of Ar and He atoms inside a nanotube junction as a nanoscale nozzle and a diffuser. Interactions with the wall, which depends on the diameter of the nanotube and especially with the junction region, lead to a characteristic distribution of number density, temperature and velocity of Ar and He atoms that are different from the equilibrium state at the nanoscale. A microscopically localised higher temperature for the fluid inside the nanotube junction indicates the heating of a small quantity of molecules, while the production of a microscopically localised higher density of fluid molecules and higher frequency of collisions between molecules may make it possible to tune the conditions of a chemical reaction at the molecular level. The control of not only the equilibrium position or the shape of the materials statically, but also controlling the dynamic motion of the molecules is a further extension of the present basic study that may become an important aspect of nanotechnology in the future.

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