# Molecular Dynamics Study of Temperature Dependence of Water Flow through Carbon Nanotube Junction using Reflecting Particle Method

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## Summary

Carbon nanotube junctions, where two nanotubes with different diameters are connected, can be viewed as a nanoscale nozzle. We have conducted molecular dynamics simulation of water flow inside a (12,12)-(8,8) carbon nanotube junction. Using the reflecting particle method, dependence of the temperature of water reservoir on the dynamics is analysed. The density and the velocity distribution of the water inside (12,12)-(8,8) carbon nanotube junction are qualitatively the same regardless of the temperature of the system as a whole when the water density in the system is large.

## Introduction

Nanofluidics is a promising field in nanotechnology in view of making it possible to transport materials to the molecular level of accuracy, producing nanoscale reactors, sensors and actuators. Carbon nanotubes can be expected as suitable for such applications since they have cylindrical shapes with an atomic accuracy, and they have the characteristics of an intersection between machine, material and device.

In this context, carbon nanotube junctions[1], which have attracted attention as molecular electronic devices[2], can be viewed as molecular nozzles and diffusers[3]. Here, we have conducted molecular dynamics simulation of water flow inside a (12,12)-(8,8) carbon nanotube junction, using the reflecting particle method[4] that yields a driving force of the flow.

## Computational Details

Two carbon nanotubes with different diameters can be connected and the structure is determined uniquely by introducing pentagon and heptagon pair in the junction[2]. In this paper, we consider (12,12)-(8,8) carbon nanotube junction, where (12,12) nanotube and (8,8) nanotube is connected with their tube axes parallel to each other. The length of each nanotube is 20 carbon rings, corresponding to $24.6\times10^{-10}$ m, and the total length of the nanotube junction is $63.9\times10^{-10}$ m. Cubic volumes of fluid reservoirs with $30\times10^{-10}$ m on a side are placed on the two sides of the nanotube junction. A schematic view is shown in Fig.1.

The potential energy function that describes carbon-carbon interactions is described by Morse function (Eq. (1)), harmonic cosine angle (Eq. (2)) and dihedral terms (Eq. (3)),

$$\phi_{\mathrm{bond}}(r^{\alpha\beta}) = D_{\mathrm{e}}\{1-\exp[-\alpha_{\mathrm{e}}(r^{\alpha\beta}-r_{\mathrm{e}})]\}^2 \quad (1)$$

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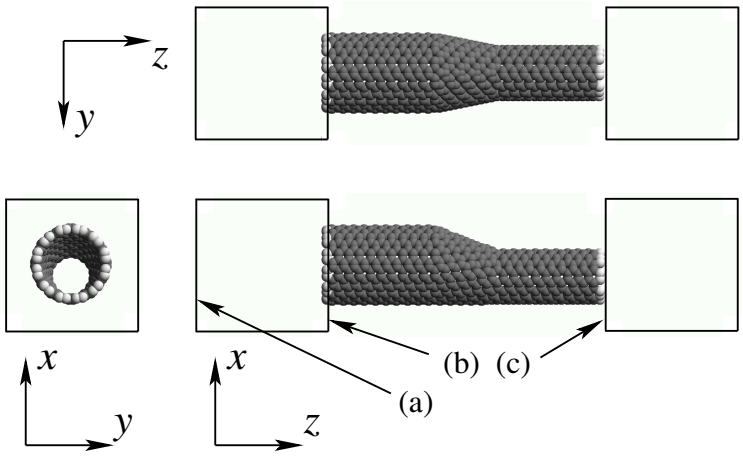



Figure 1: Computational model

$$\phi_{\mathrm{bend}}(\cos\theta^{\alpha\beta\gamma}) = E_{\mathrm{e}}(\cos\theta^{\alpha\beta\gamma} - \cos\theta_0)^2 \tag{2}$$

$$\phi_{\mathrm{torsion}}(\tau^{\alpha\beta\gamma\delta}) = C_{\mathrm{e}}(1 - \cos 2\tau^{\alpha\beta\gamma\delta}), \tag{3}$$

where $r^{\alpha\beta}$ 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 comprised of atoms $\alpha$, $\beta$, $\gamma$ and $\delta$. This potential function for carbon is developed by Guo et al.[5]. The parameters $D_{\mathrm{e}}$, $\alpha_{\mathrm{e}}$, $r_{\mathrm{e}}$, $E_{\mathrm{e}}$, $\cos\theta_0$, $C_{\mathrm{e}}$ are the same as Ref. [3].

Flexible SPC model[7] is used as the potential function of water. Intra-molecular potential $\phi_{\mathrm{intra}}$ is described by a harmonic interaction of the bonds between oxygen and hydrogen atoms and the angle subtended by three atoms. Inter-molecular interaction $\phi_{\mathrm{inter}}$ is described by Lennard-Jones potential $\phi_{\mathrm{LJ}}$ between carbon and oxygen atoms and between oxygen atoms, and smoothly truncated Coulomb potential $\phi_{\mathrm{E}}$[6],[8],

$$\phi_{\mathrm{intra}} = \frac{1}{2}K_{\mathrm{Wr}}(r^{\alpha\beta} - r_{\mathrm{W}})^2 + \frac{1}{2}K_{\mathrm{W}\theta}(\theta^{\alpha\beta\gamma} - \theta_{\mathrm{W}})^2 \tag{4}$$

$$\phi_{\mathrm{inter}} = \phi_{\mathrm{LJ}}(r^{\alpha\beta}) + \phi_{\mathrm{E}}(r^{\alpha\beta}) \tag{5}$$

$$\phi_{\mathrm{LJ}}(r^{\alpha\beta}) = 4\varepsilon\left\{\left(\frac{\sigma}{r^{\alpha\beta}}\right)^{12} - \left(\frac{\sigma}{r^{\alpha\beta}}\right)^{6}\right\} \tag{6}$$

$$\phi_{\mathrm{E}}(r^{\alpha\beta}) = \frac{1}{4\pi\varepsilon_0}\left(\frac{q^{\alpha}q^{\beta}}{r^{\alpha\beta}} - E_{\mathrm{s}}(r^{\alpha\beta})\right), \quad E_{\mathrm{s}}(r^{\alpha\beta}) = \frac{q^{\alpha}q^{\beta}}{r_{\mathrm{c}}} - (r^{\alpha\beta} - r_{\mathrm{c}})\frac{q^{\alpha}q^{\beta}}{r_{\mathrm{c}}^2} \tag{7}$$

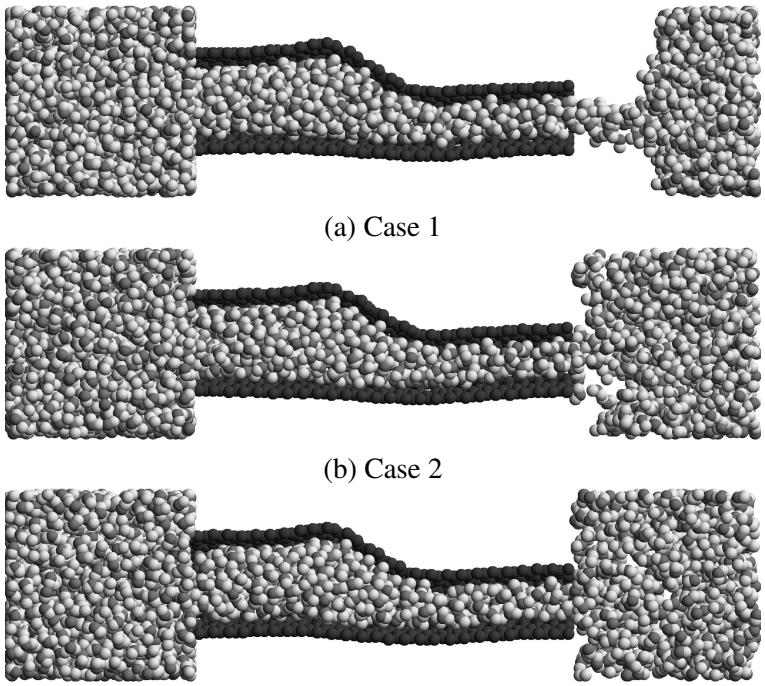
where $q^{\alpha}$ is the electric charge, and $\varepsilon_0$ is the permittivity in a vacuum. See Ref.[6] and [8] for details about parameters related to water. In this paper, all of the cutoff distances including $r_c$ are $10\times10^{-10}$ m.

Periodic boundary condition is applied in the $x$, $y$ and $z$ direction of the system. Reflecting particle method[4] is used as a part of boundary conditions and it generates the driving force of the flow (Fig.1(a)-(c)). On the plane (a) in Fig.1, particles pass through it in the positive $z$ direction with periodic boundary condition, but they are elastically reflected when they pass through in the negative $z$ direction. Atoms passing through the plane (b) in the positive $z$ direction outside (12,12) nanotube entrance and passing through the plane (c) in the negative $z$ direction outside the (8,8) nanotube entrance are also reflected. The reflection of the atoms is incorporated only by changing the sign of the velocity component in the normal direction of the boundary plane.

The water molecules are placed in the two cubic volumes in the liquid density with the initial velocity of Maxwell-Boltzmann distribution without the additional initial streaming velocity. The velocity Verlet method is used with the time step of 0.2 fs. After 200000 steps of calculation with a velocity scaling applied to the whole system, 300000 steps of the calculation without temperature control is done. The data is sampled during the last 100000 steps. Three patterns of calculation are done with goal temperature 300 K( Case 1), 500 K( Case 2), and 700 K( Case 3). The number of carbon atoms and water molecules are 1044 and 1798, respectively.

## Results and Discussions

The snapshots of the flow are shown in Fig.2, and the density distribution of water molecules inside nanotube junction is shown in Fig.3. Volume of each bin of nanotube junction is calculated by the initial center-of-mass positions of the carbon atoms. The density of water is higher in the wide (12,12) nanotube than in the narrow (8,8) nanotube, and it becomes higher as the water gets closer to the entrance of the junction region. These characteristics are the same in the previous report of Ar and He flow inside nanotube junction with different model configuration under a strong gravitational driving force[3]. The water density distribution is qualitatively the same and quantitatively quite similar regardless of the temperature difference, mainly because of the high density of water in the system. The velocity distribution of the water throughout the system is shown in Fig.4. The water is accelerated when it enters the narrow (8,8) nanotube, and there is also the nonzero velocity component in the negative $x$ direction in the junction region in all of the three cases. No streaming $y$ velocity is observed. These are also the same properties observed in the previous report[3]. The streaming velocity is larger as the total temperature of the system gets higher because the magnitude of the driving force of the flow generated by reflecting boundary is different. Since the driving force of the flow is generated by the boundaries that elastically reflect water molecules, the larger the molecular thermal velocity is, the larger the streaming velocity generated from it. The temperature distribution of water is shown in Fig.5. In this graph, the temperature is calculated by the translational motion of the molecular center of mass, subtracting the streaming velocity in $z$ direction in each bin. The temperature of the water is lower in the nanotube junction in all cases, and it



(a) Case 1

(b) Case 2

(c) Case 3

Figure 2: Snapshots of the system at 100 ps.

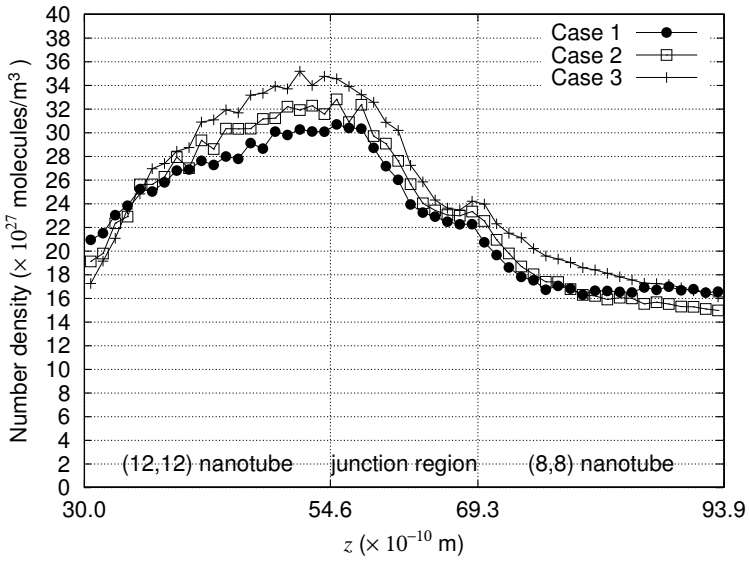



Figure 3: Density distribution of water molecules inside nanotube junction.

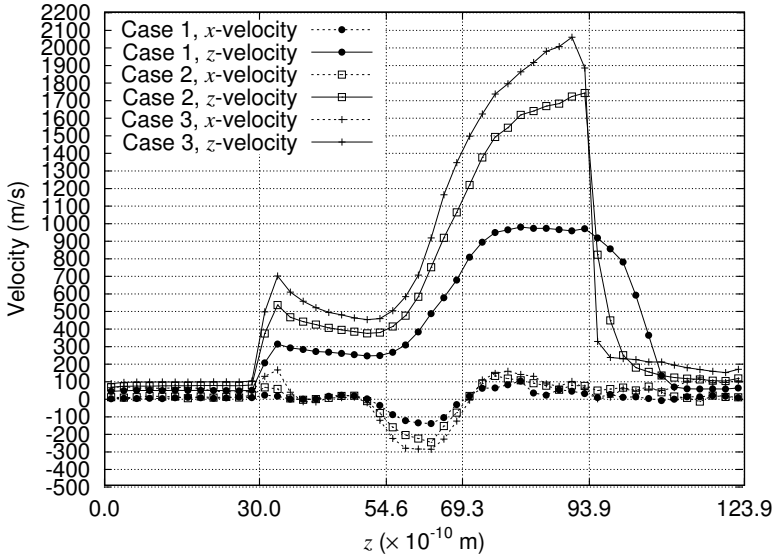



Figure 4: Streaming velocity distribution of water.

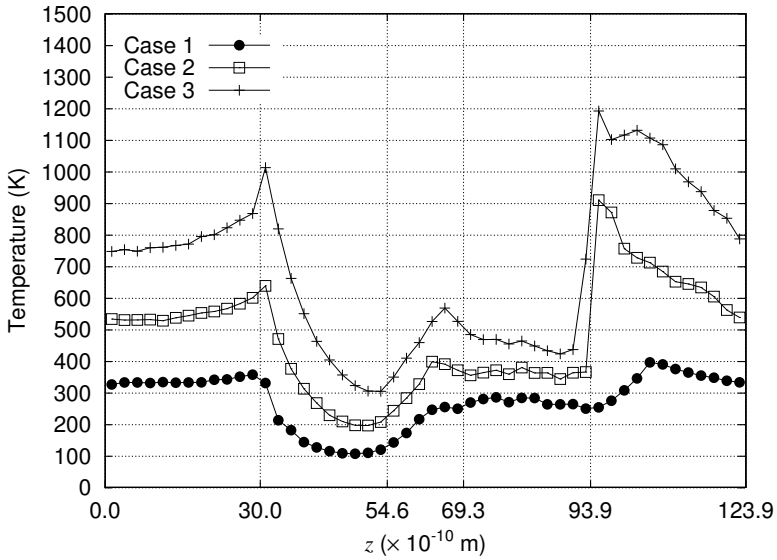



Figure 5: Temperature distribution of water.

is especially lower in the wide (12,12) nanotube than in the narrow (8,8) nanotube. The temperature of the nanotube junction continuously decreases after stopping the temperature control because of the property of the reflecting particle method which modifies the molecular velocity without changing the total energy in the system.

## Conclusion

We have conducted molecular dynamics simulation of water flow inside nanotube junction as a nanoscale nozzle, and we used reflecting particle method to induce the flow. The temperature of the nanotube junction decreased because of the inversion of the velocity direction of atoms comprising water molecules at boundaries while conserving total energy in the system. However, the observed density, velocity and temperature distribution of the water flow inside (12,12)-(8,8) carbon nanotube junction are qualitatively the same regardless of the temperature of the system as a whole when the water density in the system is large.

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