A Comprehensive Study of Water Transport Mechanisms through Carbon Nanotubes

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Abstract

Carbon nanotubes (CNT) are one of the most widely used and ideal nanofluidic devices. With an ever increasing field of applications, it becomes important to study novel mechanisms used to transport water molecules through carbon nanotubes and to compare the effectiveness and rate of fluid flow provided by them. In this study, we have considered three popular non-conventional mechanisms for pumping water through a CNT, namely, thermally driven flows, by rotating chiral CNT and by applying AC electric field to a carbon nanotube. Using molecular dynamics simulations these mechanisms are studied systematically to understand the flow behaviour inside carbon nanotubes and the pumping mechanism. Finally, a comprehensive analysis, of the efficiencies of flux obtained by the aforementioned mechanisms are presented in this work.

1 Introduction

Understanding of water transport through nanofluidic devices is of immense importance considering its potential applications in the fields of medical drug delivery systems, microbiological devices, nanorobotics, micro flow control and thermal management in MEMS/NEMS devices etc. To this front, carbon nanotubes (CNT) [1] are one of the most widely used and are also the ideal nanofluidic devices as they allow almost frictionless fluid flow through them [2]. The recent advances in the manufacturing of carbon nanotubes as well their hydrophobic properties have seen their widespread use in various industrial processes such as filtration, desalination[3] as well as in flow meter devices[4].

The transport of water molecules through the CNTs are stimulated through various mechanisms like hydrostatic pressure [5], rotation of a chiral CNT [6], AC electric fields [7], thermal flows with a temperature difference along the ends of the CNT [8] and passing Rayleigh waves along the surface of CNT [9]. The flow of water through CNT in all of the above-mentioned cases is governed through a multitude of factors, such as the nature and magnitude of the driving forces, the thermodynamic state of the system, the diameter, chirality and the length of the CNT. This clearly shows us

that there are a large number of factors involved in choosing a suitable CNT and an appropriate pumping mechanism to meet the needs of the user. Furthermore, there may possibly be more than one combination through which desired flow properties (thermodynamic state and the flow rate) can be obtained.

Three popular non-conventional mechanisms of pumping water through a CNT are, namely, thermally driven flows, rotation of chiral CNT and AC electric field driven flows. These mechanisms are explained in the following sections.

1.1 Thermally driven flows

The temperature of any system provides the thermal fluctuations associated in the molecules for the given value. Due to these thermal motions, the atoms move randomly in all the directions. When a passage for these random motions becomes restrictive than the atoms move only as the passage directs. This very nature of motions is been utilised in the transport of water molecules through carbon nanotubes. When a passage viz., CNT, is provided to water molecules present in two reservoirs at different temperatures, the asymmetric thermal fluctuations causes the water molecules to flow from one reservoir to another, as described by Zhao *et al.* [10]. They found a continuous flux of water being transported from the hot reservoir to the cold reservoir when the temperature difference is about 15-70 K, through a small (6,6) CNT. The flux obtained through this system is equivalent to that of the flux generated by a hydrostatic pressure difference which is of the orders of megapascals.

Zhao *et al.* [10] theorised that the forces working in the direction of the flow are neither the thermophoretic forces nor the thermal transpiration. This is because, as the water flows rapidly against the chemical potential barrier, the flow rate is independent of the length of the CNT, and hence, it is independent of the temperature gradient. The phenomenon that causes this flow of water from the hot reservoir to cold reservoir is not very clear and that forms one of the focuses of the current work and in order to understand the phenomenon, a number of simulations are carried out by varying the temperatures of the two reservoirs over a wide range.

1.2 AC electric field

When an electric field is applied to a CNT in the form of a travelling wave, it causes the water molecules to follow the gradients in the electric field due to their existence as dipoles. Klaus *et al.* [7] postulated an elaborate polarisation dragging theory to describe the effect of AC electric field on water molecules by simulating a system that uses discrete charged electrodes to simulate the travelling electric field wave. This travelling wave breaks the spatio-temporal symmetry of the water molecules and creates wave packets by periodically polarising the water in the direction of the local electric field. The resultant of this localised effect is that the packets of water molecules orient in opposite directions and are forced to travel along with a particular wave packet. As the wave itself travels along the CNT, this causes the water molecules to be dragged along with the wave packets and be pumped out of the tube. Dependence on the strength of electric field is studied in this work.

1.3 Rotation of CNT

Pumping water by rotating the chiral CNT is one of the unique concepts and it is possible because of the structure of CNT. The structure of a chiral CNT is such that there exists an asymmetry in one direction. This asymmetry interacts through mechanical impingement with water molecules. When a chiral CNT is rotated, this asymmetry of CNT produces the required axial force on the water molecules which moves them ahead along the length of CNT. Feng *et al.* [6] attempted to fit an empirical relation to the potential energy landscape to characterise the forces pushing the water out and came up with an empirical relation of the following form as given in Eq. 1 [6].

$$\begin{aligned} V(\theta,z,\omega,t) = {} & a\sin(n(\frac{5}{\sqrt{3}r}z+\theta-\omega t)) + b\cos(n(\frac{5}{\sqrt{3}r}z+\theta-\omega t)) \\ & + c\sin(2n(\frac{2}{\sqrt{3}r}z-\theta+\omega t)) + d\cos(2n(\frac{2}{\sqrt{3}r}z-\theta+\omega t)) \\ & + e\sin(3n(\frac{1}{3\sqrt{3}r}z+\theta-\omega t)) + f\cos(3n(\frac{1}{3\sqrt{3}r}z+\theta-\omega t)) + V_0 \end{aligned} \tag{1}$$

where, r denotes the radius of CNT, and a, b, c, d, e, f, V_0 are constants being obtained by fitting the function to the potential energy landscape.
The potential energy landscape depends on the parameters like radius and angular velocity of CNT, which can be readily changed, hence changing the flux of water being pumped through it. The flux is thought to increase with both radius and angular velocity, however Feng *et al.* [6] claim that increasing the angular velocity beyond a certain value decreases the pumping flux as the water molecules fail to adjust their structure to that of the fast rotating CNT. This is because as the time period of the oscillating potential energy landscape is faster than the relaxation time of water molecules. The interaction of the water molecules close to the wall to those near the centre transfers this axial force across the radial direction. A thick (16,32)CNT is used by [3] to ensure that the distribution of water molecules inside the CNT is unstructured and thus more efficient pumping of water is achieved.

This pumping efficiency can also be increased by decorating the CNT with any functional group. This functional group will induce a higher flow rate through physical means, such as that used in an Archimedes screw. Flow rates can also be increased with electrically charged particles, which would simulate a moving electric field on rotation of the CNT, similar to an AC electric field through the CNT. This can also be seen in the potential function proposed by Feng [6], the decoration increases the slope of the potential energy function, leading to larger forces.

In this study, we use molecular dynamics simulations to characterise various pumping mechanisms. A detailed study to estimate the flow rate of water molecules through CNT by using the above-mentioned mechanisms are attempted. In the remainder of the paper, computational details employed to describe each mechanism is provided in Sec. 2 followed by results and discussion where an elaborate description of flow rates obtained for each of the mechanisms are presented and finally concluding remarks are made in Sec. 4.

2 Computational Details

All the molecular dynamics simulations are carried out using the LAMMPS [11], an open source molecular dynamics package. Firstly, the common computational details that are been maintained constant in all the case studies that are carried out in this work are presented and later computational details that are relevant to particular mechanisms are explained. The system consists of a single carbon nanotube that connects the two reservoirs on either end of it as shown in the Fig. 1. The carbon atoms present in CNT are terminated using hydrogen at both ends. The TIP4P [12] model of water is used. The pppm style invokes a particle-particle particle-mesh solver [13] which maps atom charge to a 3d mesh, using 3d FFTs to solve PoissonвЂ˜Єs equation on the mesh and then interpolates electric fields from the mesh points back to the atoms. The radial distribution function Fig. 2, plotted for this model shows that the potential predicts the behaviour of water molecules as obtained in literature [14]. CHARMM [15] force fields are used to model the interactions between carbon and water molecules. A time-step of 1 femtosecond is considered for all the cases studied in this work.

To statistically average the data obtained, the length of CNT is divided into 40 bins, each bin 0.4 nm in length, and the centre of mass velocities from each bin is calculated to determine the flow characteristics. The CNT was also divided into 4 concentric bins, each of thickness 0.1 nm, to find the variation of the flow characteristics between the CNT axis and walls. The system is first relaxed to a state of local minimum energy using the Polak-Ribiere [16] version of the conjugate gradient (CG) minimization algorithm. Nosé [17]-Hoover [18] thermostat is used to maintain the temperatures of water molecules. The time integration for the water molecules inside the CNT is performed by NVE integrator. Periodic boundary conditions were used in all directions. The system is allowed to simulate for 11 ns out of which the system is equilibrated for 1 ns and the next 10 ns of the simulation are considered to obtain the desired results.

Now, the computational details pertaining to the specific pumping mechanism are explained in following subsections.

2.1 Thermally driven flows

To generate a thermally driven flow a (15,14) CNT of 10 nm length is used to connect the two reservoirs that are placed on either side, each consisting of 5120 water molecules and are confined between two graphene sheets, with dimensions of 100 Å x 50 Å x 32 Å as shown in Fig. 1. This corresponds closely to a density of 1 g/cc of water at STP. At the initial timestep, there are no water molecules inside CNT. The CNT is held rigid and fixed in the same position. Various cases studies are considered by varying the temperature of the two reservoirs.

2.2 AC electric field

In this case, the system dimensions follow same as that used for thermally driven flow expect that one of the reservoirs is filled with water while the other is kept

empty. A number of cases studies were carried out by varying the magnitude of the electric field from 0 to 0.1 V/Å keeping the wave number and frequency constant.

2.3 Rotation of CNT

To pump water molecules through a rotating CNT, an asymmetric (chiral) CNT is required. Therefore, a chiral (16,32) CNT of length 10 nm is used. Each reservoir has the dimension of 100 Å x 50 Å x 63 Å and possesses 10240 water molecules, corresponding to the density of 1 g/cc of water. Case studies by varying the angular velocities of CNT are carried out and also the CNT is rotated both clockwise and counterclockwise direction to better understand the pumping mechanism. Fig. 3 shows the schematic of the simulation domain for this case.

3 Results and Discussion

In this section, we present and discuss the functioning of each mechanism used to pump water molecules through CNT. The focus of the present work is to understand the pumping mechanisms and calculate the flux rate for each mechanism. We have also calculated the number density of water molecules present across the CNT. This number density distribution across the CNT helps us to analyse where the water molecules are more concentrated. In the subsequent subsections, results and their analysis for each of the mechanism to pump water is presented.

3.1 Thermally driven flows

To study the thermally driven flow, several cases were considered in which the temperature of each of reservoirs are varied so as to have a temperature difference that would drive the molecules from one reservoir to another. As mentioned in the Sec. 2, the time integration for the water molecules in the reservoir were carried out by NVT ensemble while the time integration for water molecules inside CNT was performed by NVE ensemble.

Firstly, radial number density across the channel is calculated for various temperatures considered in this work. It is observed that the number of water molecules remained larger at the centre of CNT and gradually reduced when moved towards the walls. This clearly indicates that friction offered by the walls is very less, as the reduced number density near the walls indicate lesser fluid-surface interaction. The following Fig. 4, shows the distribution of number density radially across the CNT for various cases. Fig. 4, also clearly indicates that the radial distribution of number density does not vary much with the change in temperature.

Next, the flux of water molecules flowing through the CNT is presented in Table 12. As the temperature difference increases the flux rate also increases due to increased internal energy in the molecules. The sign of flux indicates the direction of flow and it is evident that the movement of water molecules is from the reservoir having the higher temperature to that of reservoir kept at lower temperature. Observing the direction of flow of water molecules we can say that due to increased internal

energy and confinement along a passage, the water molecules are forced to move in one particular direction.

Center of mass velocity (Z component) plotted along the CNT (aligned in Z direction) as shown in Fig. 5 indicates that the water molecules in the reservoir kept at higher temperature prefers to move towards the reservoir kept at lower temperature, while the molecules from the lower temperature reservoir move towards the higher temperature reservoir. However, due to their higher kinetic energies, the molecules of the high-temperature reservoir clearly dominate over the others, thus driving a net flow. Thus, it is the thermal motion of water molecules that drives the water molecules through CNT.

3.2 AC electric field

To study the pumping mechanism by using AC electric field, a travelling electric field is applied to the water molecules present in the CNT. This travelling wave drags the water molecules along it as it is explained in Sec. 1.2 By varying the strength of electric field from 0.1 V/Å to 1 V/Å, properties like radial number density distribution across the CNT and flux of water molecules are calculated.

The behaviour of radial number density across the channel is similar to that of the thermally driven case where the number of water molecules is higher at the centre of CNT than at the walls. For all the cases considered the behaviour remained similar without much difference indicating that the effect of electric field on the number density distribution negligible. The Fig. 6 show the distribution of number density radially across the CNT for various values of electric field.

Now, the flux of water molecules flowing through the CNT due to the presence of electric field are calculated and is presented in Table 14. With the increase in strength of electric field, the flux of water molecules also increased. This is because the moving travelling electric field has greater strength to pull the water molecules with it now. It is also observed that when the phase of this electric field is shifted by 180 degrees the results obtained remained same as that without phase shift.

3.3 Rotation of CNT

We now present the results for the case of rotating CNT obtained by our molecular dynamics simulations. The system consists of thick, chiral (16,32)-CNT, connecting two reservoirs, one of which is empty while the other is filled with water as mentioned in Sec. 2.3. The CNT is rotated at various angular speeds in both clockwise and anticlockwise directions.

Interestingly, the behavior of the radial number density distribution remained the same showing the consistency in the results obtained. As the CNT used for this case has a larger diameter than the other mechanisms, the graph appears different as can be seen in Fig. 7. Here the distribution remains constant for certain distance near the centre and distribution does not vary much with the variation in rotational speeds.

We then calculate the flux of water molecules that is being pumped out of CNT. We observe that the flux of water molecules shows a significant dependence on the angular speed of CNT. Table 14 shows the flux of water molecules that have been pumped out through CNT when CNT is rotated at various angular speeds in both clockwise and anticlockwise direction. It is observed that with an increase in angular speed, there is an increase in the number of water molecules that have been pumped out. It is found to be in qualitative agreement with the results from the works of Tu *et al.* [3] and of Feng *et al.* [6], who found a strong relationship between the rotation speed and cumulative flux of water molecules through CNT. It can also be observed that the there is negligible change in flux when the CNT is rotated either in the clockwise or anticlockwise direction as indicated in Table 14.

4 Concluison

In this study, molecular dynamics simulations were employed to study three nanoscale pumping mechanisms to transport water molecules through CNT. In the case of thermally driven flow case, the temperature difference maintained between two reservoirs enabled the transport of water molecules through the CNT. Due to high temperature, the thermal modes in water molecules have agitated and by confining the movement finite flow rates were achieved. In the case of AC electric field, the travelling wave drags the water molecules along with it and thus creating a finite flux.

Though with the increase in AC electric field the flux of water molecules increases, achieving very high electric field is difficult and at very high electric fields there is a possibility of breaking the water molecule. In the last mechanism, rotation of CNT, the transport of water molecules takes place due to structure (chirality) of CNT. Only a chiral CNT can transport water when rotated. It is also observed that as the rotational speed of CNT is increased, the flux of water molecules also increased. Flux is observed not to vary much with the direction of rotation. Thus, the above-mentioned nanoscale scale pumping mechanisms have crucial applications in various fields and to increase the pumping rates with higher efficiencies one can develop a hybrid mechanism combining the above-mentioned mechanisms.

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Table 12: Table showing flux of water molecules being pumped out of CNT for various temperatures of reservoirs

Temperature (K)		Flux of water molecules
Upper Reserviour	Lower Reserviour	
300	300	0.00510
400	300	-0.0700
500	300	-0.0515
500	400	-0.0650
600	500	-0.0340

Table 13: Table showing flux of water molecules being pumped out of CNT for various electric fields

Electric Field (eV)	Flux of water molecules
0	0.198
0.025	0.254
0.05	0.254
0.075	0.260
0.1	0.295

Table 14: Table showing flux of water molecules being pumped out of CNT for various rotational speeds in both clockwise and anticlockwise rotation

Rotational Speed (rad/ns)	Flux of water molecules	
	Clockwise	Anti-Clockwise
0	0.04	0.04
6.195	0.12	0.09
12.39	0.25	0.27
24.78	0.74	0.75

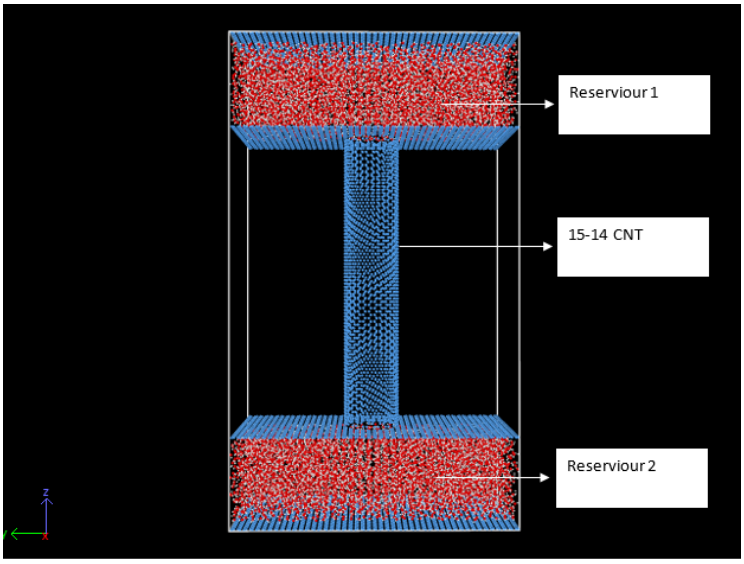

Figure 1: Schematic of simulation domain

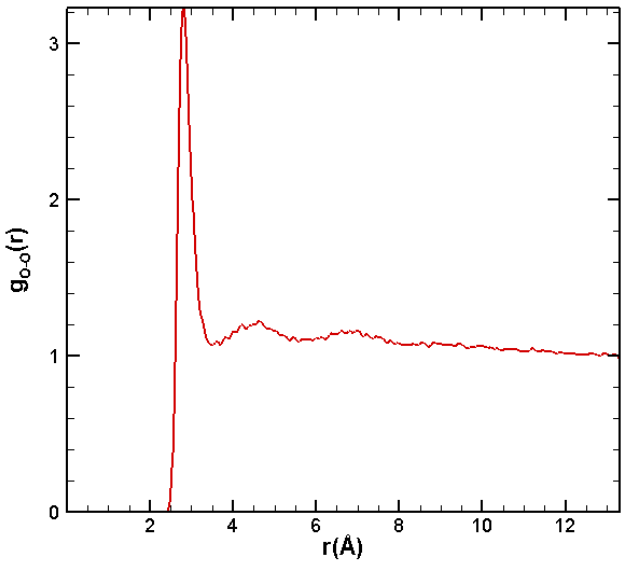

Figure 2: Radial distribution function of oxygen atoms in water molecule.

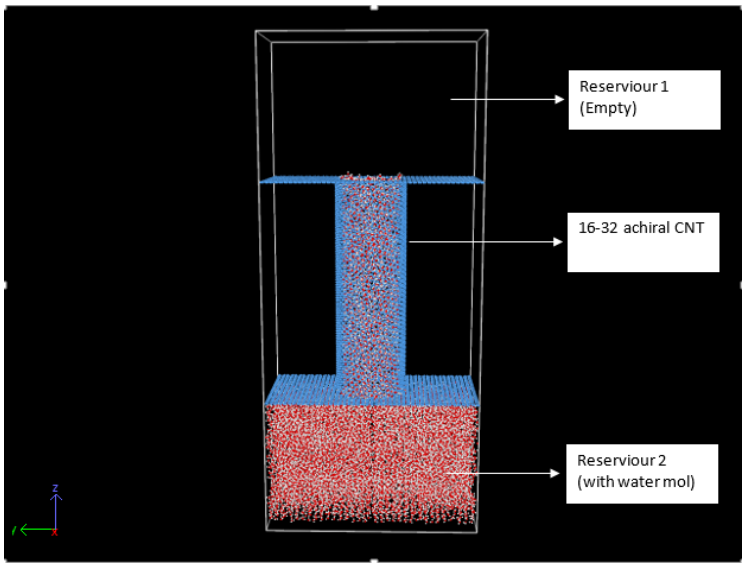

Figure 3: Schematic of simulation domain used to study rotation of CNT case

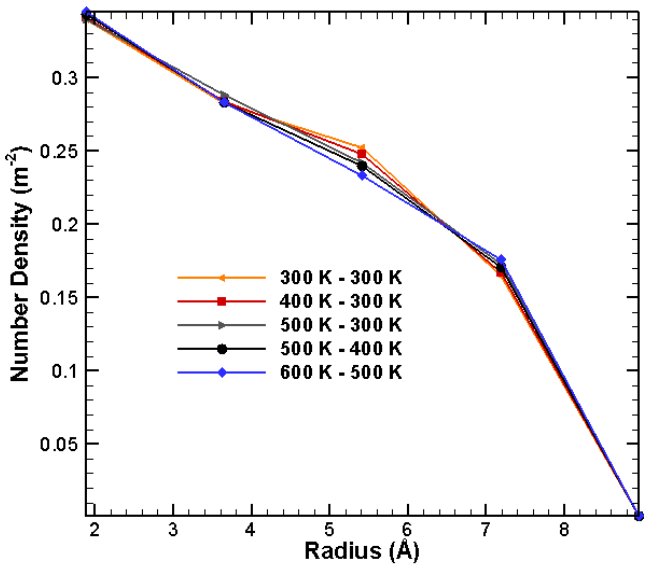

Figure 4: Cumulative radial number density of water molecules inside carbon nanotube in radial direction for various temperatures of reservoirs

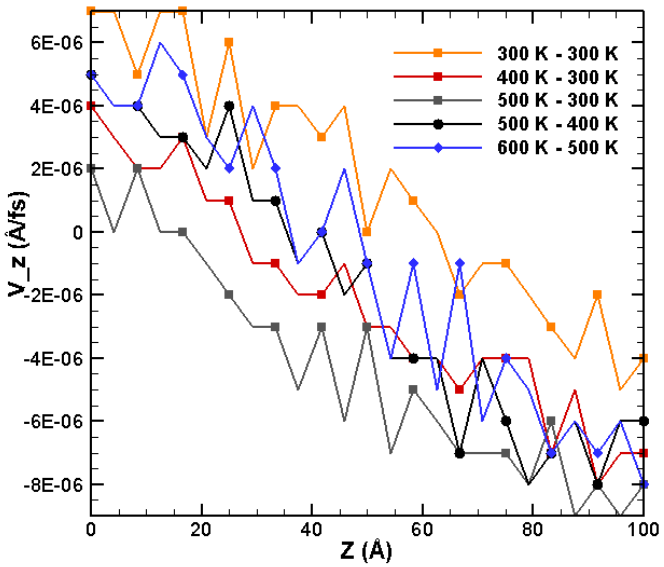

Figure 5: Center of mass velocity (Vz) of water molecules in each bin along the length of CNT

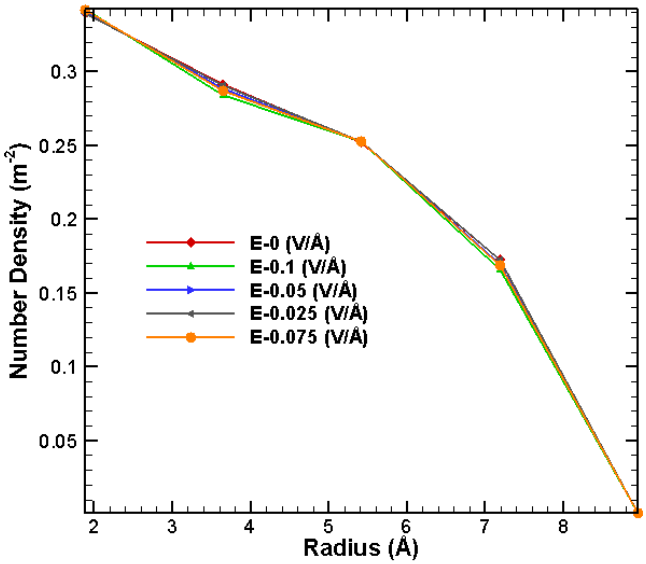

Figure 6: Cumulative radial number density of water molecules inside carbon nanotube in radial direction for various electric fields

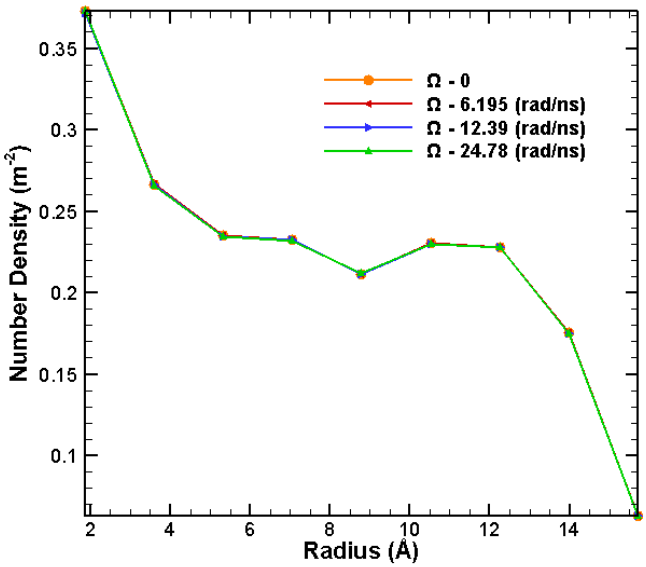

Figure 7: Cumulative radial number density of water molecules inside carbon nanotube in radial direction for various rotational speeds

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