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Study of the Effect of Temperature on Water Permeation Through Carbon Nanotubes Subjected to an Induced Pressure Gradient: A Molecular Dynamics Simulation

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Abstract

Molecular Dynamics simulations were carried out using GROMACS to study the temperature and diameter dependency of water transport through carbon nanotubes in equilibrium state and non- equilibrium state simulations. In equilibrium state simulations, the water flow has shown a linear dependency on the temperature for nanotubes. The carbon nanotube of diameter 8.1 Å may be considered as critical diameter value below which the water flow through the nanotube did not indicate a clear relationship with temperature. In non-equilibrium state simulations the nanotubes were considered as biological water channels that transport water under osmotic pressure difference. An artificial osmotic pressure difference was successfully implemented to mimic the physiological behavior of biological water channels. The osmotic permeability and hydraulic permeability have shown approximately linear dependence on the temperature for the given diameter values of nanotubes within the temperature range of 280 K and 360 K.

1. INTRODUCTION

Carbon nanotubes are molecular-scale tubes with graphitic carbon structures (can be thought of as a graphene of a hexagonal lattice of carbon) rolled into a cylinder. They are unique for their size, shape and remarkable physical properties [1]. Nanotubes have a broad range of thermal, electronic and structural properties that vary depending on different types of nanotube which are primarily defined by its diameter, length and chirality [1].

Over the years many studies have been carried out in area of carbon nanotubes as a means of water and proton transport in nano and biological channels [2,3,4]. The transport of water molecules across nano-channels acts as an important role in biological systems [5]. Investigations such as effect of temperature on water permeation could be a driving factor on the determinants of water and proton conduction rates in such biological water channels**.** Study of temperature effect on the dynamic interaction of water and carbon nanotubes can be of great importance in efficient water transport in carbon nano-channels. The water permeation through carbon nanotubes could be subjected to an induced pressure gradient to mimic a biological channel [3,6].

In present the work a Molecular Dynamic (MD) simulation studies were conducted using GROMACS (Groningen Machine for Chemical Simulations) [7] based on LINUX platform to model water permeation through carbon nanotubes at different temperatures subjected to an induced pressure gradient.

2. METHODOLOGY

2.1 Modeling carbon nanotubes

In this research three armchair type uncapped, single-walled nanotubes (SWNT) of carbon were considered with chirality of (6, 6), (8, 8), and (10, 10) having diameter values 8.1 Å, 11.0 Å and 13.75 Å respectively. The graphite sheets of area 6.25 nm^2 was chosen for this purpose were with chirality of (10, 10), with dimensions *a*, *b* equal to 2.5 nm each (Fig 1).

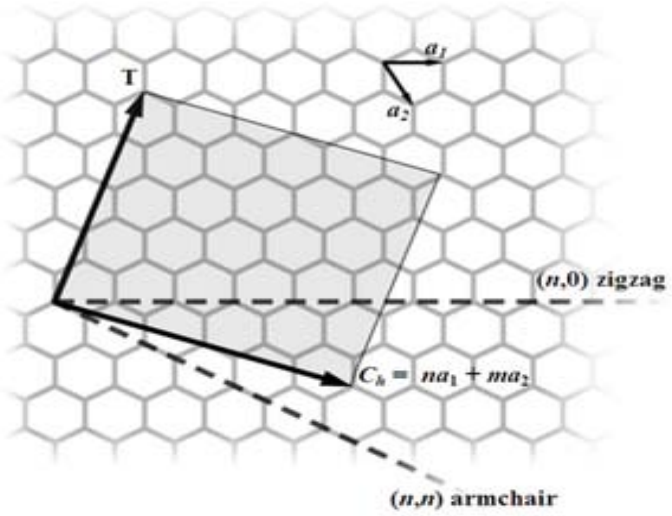

Fig. 2 Chiral vector described by integers *n, m* as $C_k = na_1 + ma_2$

(Adopted from reference [8])

The tube length chosen was 13.4 Å according to previously published results [9]. The carbon bond length was specified as 1.425 Å. In order to observe a significant water flow through the nanotubes at equilibrium and non-equilibrium states, the structure outside the nanotube was improved by adding two graphite sheets to the model [9]. All the carbon atoms in both, the carbon nanotube and the graphite sheet, were fixed in position in all simulations. Electrostatic interactions were modeled with a cut-off distance of 1 nm.

The length of the simulation box was chosen as 40 Å (more than twice the length of a nanotube) and the length of a side of the box was chosen as 25 Å. These values were chosen as to avoid water molecules permeating across the graphite sheet layer. Since periodic boundary condition was considered in all directions (x, y, z), it was important that the point distance between the end of the nanotube in the unit cell and the beginning of the

image nanotube in the image cells is smaller than the length of the carbon bond. This was to avoid carbon-carbon interaction between two nanotubes in different cells.
In the simulations carbon atoms were modeled as uncharged Lennard-Jones particles with a C–C and C–O cross section, 0.3400 nm and 0.3275 nm respectively, depth of C–C and C–O potential wells of 0.3612 kJ mol^{-1} and 0.4802 kJ mol^{-1} respectively [9]. Periodic boundary conditions were applied in all directions. All simulations were carried out at a constant volume with box size dimensions of L_x = 2.5 nm, L_y = 2.5 nm and L_z = 4.0 nm.

2.2 The simulation

All the simulations were performed with GROMACS 4.1 MD program [7]. The simulations were carried in two parts as equilibrium and non-equilibrium simulations. In non-equilibrium simulations, a method described by Zhu *et al*. was adopted to obtain a pressure difference between the two ends of the SWNT [3]. An additional acceleration of nm ps^{-2} was applied to each water molecule along the +*z* direction. For each diameter value, the simulations were run at temperatures 280 K, 300 K, 320 K, 340 K and 360 K. The temperature range was chosen to avoid the system undergoing a change from liquid to solid phase or from liquid to gaseous phase. Each system was simulated for 3.2 ns at each temperature and diameter value in both equilibrium and non-equilibrium simulations. This was done in three phases. In the initial phase, the systems were run for 1.2 ns and the first 200 ps of the simulation were discarded because initially there were no water molecules inside the tube and the system takes some time to settle into its equilibrium state. In the subsequent phases, the systems were run for 1 ns each and necessary data were extracted.
In non-equilibrium conditions, the simulation was carried out under an induced pressure gradient by applying an external force to each and every water molecule in the unit cell along the *z*-direction. Thus water molecules obtain a net directional flow of water through the nanotube. This condition was given in the non-equilibrium MD section in the mdp file. The periodic boundary conditions were applied in all directions since it was necessary to induce the hydrostatic pressure in the non–equilibrium simulations. The tool used for extracting data was the molecular graphics software VMD (Visual Molecular Dynamics).The initial configuration files of each simulation run was then loaded onto VMD and the trajectory file was then loaded on top of that. The permeation event could then be observed through the VMD interface [7].

2.3 Calculations

In equilibrium simulations water flow and the net water flow were calculated for each system using the number of permeation events. The number of permeation events occurring in the *z*-directions during a simulation run time was calculated using GROMACS program commands [7]. A permeation event was defined as a water molecule entering from one end of a nanotube and leaving the other end, therefore traversing the entire length of the nanotube [10]. The water flow was defined as the total number of water molecules per nanosecond that leaves the SWNT from one end, having entered the opposite side [9] and the net water flux was defined as the difference between the number of water molecules per nanosecond leaving from one end and the other, again having entered from the opposite

end. The calculated water flow and water flux were averaged over the three simulations runs and then plotted against temperature to obtain the best fit curve.

3. RESULTS AND DISCUSSION

3.1 Equilibrium state simulations

Using the data from the equilibrium simulations, the total water flow was calculated as function of the water flux for each system at each temperature value. The calculated values are tabulated and plotted against temperature to analyze the temperature dependency of water flow and water flux. The water flow is then expressed as a function of temperature by keeping the diameter of the nanotube fixed.

3.1. 1 Water flow as a function of temperature

The calculated water flow for SWNT (8, 8) and SWNT (10, 10) was plotted against the temperature as seen in Fig. 2. The best fit for water flow as a function of temperature for SWNT (8, 8) and SWNT (10, 10) is a straight line. Therefore it could be argued that water flow is linearly dependant on the temperature for a diameter value of 11.25 Å and 12.75 Å under equilibrium simulations. Therefore, the water flow through the tube is bulk like, which means that, water molecules transport in bulk through the tube. It does not form a single file flow but it created a room for water molecules to travel along $+z$ and $-z$ directions simultaneously. Therefore values obtained for water flow forms a clear relationship to temperature. The Fig. 2 further shows that the gradient of the graph of SWNT (10, 10) is greater than that of the graph of SWNT (8, 8). This effect is possibly due to the diameter factor of carbon nanotubes.

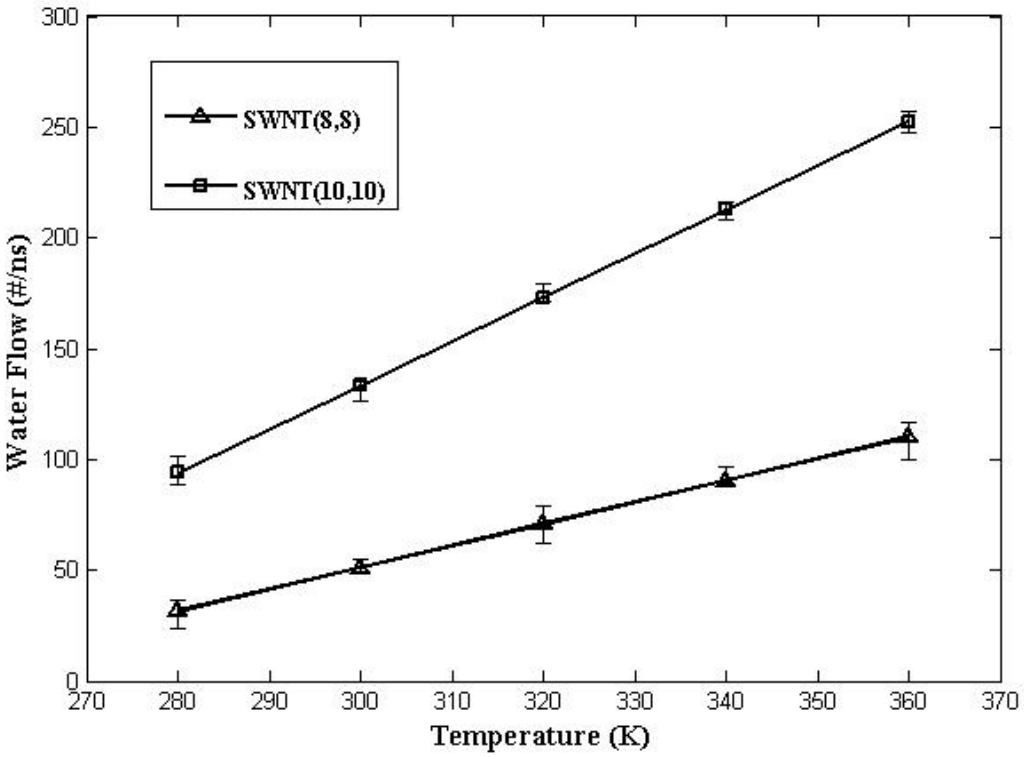

Fig. 2 Comparison of water flow as a function of temperature

However, the water flow calculated for SWNT (6, 6) was plotted against the temperature; the curve does not implicate a genuine relationship between water flow and the temperature for SWNT (6, 6) under equilibrium conditions. The possible reason behind such a behavior is the formation of 'single-file' water chains inside the nanotube as observed. This resulted in a pulse like transport of water as validated by the work of Holt *et al*. [11]. Due to this effect, water molecules are mostly confined in the nanotube and only a few number of water molecules will traverse the full length of the nanotube at any given temperature under equilibrium simulations. Thus, it justifies the small number of permeation events that occurred even at higher temperature values. The diameter value of SWNT (6, 6) can therefore be considered as a critical diameter value below which the water flow through the nanotube does not indicate a clear relationship with the temperature strictly under equilibrium states.

3.1.2 Water flux as a function of temperature

The water flux for systems SWNT (6, 6), SWNT (8, 8) and SWNT (10, 10) yielded values closer to zero at each temperature value. Even though ideally these values should be zero, these results are acceptable since thermal fluctuations can cause a net water flow at equilibrium simulations.

3.2 Results for non-equilibrium state simulations in the presence of a hydrostatic pressure difference

Under non-equilibrium simulations carbon nanotubes were considered to mimic a biological channel. The ability of a membrane to conduct water is characterized by the ratio of net water flow to the hydrostatic or osmotic pressure difference, ΔP across the membrane [3]. It is known that an osmotic pressure is equivalent to a hydrostatic pressure. Therefore, if one can generate a hydrostatic pressure difference in MD simulations, one can set up an osmotic pressure difference to mimic a biological channel in order to study water channels.

For a single water channel, hydraulic permeability, l_p ($cm^5N^{-1}s^{-1}$), is defined through [3];

$$j_v = l_p \Delta P = l_p \frac{4nf}{A} \qquad (1)$$

where, $j_v (cm^3s^{-1})$ is the volume flux through a single channel and ΔP is the hydrostatic pressure difference across the nanotube, n is the total number of water molecules in the simulation box, f is the force applied on a molecule, and A is the area of the graphite sheet which is 2.5 nm x 2.5 nm).

Similarly, osmotic permeability, P_f (cm^3s^{-1}), can be defined through;

$$J_w = P_f \Delta C \qquad (2)$$

where J_w (mol / s cm^2) is the molar flux presented as the number of moles of water passing through the unit area of the membrane per second; ΔC (mol / cm^3) is the solute (water) concentration difference.

Since the osmotic pressure difference ΔP of a dilute solution is approximated by;

$$\Delta P = RT\Delta C \qquad (3)$$

Osmotic permeability is now related to hydraulic permeability l_p by Eq. 4;

$$p_f = (\frac{RT}{V_w}) l_p \qquad (4)$$

where V_W is the molar volume of water ($V_W = 18\ cm^3mol^{-1}$), R is the universal gas constant ($R = 8.314 \times 10^7$ erg $K^{-1}mol^{-1}$) and T is the absolute temperature of the system.

In order to determine the permeability of water in each nanotube, the hydraulic permeability of the channel was calculated according to Eq. 1 at each temperature and the hydraulic permeability was found as a function of temperature where a polynomial of 2nd degree was found to fit the values best for each diameter value. Substituting these data in Eq. 4, the osmotic permeability of each channel was found and plotted against the temperature to determine the temperature effect on the water permeation through nanotubes (Fig. 3).

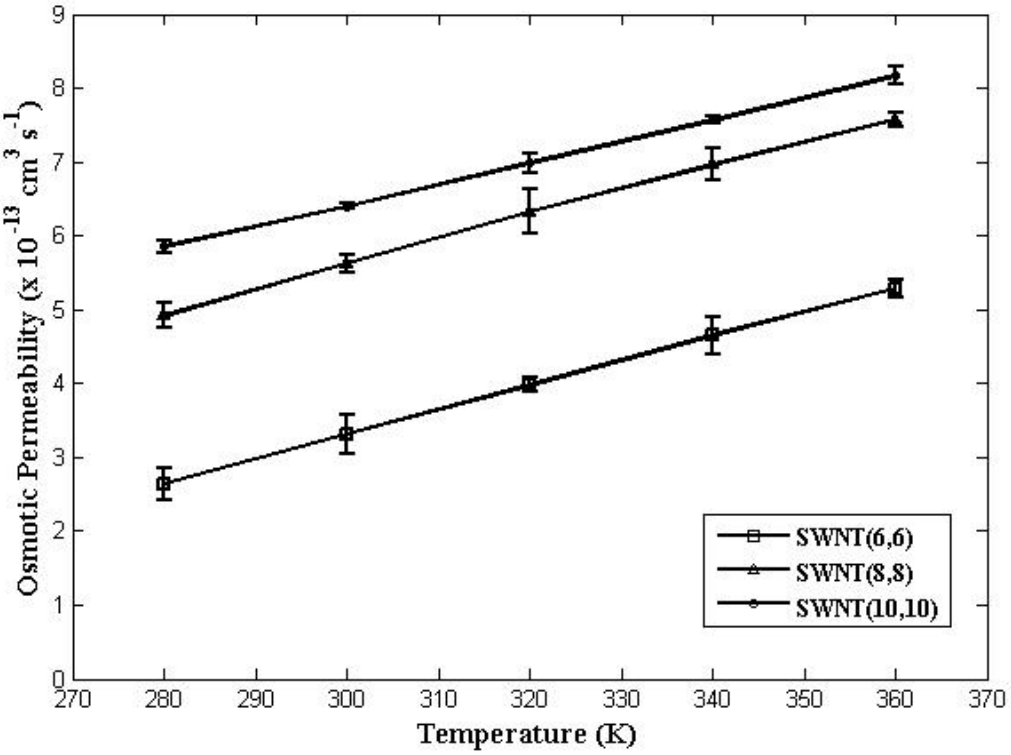

Fig. 3 Comparison of Temperature dependency on Osmotic permeability

When osmotic permeability is expressed in terms of hydraulic permeability for the three systems, SWNT (6, 6), SWNT (8, 8) and SWNT (10, 10), the Eq. 5, Eq. 6 and Eq. 7 respectively gives Osmotic permeability as a function of temperature.

$$P_f = \left(0.0022T^2 - 3.3114T\right)\times 10^{-15} \quad (5)$$

$$P_f = \left(0.0217T^2 - 2.1861T\right)\times 10^{-15} \quad (6)$$

$$P_f = \left(0.0033T^2 + 1.2993T\right)\times 10^{-15} \quad (7)$$

Fig 3 and Eq 5 – 6 show that for the given diameter of a nanotube, the osmotic permeability increases approximately linearly with the increasing temperatures in range of 280 K – 360 K. The calculated values for osmotic permeability and hydraulic permeability in each system agree with already published values [3]. Furthermore, from Fig. 3, for a given temperature, osmotic permeability is increased when the diameter of the nanotube is increased. However the gradients of the three curves are very much close to one another, the osmotic permeability of nanotube membrane varies with the temperature in the same way for different diameter values.

4. CONCLUSIONS

Molecular Dynamic simulations were carried out to study the temperature and diameter dependency of water transport through carbon nanotube. The study was carried out in two parts as equilibrium state simulations and non equilibrium state simulations. In equilibrium state simulations, the water flow has shown a linear dependency on the temperature for nanotubes. It was observed that temperature has a direct influence on the water flow through the nanotubes of diameter 11 Å and 13.25 Å. The carbon nanotube of diameter 8.1 Å indicated a random behavior with respect to temperature. The carbon nanotube of diameter 8.1 Å may be considered as critical diameter value below which the water flow through the nanotube did not indicate a clear relationship with temperature. In non-equilibrium state simulations the nanotubes were considered as biological water channels that transport water under osmotic pressure difference. An artificial osmotic pressure difference was successfully implemented to mimic the physiological behavior of biological water channels. The osmotic permeability as well as hydraulic permeability has shown an approximate linear dependence on the temperature for the given diameter values within the temperature range of 280 K – 360 K.

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