MODELING WATER FLOW THROUGH CARBON NANOTUBE MEMBRANES WITH ENTRANCE/EXIT EFFECTS

Myung Eun Suk\textsuperscript{a} and Narayana R. Aluru\textsuperscript{b}

\textsuperscript{a}New Transportation Research Center, Korea Railroad Research Institute, 176, Cheldobangmulgwan-ro, Uiwang-si, Gyeonggi-do, South Korea; \textsuperscript{b}Department of Mechanical Science and Engineering, Beckman Institute for Advanced Science and Technology, University of Illinois at Urbana–Champaign, Urbana, Illinois, USA

ABSTRACT
Carbon nanotube–based membranes have gained significant attention due to their transport efficiency and wide range of applications, including molecular sieving and sensing. Recently, in order to attain high transport rates, many studies have focused on reducing membrane thickness. A reduction in membrane thickness results in the dominance of entrance/exit effects over surface effects, particularly for carbon nanotubes (CNTs), due to their hydrophobicity. However, experimentally obtained nanoscale flow rate data span a wide range, and entrance/exit effects are often neglected when analyzing these data. In this study, we modeled the water flow rate through various lengths and radii of CNTs using molecular dynamics simulations while also taking entrance/exit effects into consideration. Based on viscosity and slip length calculations, a water flow model is proposed that covers various lengths and radii of CNTs. Moreover, the enhancement factor of CNT membranes is reassessed using entrance/exit effects. The results of this study can be used for the optimal design of ultraefficient CNT membranes for potential applications such as water filtration.

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INTRODUCTION
Studies on water flow through carbon nanotubes (CNTs) have been frequently conducted because of the high rate of water flow through them [1–3], their ion selectivity [4–6], and other factors [7–9]. In 2006, Holt et al. successfully grew a CNT forest with a diameter of less than 2 nm to produce a CNT membrane [2]. The CNT membrane showed about 100 to 1,000 times higher water permeability than existing polymeric membranes [2]. Thereafter, many studies were conducted using molecular dynamic simulations, including observations of water flow through [10] CNTs and between [11] CNTs, discussions of the main factors and mechanisms governing fast water flow [12], and studies on ion rejection according to CNT diameter and the resulting possibility of their application for desalination [4].

CNT membranes with various diameters and matrix fillers have been fabricated experimentally [7, 8, 13–15]. Baek et al. fabricated a CNT membrane with a diameter of \( \sim 4.8 \) nm using epoxy filler [8]. Recently, CNT–parylene membranes with a diameter of \( \sim 3.3 \) nm were studied by Bui et al. [7]. CNT–wall membranes consisting only of CNTs were fabricated by Lee et al. [15]. Through mechanical densification, the CNT–wall membranes can be produced with 6-nm-wide inner pores and 7-nm-wide outer pores [15]. The porosity is greatly increased in this case, compared to previous/existing CNTs filled with a polymer [7] or an Si\textsubscript{3}N\textsubscript{4} matrix [2], and the permeability is also increased.

CONTACT
Myung Eun Suk  
msuk2@krri.re.kr  
New Transportation Research Center, Korea Railroad Research Institute, 176, Cheldobangmulgwan-ro, Uiwang-si, Gyeonggi-do 16105, South Korea.

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by over 10 times. In addition, it has been shown that the permeability is further increased by making the entrances of the CNTs hydrophilic via an oxygen-reactive ion etching process [15].

Due to the fast water flow rate through CNTs [1–3], the gradually decreasing manufacturing costs, and a greater feasibility of commercialization [16], the chances of CNT membranes replacing existing filtration membranes have risen [17]. Depending on the size of the membrane, not only water but also protons [18, 19], ions [20], biomolecules [21], and other molecules can be transported highly efficiently. Therefore, the applications of CNT membranes are being expanded to include a variety of fields, including fuel cells [18], drug delivery [21], ion separation [22] and supercapacitors [23, 24]. For expanded applications of CNT membranes and the interpretation of various experimental results, an accurate comprehension is needed of the relationship between the mass transfer rate and the dimensions of a CNT, particularly its radius and length. In experimental setups, the fine control of CNT size and the accurate measurement of the physical properties of the fluid inside the CNT and its mass transfer rate are difficult to achieve [25]. Therefore, molecular dynamics simulation is a useful tool for a comprehensive understanding of the matter.

There have been previous studies investigating the effects of CNT dimensions on the water flow rate using molecular dynamics (MD) simulations [26–30]. Su and Yang [26] and Su and Guo [30] tested (6,6)–(15,15) CNTs, corresponding to radii of 0.41–1.01 nm, for a given CNT length of 2.56 nm. For a given CNT radius of 0.54 nm, CNT length varied from 1.34 to 9.89 nm [26, 30]. The unidirectional water flow rate was calculated by applying the pressure gradient, and changes in the flow rate with CNT radius for a given CNT length were described by an exponential function. As noted in Su and Guo [30], the exponential dependency of water flow rate on CNT radius is not expected from the continuum relationship (Hagen-Poiseuille relationship), which is scaled by $Q \sim R^4$ and $Q \sim L^{-1}$. Their studied CNT radius ranged from 0.41 to 1.01 nm, mostly corresponding to the subcontinuum regime [29]. For a (7,7) CNT with a radius of 0.48 nm, Nicholls et al. [27] tested the effects of varying lengths on water flow rate; they observed an invariant water flux with changing lengths of the CNT. In this subcontinuum regime, water molecules are transported by collective motion rather than by frictional flow [31]. The energy barrier at the entrance determines the water transport rate, and hydrophilic pores provide a higher transport rate than hydrophobic pores by lowering the energy barrier at the entrance [10].

The transition from the continuum to the subcontinuum regime of water flow through CNTs was studied in detail by Thomas and McGaughey [28]. By comparing the MD simulation results to a modified Hagen-Poiseuille (HP) relationship with a slip boundary condition and reduced water viscosity inside the CNT, the transition was reported to occur at $R \sim 0.7$ nm [29]. For a CNT radius smaller than $\sim 0.7$ nm, a deviation in the MD resulting from the modified HP relationship was found. Thomas and McGaughey [29] tested CNTs with two different lengths (75 and 150 nm) to eliminate the pressure loss at the entrance and exit regions and thus extract the hydraulic conductivity inside the CNT. This hydraulic conductivity, corresponding to the permeability of the CNT without entrance/exit effects, is compared to the modified HP relationship in the study by Thomas and McGaughey [29]. The enhancement factor is also calculated by dividing the hydraulic conductivity over a no-slip HP relationship in the absence of entrance/exit effects [29].

Entrance/exit effects will be negligible when frictional loss along the tube wall is dominant. In the case of CNTs, the smooth surface and hydrophobicity provide low frictional loss, and these characteristics are known to be the major factors responsible for the fast mass transport rate through CNTs [12]. Because the frictional loss inside CNTs is very low, the entrance/exit effects become dominant, especially for short CNTs. Therefore, in understanding the relationship between CNT dimensions (radius and length) and water flow, it is necessary to factor in the entrance/exit effects. Our study aims to comprehensively explain the water permeability and flow enhancement of CNTs and the dependence of these characteristics on CNT radius and length, including the consideration of entrance/exit effects. Using MD simulations, we obtained the flow rate and permeation coefficient of water flowing through CNTs with varying radii and lengths. The CNT radii used were approximately 0.813–2.046 nm, and the lengths were about 5–60 nm. A water transport model including the entrance/exit effects was derived and compared to the measured values. Furthermore, we recalculated the enhancement factor by factoring in
the entrance/exit effects, thereby quantifying the efficiency of CNTs and establishing a relationship between the changes in efficiency and the dimensions of CNTs, particularly the radius and length.

**Methods**

**Pressure-Driven flow simulation**

Figure 1 shows the simulation setup. CNTs with various radii were tested: (12,12), (16,16), (20,20), (24,24), (27,27), (30,30), and (34,34) armchair CNTs. The corresponding center-to-center radii were 0.813–2.046 nm, given by $R_{c-c} = \frac{\sqrt{3}n}{2\pi}d$, where $R_{c-c}$ is the center-to-center CNT radius, $n$ is the chiral index, and $d$ is the lattice constant of 0.246 nm. The CNT radius, $R$, used in this work was defined by subtracting the width of depletion layer (~0.27 nm) near the CNT surface from the center-to-center CNT radius \[12,32\]. In this way, the effective radius accessible to water molecules was used, and the calculations of flow rate and permeability were more accurate. The effective CNT radius, $R$, ranged from 0.55 to 2.05 nm. The CNT lengths ($L$) varied from 5 to 60 nm. The water bath sizes in the $x$ and $y$ dimensions ($L_x$, $L_y$) ranged from 4 to 8 nm depending on the CNT radius in order to keep the porosity constant. The water bath size in the $z$ dimension ($L_z$) was fixed at 6 nm.

Simulations were performed using the LAMMPS package \[33\]. A time step of 1 fs was used. A Nosé-Hoover thermostat \[34\] was used to maintain the temperature at 300 K with a time constant of 0.1 ps. A periodic boundary condition was applied in all three dimensions. A particle–particle–particle–mesh method \[35\] was used for long-range electrostatic interactions. An SPC/E (extended simple point charge) water model \[36\] was used with a shake algorithm to constrain the angle and bond length. The SPC/E water model was used because various water properties, such as the diffusion coefficients \[37\], viscosities \[38\], and surface tension \[39\], were in good agreement with the experimental values. The carbon atoms were modeled with Lennard-Jones interactions with the parameters $\sigma_{C-C} = 0.339$ nm and $\varepsilon_{C-C} = 0.0692$ kcal/mol \[40\]. The Lennard-Jones parameters between water and carbon atoms were obtained from Lorentz-Berthelot mixing rules: $\sigma_{C-O} = 0.328$ nm and $\varepsilon_{C-O} = 0.104$ kcal/mol.

**Water permeability measurement and modeling**

The water permeability of CNTs with varying lengths and radii was obtained by performing nonequilibrium molecular dynamics (NEMD) simulations. By applying a pressure drop, water flows through the CNTs were successfully simulated. The water flow rate was calculated by directly counting the net number of water molecules transported through the CNT during the simulation. The CNT permeability was then obtained using $p_Q = Q/\Delta P$, where $p_Q$ is the permeation coefficient, $Q$ is the volumetric flow rate, and $\Delta P$ is the applied pressure drop. The pressure drops employed were 10–300 MPa. After confirming the linear relationship by plotting the respective pressure drop and volumetric flow rate, the permeability was obtained from the linear slope. The applied pressure was very high compared to the

![Figure 1](image-url) Simulation setup for water flow through a CNT. $R$ and $L$ are the CNT radius and length, respectively. $L_y$ and $L_z$ are the dimensions of the water bath in the $y$ and $z$ directions, respectively.
Experimental operating pressure (~10 MPa) [41]; this was to reduce statistical error caused by the high thermal motions of water molecules during the limited simulation time. The permeability obtained in the high pressure range was reported to be the same as that obtained in standard operating pressure range [4]. The linearity between the water flow rate and the pressure drop was shown in a wide pressure range, up to 500 MPa during the MD simulation [4, 42, 43]. The relational expression for modeling was based on hydrodynamic equations and circuit analogy. When plotting the pressure along the length direction, as shown in Figure 2, the pressure gradient varied in the interior and at the entrance/exit points. By comparing the pressure to voltage and the flow rate to current, it was shown that the entrance/exit resistance and the interior resistance were serially connected. Therefore,

$$Q = \frac{1}{E_R + I_R} \Delta P$$

and

$$p_Q = \frac{1}{E_R + I_R}$$,

where $E_R$ is the resistance in the entrance/exit region and $I_R$ is the resistance in the interior region.

The interior resistance can be calculated using the Navier-Stokes equation. Instead of the no-slip boundary condition, wherein the fluid velocity is assumed to be zero along the CNT wall, a slip boundary condition needs to be applied. Because of the weak water–carbon interaction (hydrophobicity) and smooth surface, strong slip behavior at the CNT wall was observed [12]. The slip boundary condition is given by

$$u(R) = -\delta \left( \frac{du}{dr} \right)_{r=R}$$,

where $u$ is the water velocity, $R$ is the CNT radius, and $\delta$ is the slip length.

After applying the slip boundary condition, the water velocity was calculated as shown below in Eq. (4):

$$u(r) = \left( -\frac{1}{4\mu} r^2 + \frac{R^2}{4\mu} + \frac{R}{2\mu} \delta \right) \frac{dP}{dz}$$.

Figure 2. Pressure distribution along the CNT axial direction during pressure-driven flow simulations. Local pressure is calculated using the Irving-Kirkwood expression [44]. The applied pressure drops were 100, 200, and 300 MPa. The CNT membrane was positioned between $z = 6$ and 21 nm. The pressure drop was large at the entrance and exit regions and small in the interior region.
Here, \( r \) refers to the dimension of the CNT in the radial direction; at the center of the pore, \( r = 0 \), and at the CNT wall, \( r = R \). The variable \( z \) refers to the dimension in the length direction of the CNT, and \( \mu \) refers to the dynamic viscosity of water. Upon integrating from \( r = 0 \) to \( r = R \), a volumetric flow rate similar to that of the HP equation was obtained from 

\[
Q = \int_0^R u(r)2\pi r dr.
\]

This is shown as Eq. (5):

\[
Q = \frac{\pi(R^4 + 4R^3\delta)}{8\mu L}\Delta P. \tag{5}
\]

The interior resistance is denoted as in Eqs. (6) and (7):

\[
I_R = i_R L \tag{6}
\]

and

\[
i_R = \frac{8\mu}{\pi(R^4 + 4R^3\delta)}. \tag{7}
\]

where \( i_R \) is the interior resistivity.

The entrance resistance can be obtained using the flow resistance of an infinitely thin orifice. This can be expressed by using the Sampson equation [45]:

\[
E_R = \frac{3\mu}{R^4}. \tag{8}
\]

An infinite-series solution for a fluid moving through finite-length pores was obtained by Dagan et al. [46]. They found that a simple approximate solution for combining Poiseuille flow at the interior with Sampson flow at the entrance/exit was close to the exact solution within 1% error [46].

**Calculation of viscosity and slip length**

To obtain the entrance/exit resistance and interior resistance using Eqs. (6), (7), and (8), accurate values of the viscosity and slip length depending on the CNT radius are required. When water molecules are confined in nanosized tubes, water properties such as diffusivity and viscosity deviate from their bulk values due to the change in water structure [47, 48]. The slip length is also influenced by the CNT radius [28, 49]. For an accurate calculation of the resistance that factors in the CNT radius, the values of the viscosity and slip length should be obtained in advance.

With the water bath removed, the periodic boundary condition was applied to calculate the viscosity and slip length inside the CNT, thus allowing the simulation of an infinitely long CNT. The calculations of viscosity and slip length were carried out using the Green-Kubo equations [32, 50] in an equilibrium MD simulation without any external forces. Some studies have calculated the viscosity and slip length indirectly by fitting the flow velocity profile obtained from NEMD to a theoretical model such as Eq. (4) [28, 51]. However, in this study, this method was not adopted for several reasons. First, the velocity profile is flat because of the relatively large slip length compared to the CNT radius. In this case, a huge error may occur in the obtained viscosity and slip length [52]. Second, when determining the validity of our model by comparing the NEMD result with the modeling result, the judgment would have been compromised by using results obtained from an identical simulation. An independent equilibrium MD simulation was conducted in order to avoid relating the modeling result to the data points based on NEMD.
Results and analysis

Viscosity and slip length variation with CNT radius

The viscosity and slip length were calculated for each CNT radius, and they are shown in Figure 3. As shown in Figure 3a, the viscosity of the water inside the CNT was lower than the bulk value. The viscosity also decreased with decreasing CNT radius. At the hydrophobic surface of the CNT, the number of hydrogen bonds among the water molecules was reduced, and “dangling” OH bonds were observed [12]. The reduced amount of hydrogen bonding of the water molecules resulted in an increase in the degree of freedom of each water molecule, which led to an increase in the diffusion coefficient and a decrease in the viscosity. A similar mechanism of enhanced diffusion was observed at the liquid–vapor interface [53]. At the interfacial region, a 58% greater diffusion coefficient than that in the bulk water was observed due to the breaking up of the bulk liquid hydrogen bonding [53].

The changes in viscosity caused by changes in the CNT radius can be expressed as the fractional average of the water viscosity at the surface region and the bulk water viscosity of the corresponding area, as shown in Eq. (9) [28]. Considering the surface viscosity to be 0.32 mPa·s and the surface layer thickness to be 0.38 nm, Eq. (9) well describes the changes to viscosity, which are shown in Figure 3a as a solid line.

$$\mu(R) = \mu_s \frac{A_s(R)}{A_T(R)} + \mu_{\text{bulk}} \left(1 - \frac{A_s(R)}{A_T(R)}\right).$$

Figure 3. Change in (a) viscosity and (b) slip length against CNT radius. As the radius increases, the viscosity approximates the bulk value (0.855 mPa·s), and the slip length approximates the case of a flat graphene surface (66.1 nm). These limit values are depicted using a blue dashed line. The solid red lines in (a) and (b) depict Eqs. (10) and (11), respectively.
Here, \( A_T \) and \( A_s \) refer to the total cross-sectional area and the cross-sectional area at the surface region inside the CNT, respectively. In other words, \( A_p = \pi R^2 \) and \( A_s = \pi R^2 - \pi (R - 0.38\text{nm})^2 \). The variable \( \mu_{\text{bulk}} \) is the viscosity of the bulk water (0.855 mPa-s at 300 K \([54]\)), and \( \mu_s \) is the viscosity at the surface region (0.32 mPa-s). Rewriting Eq. (9) using the relational expression for the CNT radius,

\[
\mu(R) = \frac{C_1}{R^2} + \frac{C_2}{R} + \mu_{\text{bulk}},
\]

(10)

Here, \( C_1 = 0.075 \text{ mPa-s-nm}^2 \) and \( C_2 = -0.4 \text{ mPa-s-nm} \).

Figure 3b plots the slip length against the CNT radius. The power law was applied to the variation in slip length with CNT radius as follows:

\[
\delta(R) = AR^B + \delta_{R \to \infty},
\]

(11)

where \( \delta_{R \to \infty} \) is the slip length for an infinite pore radius, \( R \) is the CNT radius in nanometers, and \( A \) and \( B \) are power law coefficients, which were determined using the least squares method. Their values were 21.06 nm^2 and −1.36 (dimensionless), respectively. The value of \( \delta_{R \to \infty} \) is obtained from the slip length of the flat graphene surface to capture infinitely small curvature as \( R \to \infty \). The computed slip length of the graphene surface (\( \delta_{R \to \infty} \)) was 66.1 nm, which falls between the reported values of 30 nm computed by Thomas and McGaughey \([28]\) and 80 nm computed by Falk et al. \([49]\). The obtained slip length of 66.1 nm was also close to the value of 60 nm reported by Kannam et al. \([52]\) and 64 nm by Koumoutsakos et al. \([55]\).

Change in water permeability with CNT radius and length

The permeability of a CNT depends on its radius and length, so to investigate this phenomenon, we varied the radius and length. First, the CNT length was fixed at 10 nm, and the CNT radius was adjusted from 0.5 to 2 nm. The measured permeability from NEMD simulations is represented by the points in Figure 5. As mentioned previously, the permeation coefficient is obtained from the slope of the linear fit between the water flow rate and the applied pressure. The error bars in Figure 5 indicate the standard errors of the linear fit coefficients. The modeling results of Eqs. (2) and (6) through (8) are represented by solid lines. The viscosity and slip-length models (Eqs. (10) and (11)) obtained from the previous section are also applied to take into account their variation with CNT radius.
When applying the bulk viscosity value without considering the changes to the structure of the water molecules and their properties caused by nanoscale confinement inside a CNT [57, 58], the resistance was overestimated compared to the case that applied the actual viscosity values inside the CNT. The overestimate can result in a large difference between the predicted value using the flow model and the actual measured value for a small CNT radius. As shown in Figure 5, the water flow model represents the variation in permeability with CNT radius reasonably well when properly assessing the entrance resistance and interior resistance by including the viscosity and slip length variations that depend on the radius.

Next, using a fixed CNT radius, the permeability changes due to changes in CNT length were observed in (20,20) and (30,30) CNTs. With an increasing length of the CNT up to 60 nm, the permeability measured through NEMD simulation is represented by the round points in Figure 6. The modeling results of Eqs. (2) and (6) through (8) are represented by solid lines. Approximately,
the changes in permeability over a length of 5 nm were well predicted by our proposed model. Below a length of 5 nm, the prediction deviated due to the coupling between the entrance and exit regions. When the entrance and exit regions are overlapped, water molecules form a layered structure in the axial direction, and the physical properties of the water change according to its structure [32].

Note that the permeability changes with CNT length are relatively small compared to the statistical error of the MD simulations. The water flow rate or permeability variations with length may not be properly captured if narrow length ranges are tested [26, 27]. Simulations of CNTs with micrometer-scale lengths are computationally expensive, especially for CNTs with a large radius, because a large number of water molecules are needed to fill the CNT at the density of liquid water. Despite the high computational cost, a simulation of a CNT up to 2 μm in length was attempted by Walther et al. with a (15,15) CNT [58]. In our study, it was shown that the water flow model predicts the water flow rate and the permeability of a CNT reasonably well; the analysis for CNTs with micrometer-scale lengths can be performed using the water flow model without a high computational expense.

Entrance and exit effects of CNTs

We examined the entrance/exit effects and surface effects of CNTs by modulating the slip length in the water flow model. The changes in water permeability when there are only entrance/exit effects (no surface effects; $\delta = \infty$) are illustrated in Figure 7. The solid red line shows the perfect slip case, which has only entrance/exit effects. In the perfect slip case, the interior resistance (Eq. (7)) is zero when the infinite slip length is applied. In this case, the permeation coefficient is reduced to $1/E_R$, and there are no changes in permeability with length.

The water permeability changes under no-slip surface conditions (maximum surface effect; $\delta = 0$) are also illustrated in Figure 7. The solid purple line shows the case when no-slip surface conditions occur, plotted by applying the zero-slip length in Eq. (7). The solid yellow line shows the partial-slip case, which refers to the hydrophobicity of CNTs, plotted by applying a slip length of...
84.93 nm corresponding to the (20,20) CNT in Eq. (7). NEMD data points for a (20,20) CNT are shown for reference in Figure 7.

In partial-slip or no-slip cases, the interior resistance increases proportionally to the tube length. Therefore, as the length increases, the permeability decreases. In the no-slip case, the rate of decrease is very high, whereas the rate of decrease is moderate in partial-slip case such as CNTs (only an ~13% reduction for a 50-nm-long CNT). Therefore, in the case of a membrane with a nanoscale

Figure 7. Entrance/exit effects and surface effects on water permeability variation with CNT length. Permeability is largely reduced in the no-slip surface conditions corresponding to a hydrophilic surface. In case of CNTs, the reduction is small due to the slip surface.

Figure 8. Fraction of entrance resistance \( \frac{E_R}{(E_R + I_R)} \). The percentage of entrance resistance decreases with CNT length starting from 100%. (Inset) The critical length is obtained from the length when the percentage of entrance resistance reaches 5% of the total resistance. Above this critical length, the entrance/exit effects can be neglected.
thickness, the entrance/exit effects rather than the surface effects should be considered. In addition, it shows that the slip surface condition of CNTs is a major factor in the high permeability of CNTs. In the analysis of water flow through CNT membranes, the entrance/exit resistances have seldom been considered [2, 12, 28, 29]. In the case of a hydrophilic surface where no surface slip occurs, the entrance/exit resistance is negligible because the interior resistance is relatively much higher than the entrance/exit resistances. However, when the interior resistance is low, as for a CNT membrane, the entrance/exit resistances are important. Therefore, the length criteria, which can ignore the entrance/exit resistances, were estimated by extrapolating the modeling results and observing the ratio between the entrance/exit resistances and the total resistance up to a microscale length (see Figure 8). The length criteria are determined when the entrance/exit resistances are lower than 5% of the entire resistance—in our case, mostly determined to be between 5 and 20 µm at a pore radius of less than 2 nm.

**Recalculation of CNT enhancement factor**

Finally, the enhancement factor, which is a figure that quantitatively represents the efficiency of a CNT membrane, was recalculated by considering the entrance/exit effects. The enhancement factor is defined as [2]

$$E = \frac{Q_{CNT}}{Q_{HP}}.$$  \hspace{1cm} (12)

Here, $E$ is the enhancement factor, $Q_{CNT}$ is the measured water flow rate through the CNT, and $Q_{HP}$ is the water flow rate according to the Hagen-Poiseuille equation. Without considering the entrance/exit resistances, $Q_{CNT}$ can be expressed by Eq. (5). Therefore, the enhancement factor without entrance/exit effects is as follows [28]:

$$E = \left[ 1 + \frac{4\delta R}{R^2} \right] \frac{\mu_{Bulk}}{\mu_{CNT}}.$$  \hspace{1cm} (13)

Equation (13) is independent of the CNT length by excluding the entrance/exit effects.

Considering the entrance/exit resistances, the HP flow model should also be corrected. The flow rate relational equations for each case are arranged in Table 1, and the corrected enhancement factor can be finally expressed as follows:

$$E_{corr} = \frac{Q_{CNT,corr}}{Q_{HP,corr}} = \left( 1 + \frac{32L\delta}{3\pi R^2 + 8LR + 12\pi\delta R} \right) \left( \frac{\mu_{Bulk}}{\mu_{CNT}} \right).$$  \hspace{1cm} (14)

In addition to the water flow rate $Q$, as shown in Eq. (14), the enhancement factor is also a function of both the length and radius of the CNT. Moreover, the dependence of the slip length and viscosity on the CNT radius indirectly affects the variation of enhancement with CNT radius.

The corrected enhancement factor (Eq. (14)) obtained from the suggested model, the value obtained from the NEMD of the present study, and the published values obtained from either

<table>
<thead>
<tr>
<th>Case</th>
<th>Without entrance/exit effects</th>
<th>With entrance/exit effects</th>
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<tbody>
<tr>
<td>No-slip and bulk viscosity</td>
<td>$Q_{HP} = \frac{\pi R^4}{8\mu_{Bulk}} \Delta P$</td>
<td>$Q_{HP,corr} = \left( \frac{\mu_{Bulk}}{\mu_{Bulk} + \frac{\Delta P}{2}} \right)^{-1} \Delta P$</td>
</tr>
<tr>
<td>Slip and reduced viscosity</td>
<td>$Q_{CNT} = \frac{\pi R^4}{8\mu_{Bulk} + \frac{32\pi L\delta}{3\pi R^2 + 8LR + 12\pi R + 32\pi \delta R}} \Delta P$</td>
<td>$Q_{CNT,corr} = \left( \frac{\mu_{Bulk}}{\mu_{Bulk} + \frac{\Delta P}{2}} \right)^{-1} \Delta P$</td>
</tr>
<tr>
<td>Enhancement factor</td>
<td>$E = \left[ 1 + \frac{4\delta R}{R^2} \right] \frac{\mu_{Bulk}}{\mu_{Bulk} + \frac{\Delta P}{2}}$</td>
<td>$E_{corr} = \left( 1 + \frac{32L\delta}{3\pi R^2 + 8LR + 12\pi\delta R} \right) \frac{\mu_{Bulk}}{\mu_{Bulk} + \frac{\Delta P}{2}}$</td>
</tr>
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Table 1. Water flow model for each case and enhancement factor.
simulations or experiments were compared. Many CNT membranes are being experimentally manufactured and tested, and some of the results include permeation not only into the CNT but also into the polymer matrix [14]. Such cases were excluded in our comparison, because this study considers only the permeation through the inside of the CNT. The CNT–wall membranes fabricated recently were also excluded in the comparison, because the water flows through both the inside and the outside of the CNT. A theoretical study of water flow through in between CNTs can be found in Tajiri et al. [11].

First, the enhancement factor changes due to the length change were examined. The experiment/simulation results with radii of ~0.8 and ~1.7 nm and the theoretical estimation using Eq. (14) are shown in Figures 9a and 9b. When the CNT length is short, the entrance/exit effects are relatively strong. In this case, the enhancement factor is not very large. As the CNT length increases, so does the total area of the hydrophobic surface within the CNT. Compared to the HP flow of the same

Figure 9. Enhancement factor variations with CNT length. (a) Comparisons of published data and theoretical models for CNT radii ranging from 0.6 to 1.0 nm. The red diamonds represent simulation results obtained from the current work using the LAMMPS program [33], using a CNT radius of 1.09 nm. The open circles show simulation results obtained from Walther et al.’s work [58] with a CNT radius of 0.75 nm. The blue and red circles are the results from the NAMD program with pressure drops of 20 and 2 MPa, respectively. The green circles show the results from the FASTTUBE program. The brown squares are experimental results obtained from Holt et al.’s work [2] with an average CNT radius estimated as ~0.8 nm. (b) Comparisons of published data and a theoretical model for a CNT with a radius of ~1.7 nm. The red diamonds show simulation results obtained from current work with a CNT radius of 1.77 nm. The brown squares show experimental results obtained from Bui et al.’s work [7], with an average CNT radius estimated as 1.65 nm. The blue circles show experimental results obtained from Kim et al.’s work [13] with an average CNT radius estimated as 1.65 nm.
length, the enhancement factor also increases consequentially as the water flux increases. When \( L \to \infty \), Eq. (14) approximates Eq. (13). In other words, this case does not need to consider the entrance/exit effects, and the enhancement factor asymptotes to the single value, which lies between 100 and 10,000 for a radius < 2.5 nm.

The published values usually show a large uncertainty, possibly caused by the experimental challenges associated with accurately calculating the porosity based on open CNTs, measuring the CNT radius, and measuring the distribution of the CNT radii [25]. Despite large uncertainties among different sets of experimental data, Eq. (14) represents the trend of variation in the enhancement factor reasonably well. Moreover, Eq. (14) shows the best match to the results of Bui et al. [7], which were recently presented (Figure 9b, brown square).

The changes in the enhancement factor with the radius are shown in Figure 10 for the cases \( L = 10 \) nm, 100 nm, 1 \( \mu \)m, and approaching infinity as the most representative. Similarly, the values obtained from an MD simulation of the present study and the values obtained from experiments were compared. The case of \( L \to \infty \) corresponds to the upper limit of the enhancement factor. The experimental values presented by Holt et al. [2] show a wide range, and the value of the lower bound is within the theoretical range. The experimental values presented by Qin et al. [59] are usually lower than the theoretical values when considering a micrometer-scale length. Qin et al. [59] showed the possibility of uncertainty when estimating the driving force [25]. Holt et al. [2] showed the possibility of uncertainty when estimating the open CNT number [25]. Although published results show large deviations, the trend in variation of the enhancement factor is described by our proposed model (Eq. (14)) reasonably well.

![Figure 10. Variations in enhancement factor with CNT radius. The red diamonds show simulation results obtained from the current work with a CNT length of 0.01 \( \mu \)m. The brown squares show experimental results obtained from Qin et al.’s work with a 280-\( \mu \)m CNT length [59]. The green circles show experimental results obtained from Bui et al.’s work with a 23-\( \mu \)m CNT length [7]. The purple triangles show experimental results obtained from Kim et al.’s work with a CNT length of 20–50 \( \mu \)m [13]. The blue inverted triangles show experimental results obtained from Holt et al.’s work with a CNT length of 2–3 \( \mu \)m [2].](image-url)
Conclusions

In this study, the relationship between the water flow rate through CNT membranes and the CNT dimensions (radius and length) was examined with consideration of the entrance/exit effects. Molecular dynamics simulations were performed to measure the water flow rate through CNTs with radii of approximately 0.813–2.046 nm and lengths of 5–60 nm. The obtained water flow rate was compared to a flow model based on continuum hydrodynamics and a circuit analogy. The entrance/exit resistance and the interior resistance were obtained from a modified Hagen-Poiseuille’s equation with a slip boundary condition and the Sampson equation, respectively. In the application of the flow model, the variations in water viscosity and slip length with the CNT radii were also calculated and applied. The derived water flow model was in good agreement with the measured flow rate using molecular dynamics simulations. Based on the water flow model, the critical tube length for the consideration of entrance/exit effects was estimated to be about 5–20 µm for a pore radius of about 0.5–2 nm. The enhancement factor was also recalculated considering the entrance/exit effects, and it showed a decrease due to the relative increase in the entrance/exit effects as the CNT length decreased. Through comparison with the simulation/experimental values reported from previous studies, it was revealed that the suggested model could be useful for predicting and analyzing the water flow inside the CNT membrane.

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References