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**Nanoscopic insights of saline water in Carbon Nanotube Appended Filter
using Molecular Dynamics Simulations**

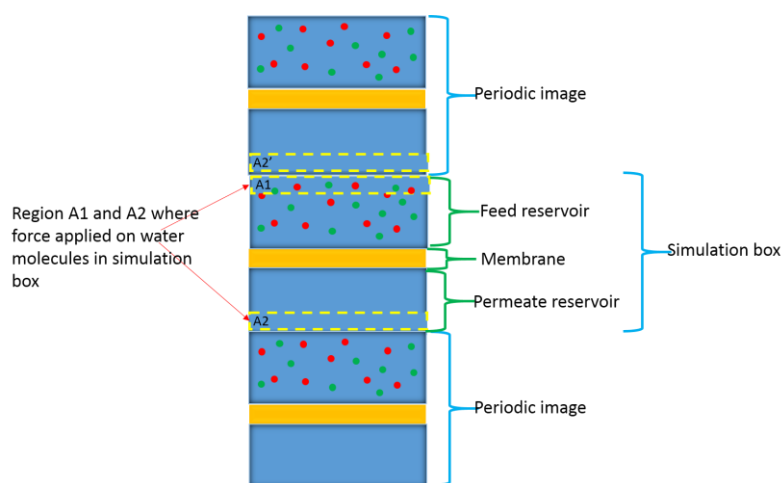
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Text.S1

In the present simulations, the pressure gradient was implemented using method of Zhu. et. at (Biophysical Journal Volume 83 July 2002 154–160). This method is applied with periodic boundary conditions as shown below image. The upper reservoir represents the feed (water + ions) and the lower one represents permeate. Now force f is applied to oxygen atoms of water molecules in region A1 and A2, both of same width (2\AA in the present study). $A2'$ is the periodic replica of A2. Even though the same amplitude of force was applied in region A1 and A2, however, having the different concentration of water in both reservoir, a pressure difference of $\Delta P = nf/A$ (where n , f and A respectively represent the force on each water, area and number of water molecules in region $A1+A2$) will be developed across the membrane.



It might be worthwhile to mention that the pressure applied for filtration was much larger than the being used in the real experimental range 1 MPa-10 MPa in order to capture the molecular events within the simulated timeframe. Since, in the Zhu et al. proposed method, pressure is applied in terms of force over a small region only, in order to avoid the artificial increase in the conduction rate due to force on water molecules. Selection of small region insures that flow through nanotubes is only due to pressure difference across the membrane, and not directly by forces on the water molecules inside the channel. Though, the one directional permeation with much pressure gradient is possible if pressure gradients are applied using piston as shown by many studies (*Desalination and Water Treatment, vol 57 (2016) 20169–20176*), however, the major advantage of Zhu method is that it provides the continuous flow the water from feed reservoir to collector reservoir as implemented with periodic boundary conditions. This on the other hand, allows to generate data from very long simulation trajectories, and so the statistical averaging

can be performed over a long time, making the system ergodic, and the estimated time average properties will be akin to experimental average properties.

Text.S2

Entropy: Entropy of the water and ions in the system was estimated using the robust 2PT method, developed by Lin et al.^{33, 34}, which is based on the assumption that a liquid can be anticipated as combination of solid phase and gas phase. Partition function of liquid therefore can be decomposed into solid partition function and gas partition function. And so, the density of state (DOS) of liquid can be written as sum of solid-like DOS and gas-like DOS. Furthermore, the information about orientation distribution can be gathered by decomposition of complete DOS of gas and solid into translational and rotational DOS.

Ions, being monoatomic, consist of only translational entropy component. On the other hand, the entropy of water molecules, which are simulated using TIP3P rigid water model, will be contributed from translational and rotation entropy components. However, since this present work is focused on permeability and the flux of ions and water, which are supposed to be related with the translational events of ion/water from one end of CNT to other end, only translational entropy was estimated using the translational density of state function as shown by **equation.s1**

$$\psi(v) = \frac{2}{kT} \lim_{\tau \rightarrow \infty} \int_{-\tau}^{\tau} \psi(t) e^{-i2\pi vt} dt \quad (\text{s1})$$

Where k and T represent the Boltzmann constant and the temperature of the system respectively and $\psi(t)$ is defined as velocity autocorrelation function, which was estimated using the following relation

$$\psi_T(t) = \sum_{i=1}^N \sum_{k=1}^3 \langle m_i c_i^k(t) \rangle \quad (\text{s2})$$

Where

$$c_i^k(t) = \lim_{\tau \rightarrow \infty} \frac{1}{2\tau} \int_{-\tau}^{\tau} v_i^k(t'+t) v_i^k(t') dt' \quad (\text{s3})$$

where m_i represents the mass of i^{th} water molecule, $v_i^k(t)$ is the k^{th} velocity component of i^{th} water molecule at time t and $c_i^k(t)$ is defined as velocity autocorrelation function for molecule i in the k^{th} direction at time t .

Further, the fluidicity factor (f) was determined to decompose translational DOS into gas-like nondiffusive component and solid-like diffusive components.

$$2\delta^{-9/2} f^{15/2} - 6\delta^{-3} f^5 + 6\delta^{-3/2} f^{7/2} + 6\delta^{-3/2} f^{5/2} + 2f - 2 = 0 \quad (\text{s4})$$

where δ is defined by

$$\delta(T, V, N, m, \psi^0) = \frac{2\psi^0}{9N} \left(\frac{\pi k T}{m} \right)^{1/2} \left(\frac{N}{V} \right)^{1/3} \left(\frac{6}{\pi} \right)^{2/3} \quad (\text{s5})$$

where ψ^0 is the zero frequency component of DOS function i.e. $\psi^0 = \psi(0)$.

Using the f , the gas component of DOS function and solid component of DOS function can be obtained using **eqn.s6** and **eqn.s7** respectively.

$$\psi^g(v) = \frac{\psi^0}{1 + \left[\frac{\pi \psi^0 v}{6fN} \right]^2} \quad (\text{s6})$$

$$\psi^s(v) = \psi(v) - \psi^g(v) \quad (\text{s7})$$

where superscript 0 indicates the zero frequency component of DOS function and superscript s and g, respectively, refer to solid-like and gas-like components of DOS function.

Given DOS decomposition, the entropy components are then calculated by using solid-like and gas-like DOS functions and corresponding weighting factors⁴⁴ as below.

$$S = k \left[\int_0^\infty dv \cdot \psi^g(v) W^g(v) + \int_0^\infty dv \cdot \psi^s(v) W^s(v) \right] \quad (\text{s8})$$

where, the weighting factors $W^g(v)$ and $W^s(v)$ for gas-like and solid-like contribution of entropy are determined by using the relation as shown in **eqn.14** and **eqn.15** respectively.

$$W^g(v) = \frac{S^{HS}}{3k} \quad (\text{s9})$$

$$W^s(v) = \frac{\beta h v}{e^{\beta h v} - 1} - \ln \left[1 - e^{-\beta h v} \right] \quad (\text{s10})$$

In the above expressions, h is plank constant and S^{HS} represent the entropy of hard sphere fluid. 2PT method was successfully applied for polar and non-polar fluids with CNT and deriving a universal scaling law using excess entropy and diffusivity of fluids under confinement.

Fig. S1. Ion concentration (C_{ion}) for axial position of CNT(9,9), considered for feed concentration of 0.6M and 1.2M at pressure gradient of 350 MPa.

Figure shows increased accumulation (concentration) of ions near nanotube-water interface with increase in ion concentration from 0.6M to 1.2M in the system.

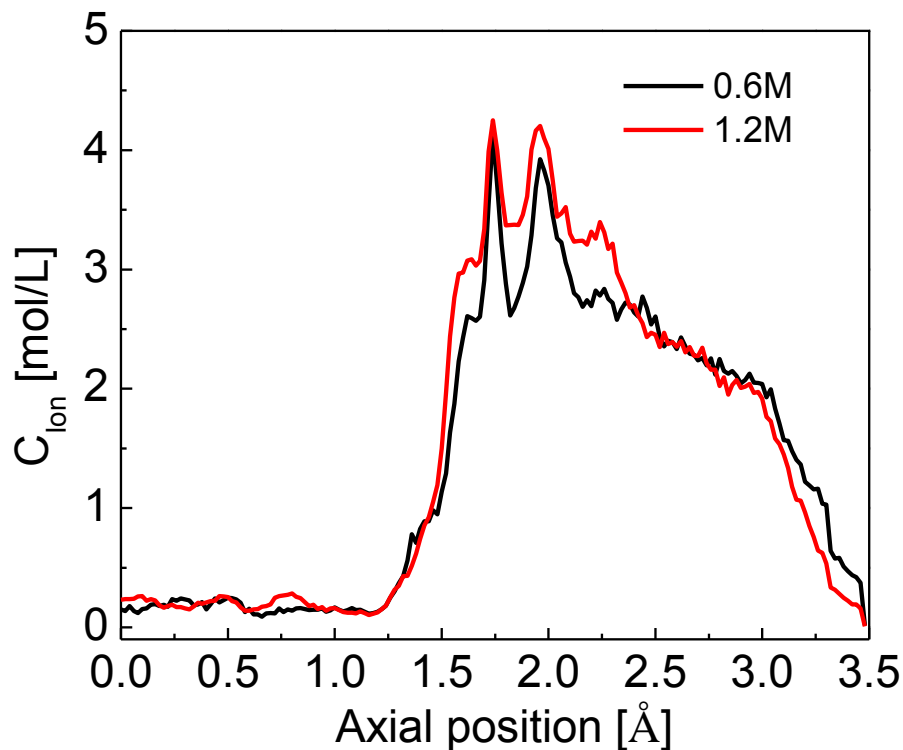


Fig. S2. Water flux vs. pressure gradient in absence of ions for CNT(9,9)

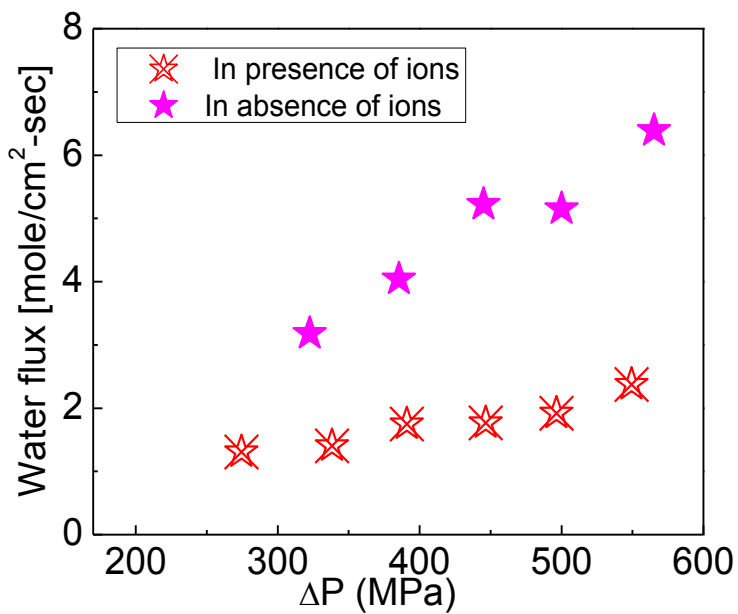


Fig. S3. PMF profiles of water (left) and ion (right) in bulk, nanotube confinement and nanotube-water interface, estimated from normalized axial density profiles with effect of nanotube diameter (top) and pressure gradient (bottom)

The PMF profiles were generated using normalized density i.e. local density/global density, which also represents the axial density correlation function ($\rho(z)$). To calculate the local density of water/ion, the nanotube volume was divided into the cylindrical bins of length 1\AA and radius same as nanotube diameter. Such bins were extended to bulk solution. The local density of water/ion in each cylindrical bin was estimated and divided by global density of water/ion in order to estimate the density correlation distribution function ($\rho(z)$). Further, using the $\rho(z)$, the PMF was estimated using expression $PMF = -RT \ln(\rho(z))$

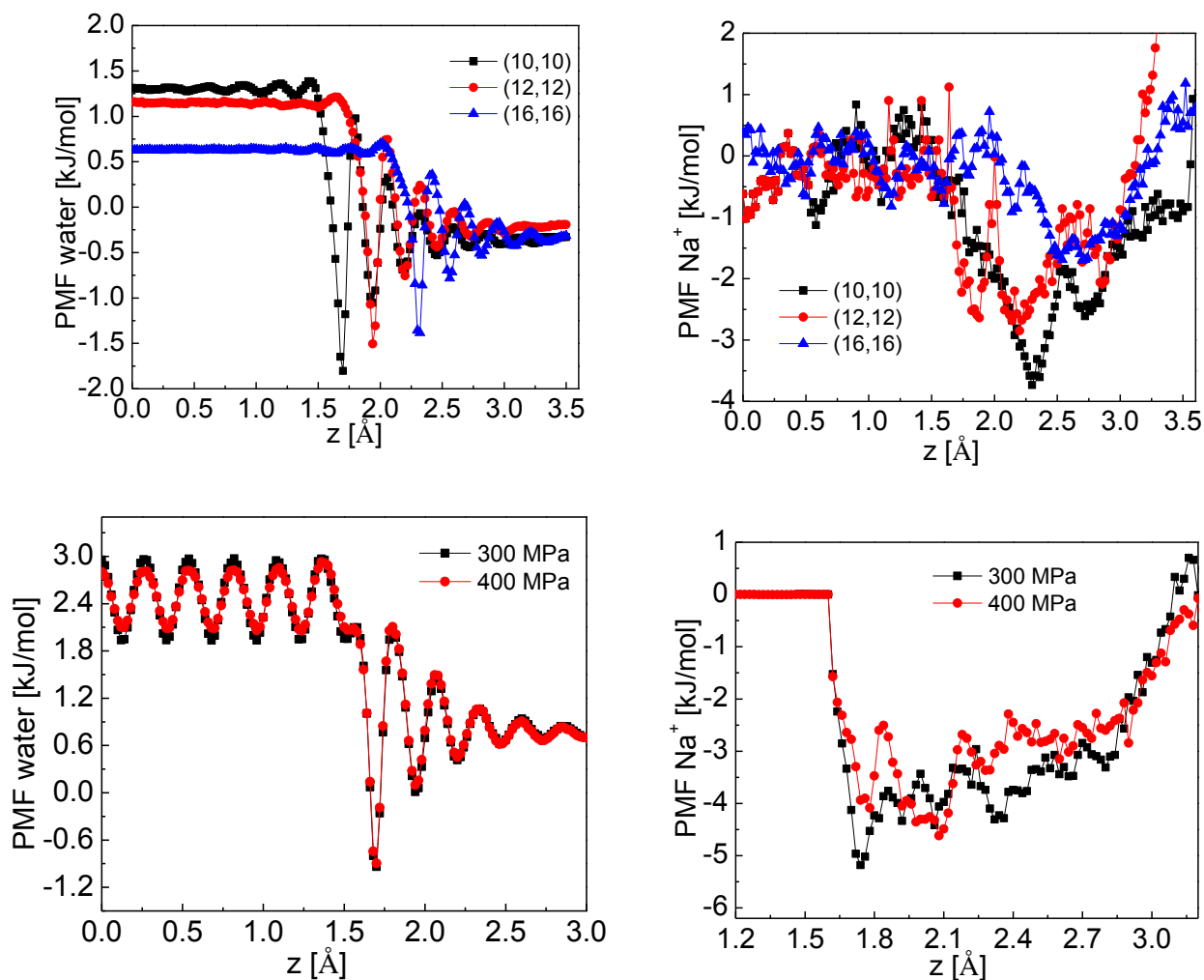


Fig. S4. Axial density profile of water along the nanotube axis for varied (a) pressure gradient and (b) nanotube diameter.

