Carbon Nanotubes
Hydrophobic channels - Perfect Models for Membrane Water Channels

A balance between the size and hydrophobicity
Water-nanotube interaction can be easily modified

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- Much better statistics
- No need for membrane and lipid molecules
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Water Single-files in Carbon Nanotubes

Water files form polarized chains in nanotubes
Calculation of Diffusion Permeability from MD

$\Phi_0$: number of water molecules crossing the channel from the left to the right in unit time

$$p_d = \frac{V_w}{N_A} \Phi_0$$

$\Phi_0$ can be directly obtained through equilibrium MD simulation by counting “full permeation events”
Chemical Potential of Water

\[ \mu_w = \mu^0_w + RT \ln X_w + PV_w \]

- \( \mu^0_w \): standard chemical potential of water
- \( X_w \): molar fraction of water
- \( R \): the gas constant
- \( T \): temperature
- \( P \): pressure
- \( V_w \): molar volume of water

Water flow in either direction is the same, i.e., no net flow of water.

\[ X_w = 1 \Rightarrow \ln X_w = 0 \]
Solutes Decrease the Chemical Potential of Water

\[ \mu_w = \mu_w^o + RT \ln X_w + PV_w \]

Addition of an impermeable solute to one compartment drives the system out of equilibrium.

\[ RT \ln X_w(1) < RT \ln X_w(2) \]

\[ \Rightarrow \mu_w(1) < \mu_w(2) \]

Water establishes a net flow from compartment (2) to compartment (1).
Establishment of Osmotic Equilibrium

At equilibrium, the chemical potential of any species is the same at every point in the system to which it has access.

\[ \mu_w^0(1) + RT \ln X_w(1) + P(1)V_w = \mu_w^0(2) + RT \ln X_w(2) + P(2)V_w \]

\[ RT \ln X_w(1) + P(1)V_w = P(2)V_w \]

\[ \Delta PV_w = -RT \ln X_w(1) \]

\[ X_w(1) < 1 \quad X_w(2) = 1 \]
Establishment of an Osmotic Equilibrium

\[ \Delta PV_w = -RT \ln X_w (1) \]

Solute molar fraction in physiological (dilute) solutions is much smaller than water molar fraction.

\[ X_w + X_s = 1 ; \quad X_s << 1 \]

\[ \Rightarrow \ln X_w = \ln(1 - X_s) \approx -X_s \]

\[ \Delta PV_w = RTX_s \]

\[ \Rightarrow \Pi = \Delta P = \frac{RT}{V_w} X_s \]

Osmotic pressure
Establishment of an Osmotic Equilibrium

\[
\Pi = \Delta P = \frac{RT}{V_w} X_s
\]

Solute concentration (~0.1M) in physiological (dilute) solutions is much smaller than water concentration (55M).

\[
X_s = \frac{n_s}{n_s + n_w} \approx \frac{n_s}{n_w} = \frac{n_s}{n_w} \frac{V_w}{V_w}
\]

\[
= \frac{n_s}{V_{tot}} V_w = C_s V_w
\]

\[
\Pi = \Delta P = \frac{RT}{V_w} C_s V_w = RT C_s
\]

\[X_w(1) < 1 \quad X_w(2) = 1\]
Simulation of osmotic pressure induced water transport may be done by adding salt to one side of the membrane.

\[ \text{NaCl} \rightarrow \text{Na}^+ + \text{Cl}^- \]

There is a small problem with this setup!
Problem: The solvents on the two sides of a membrane in a conventional periodic system are connected.
We can include more layers of membrane and water to create two compartments of water that are not in contact.
Semipermeable membrane

UNIT CELL

NaCl
(1)

NaCl
(2)

Semipermeable membrane

Semipermeable membrane
The overall translation of the system is prevented by applying constraints or counter forces to the membrane.

Realizing a Pressure Difference in a Periodic System

\[ P_1 = P_2 + nf \implies \Delta P = nf / A \]

\( f \) is the force on each water molecule, for \( n \) water molecules.

Applying a Pressure Difference Across the Membrane

\[ \Delta P = \frac{nf}{A} \]

Applying force on all water molecules.

Not a good idea!
Applying a Pressure Difference Across the Membrane

\[ \Delta P = n f / A \]

Applying force on bulk water only.

Very good
Applying a Pressure Difference Across the Membrane

\[ \Delta P = nf / A \]

Applying force only on a slab of water in bulk.

Excellent

\[ \Phi_w = P_f A \left( \frac{\Delta P}{RT} - \Delta C_s \right) \]
Calculation of osmotic permeability of water channels

GlpF

\( p_f: 1.4 \times 10^{-13} \text{ cm}^3/\text{s} \)

Aquaporin-1

\( p_f: 7.0 \pm 0.9 \times 10^{-14} \text{ cm}^3/\text{s} \)

Exp: 5.4 – 11.7 \times 10^{-14} \text{ cm}^3/\text{s}
Interactive Molecular Dynamics

VMD ← NAMD
Evidence for **Stereoselectivity**

**Ribitol**
Optimal hydrogen bonding and hydrophobic matching

**Arabitol**
10 times slower