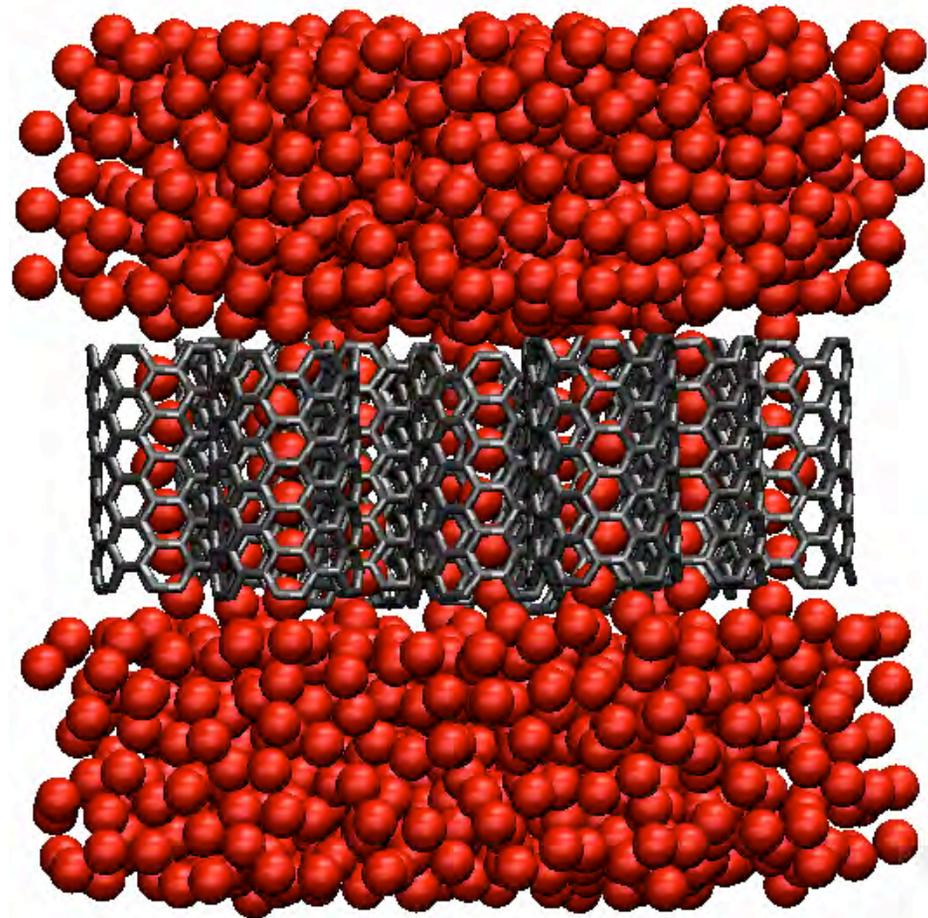


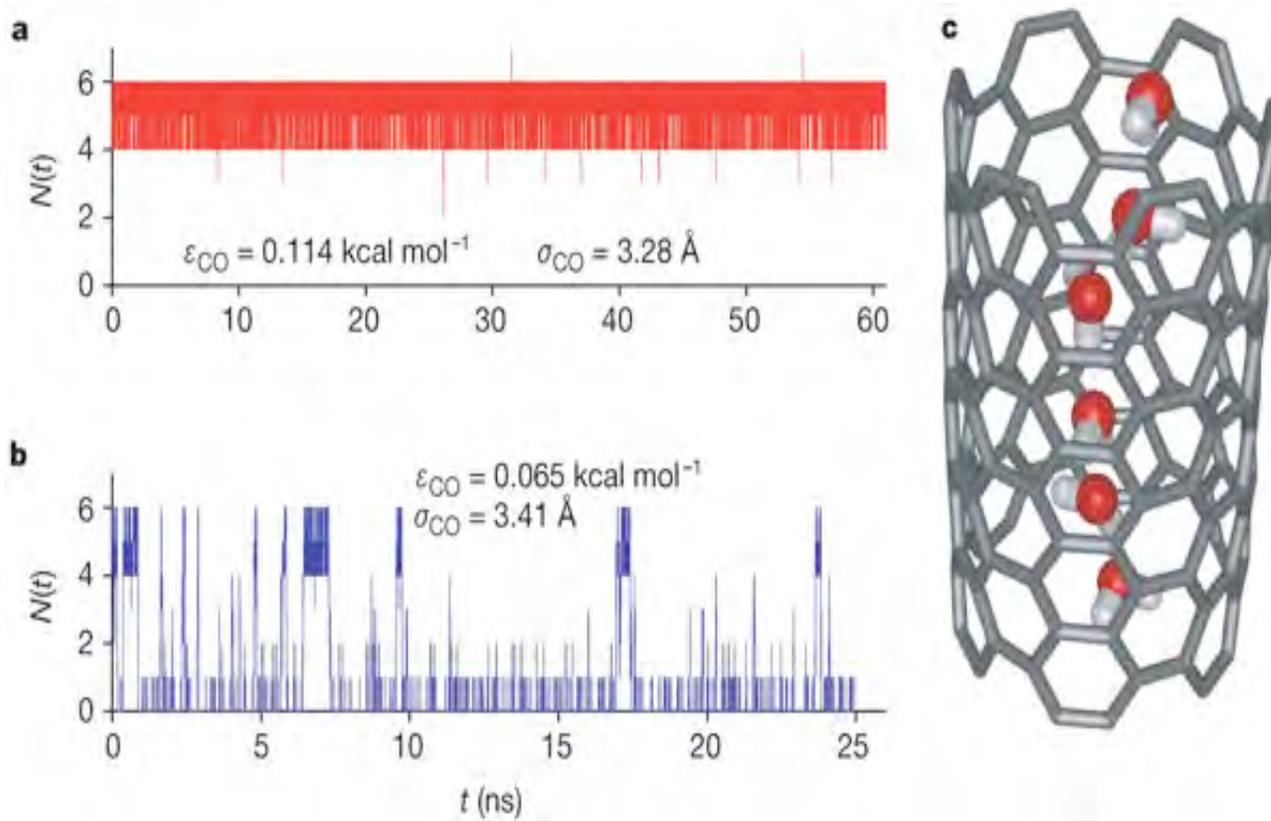
Carbon Nanotubes

Hydrophobic channels - Perfect Models for Membrane Water Channels



A balance between the size and hydrophobicity

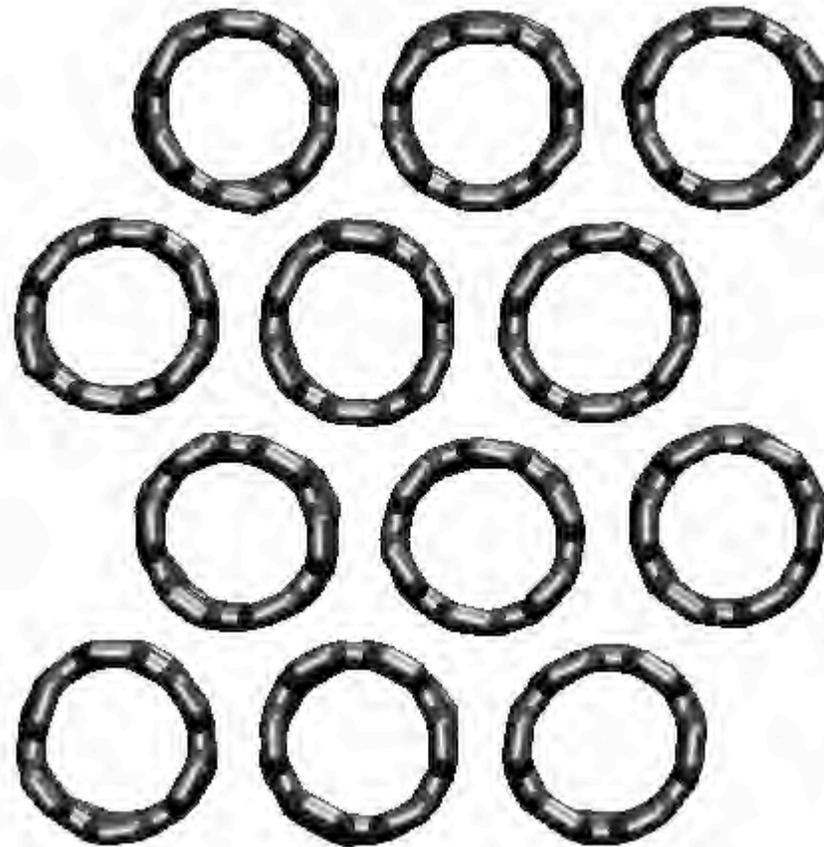
Water-nanotube interaction can be easily modified



Modifying charges
Modifying vdW parameters

Carbon Nanotubes

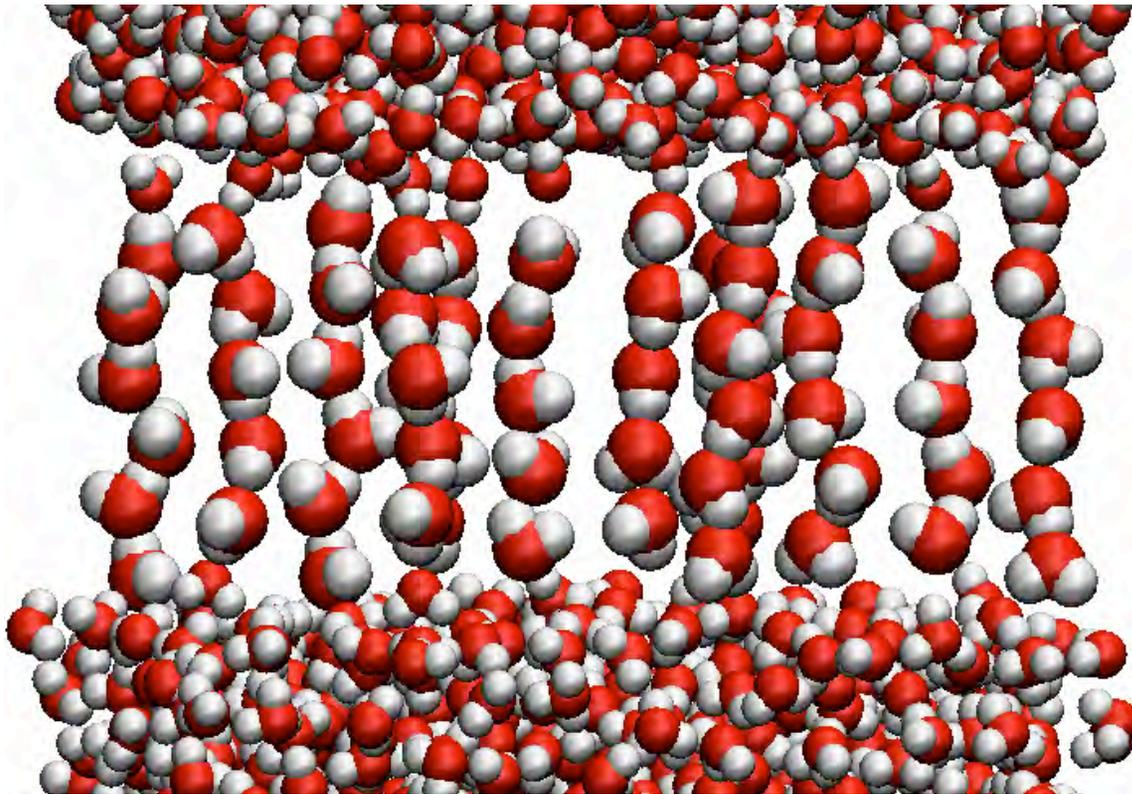
Hydrophobic channels - Perfect Models for Membrane Water Channels



- Much better statistics
- No need for membrane and lipid molecules

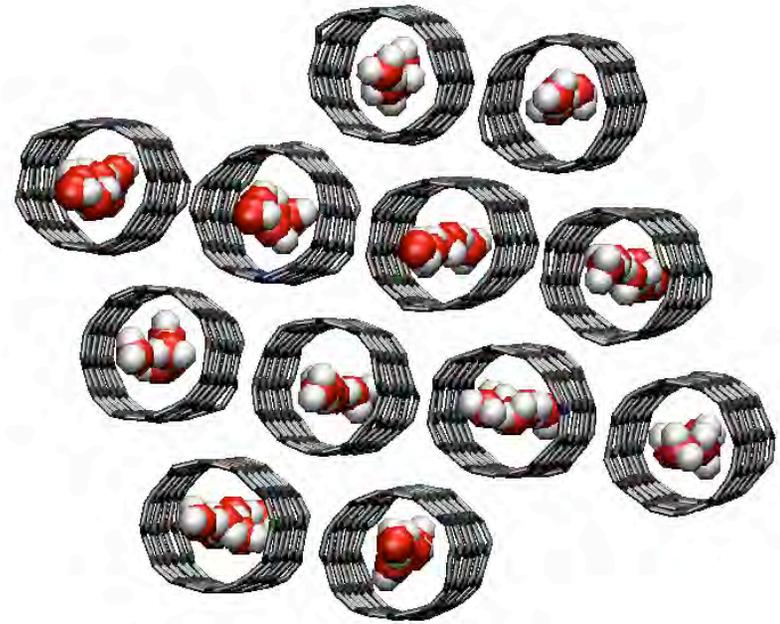
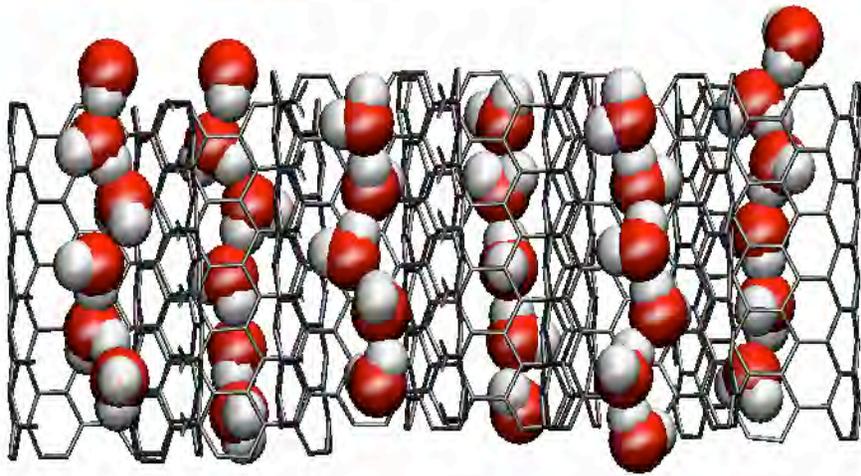
Carbon Nanotubes

Hydrophobic channels - Perfect Models for Membrane Water Channels



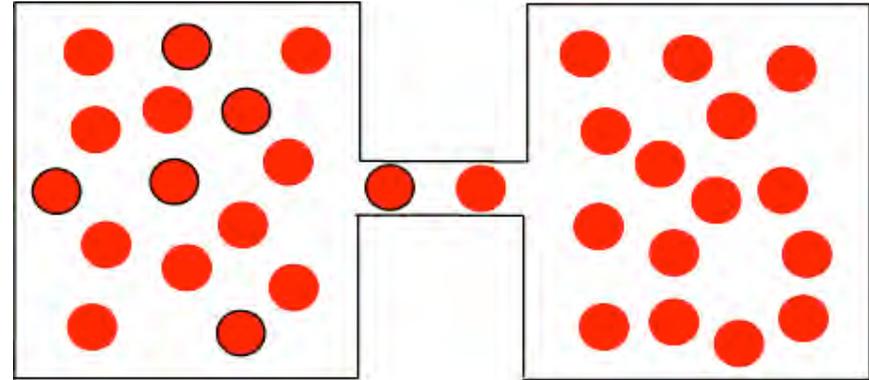
- Much better statistics
- No need for membrane and lipid molecules

Water Single-files in Carbon Nanotubes



Water files form polarized chains in nanotubes

Calculation of Diffusion Permeability from MD



Φ_0 : number of water molecules crossing the channel from the left to the right in unit time

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

Φ_0 can be directly obtained through **equilibrium MD** simulation by counting “full permeation events”

Chemical Potential of Water

$$\mu_w = \mu_w^o + RT \ln X_w + PV_w$$

μ_w^o : standard chemical potential of water

X_w : molar fraction of water

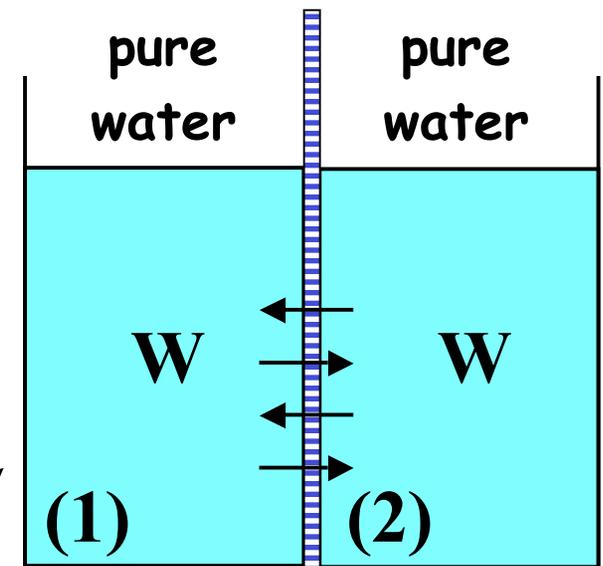
R : the gas constant

T : temperature

P : pressure

V_w : molar volume of water

$$X_w = 1 \Rightarrow \ln X_w = 0$$



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

membrane

Solutes Decrease the Chemical Potential of Water

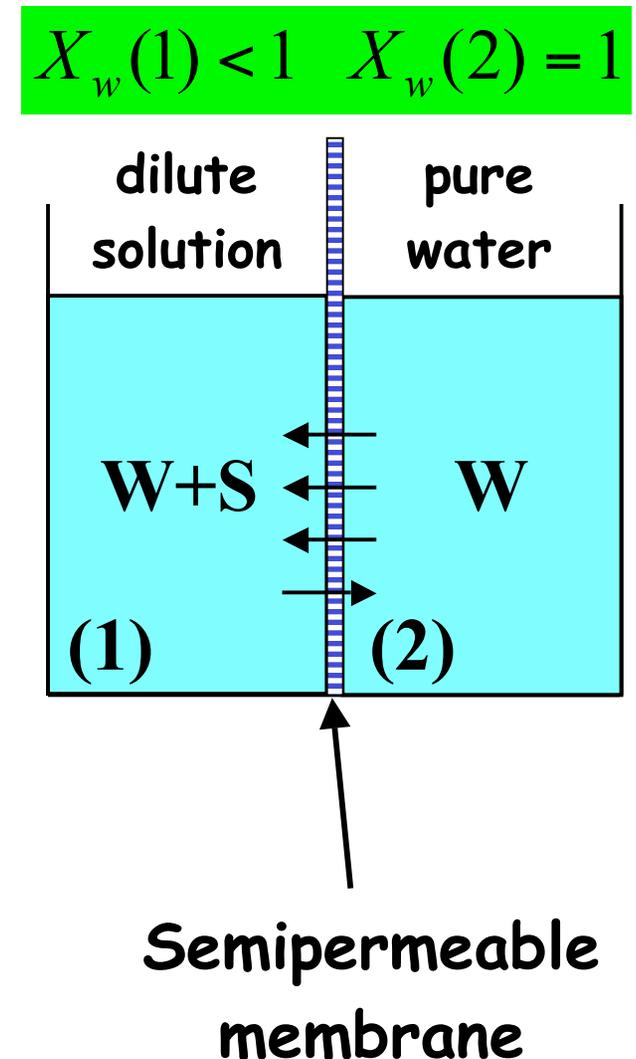
$$\mu_w = \mu_w^o + RT \ln X_w + PV_w$$

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

$$\text{@equilibrium : } \mu_w(1) = \mu_w(2)$$

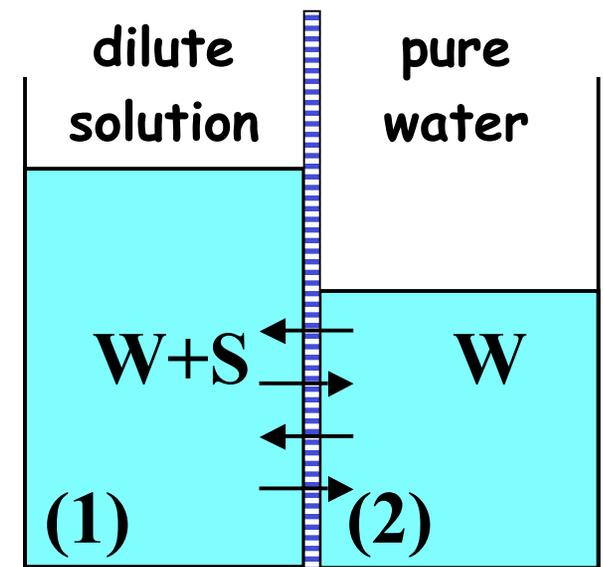
At equilibrium, the chemical potential of any species is the same at every point in the system to which it has access.

$$\mu_w^o(1) + RT \ln X_w(1) + P(1)V_w = \mu_w^o(2) + RT \ln X_w(2) + P(2)V_w$$

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

$$\Delta P V_w = -RT \ln X_w(1)$$

$$X_w(1) < 1 \quad X_w(2) = 1$$



Semipermeable
membrane

Establishment of an Osmotic Equilibrium

$$\Delta PV_w = -RT \ln X_w \quad (1)$$

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

$$X_w + X_s = 1 ; X_s \ll 1$$

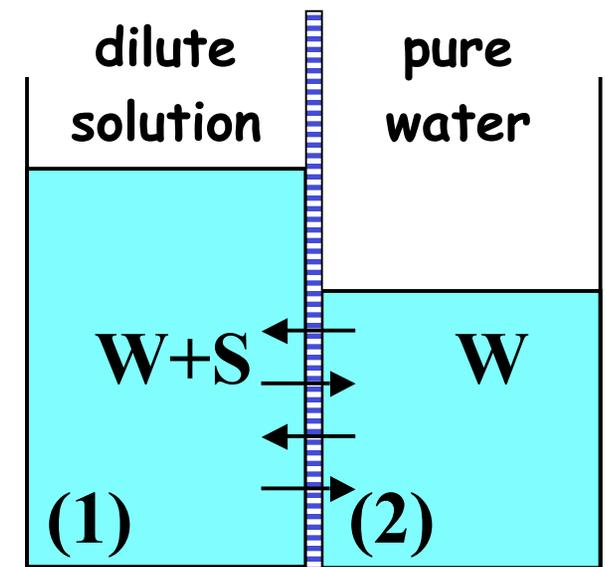
$$\Rightarrow \ln X_w = \ln(1 - X_s) \cong -X_s$$

$$\Delta PV_w = RT X_s$$

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

Osmotic pressure

$$X_w(1) < 1 \quad X_w(2) = 1$$



Semipermeable membrane

Establishment of an Osmotic Equilibrium

$$\Pi = \Delta P = \frac{RT}{V_w} X_s$$

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

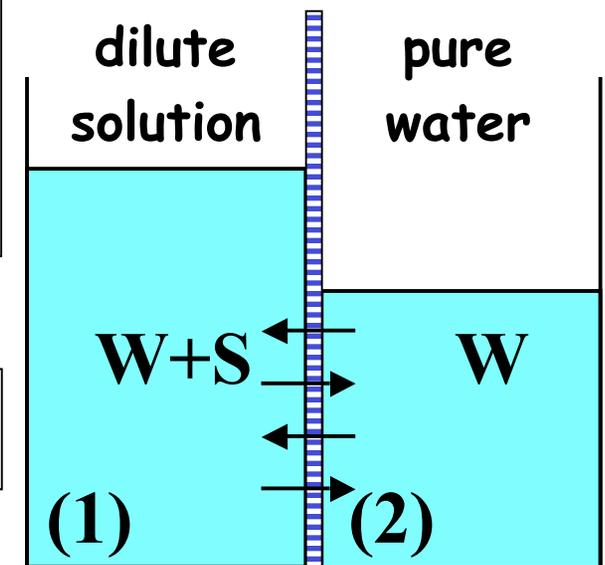
$$X_s = \frac{n_s}{n_s + n_w} \approx \frac{n_s}{n_w} = \frac{n_s}{n_w} \frac{V_w}{V_w}$$

$$n_s \ll n_w$$

$$= \frac{n_s}{V_{tot}} V_w = C_s V_w$$

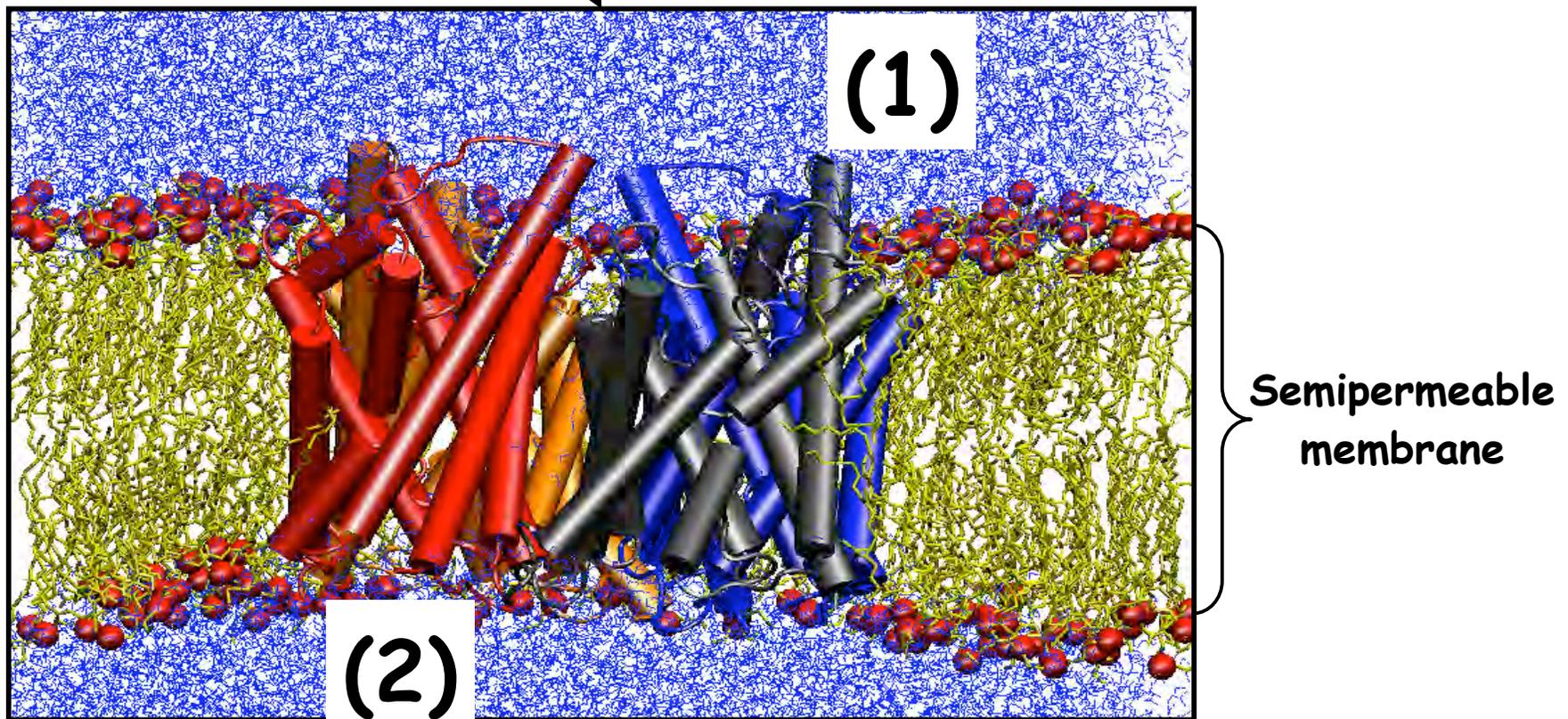
$$\Pi = \Delta P = \frac{RT}{V_w} C_s V_w = RTC_s$$

$$X_w(1) < 1 \quad X_w(2) = 1$$



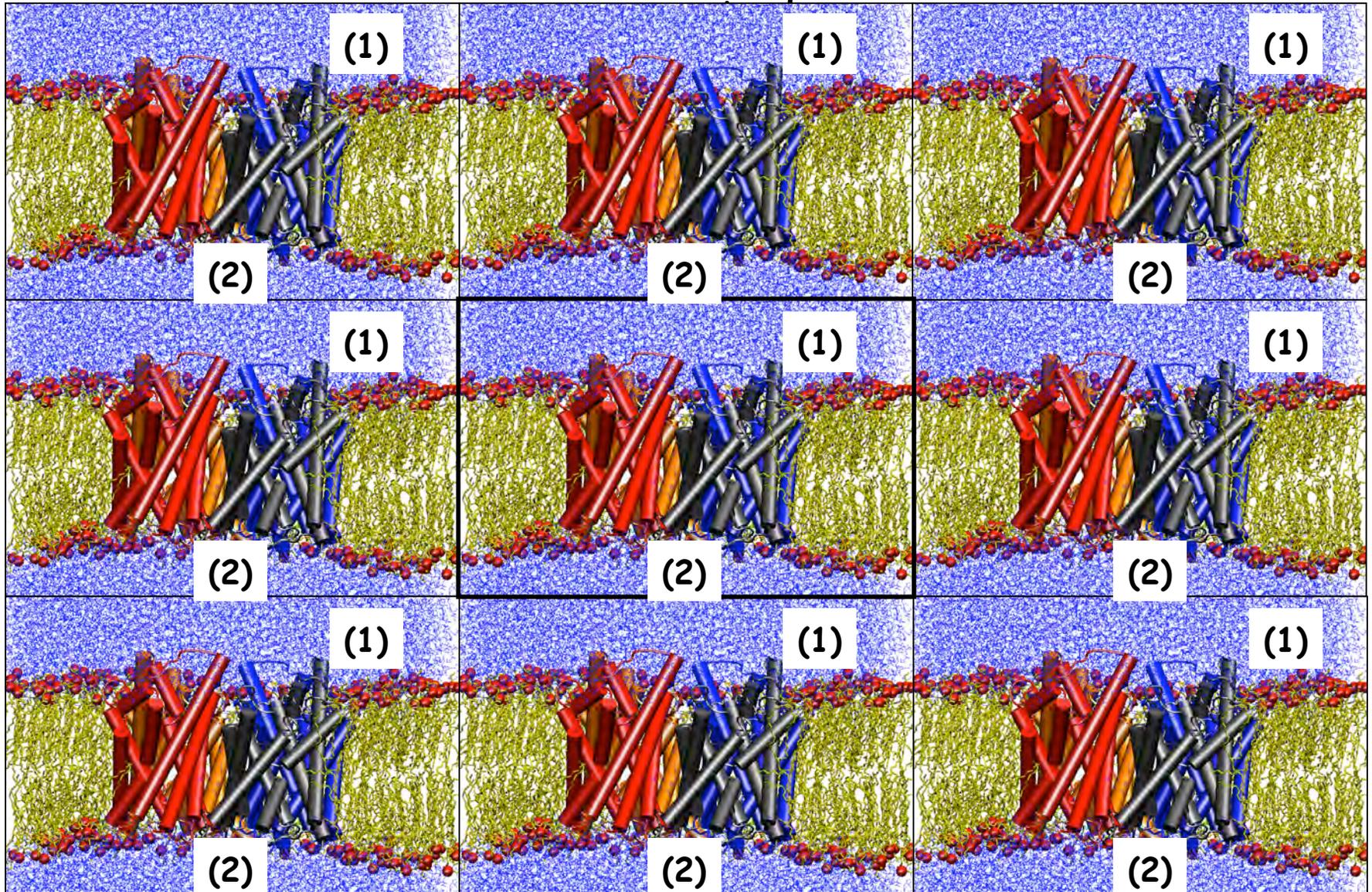
$$\Delta \Pi = \Delta P = RT \Delta C_s$$

Simulation of osmotic pressure induced water transport may be done by adding salt to one side of the membrane.



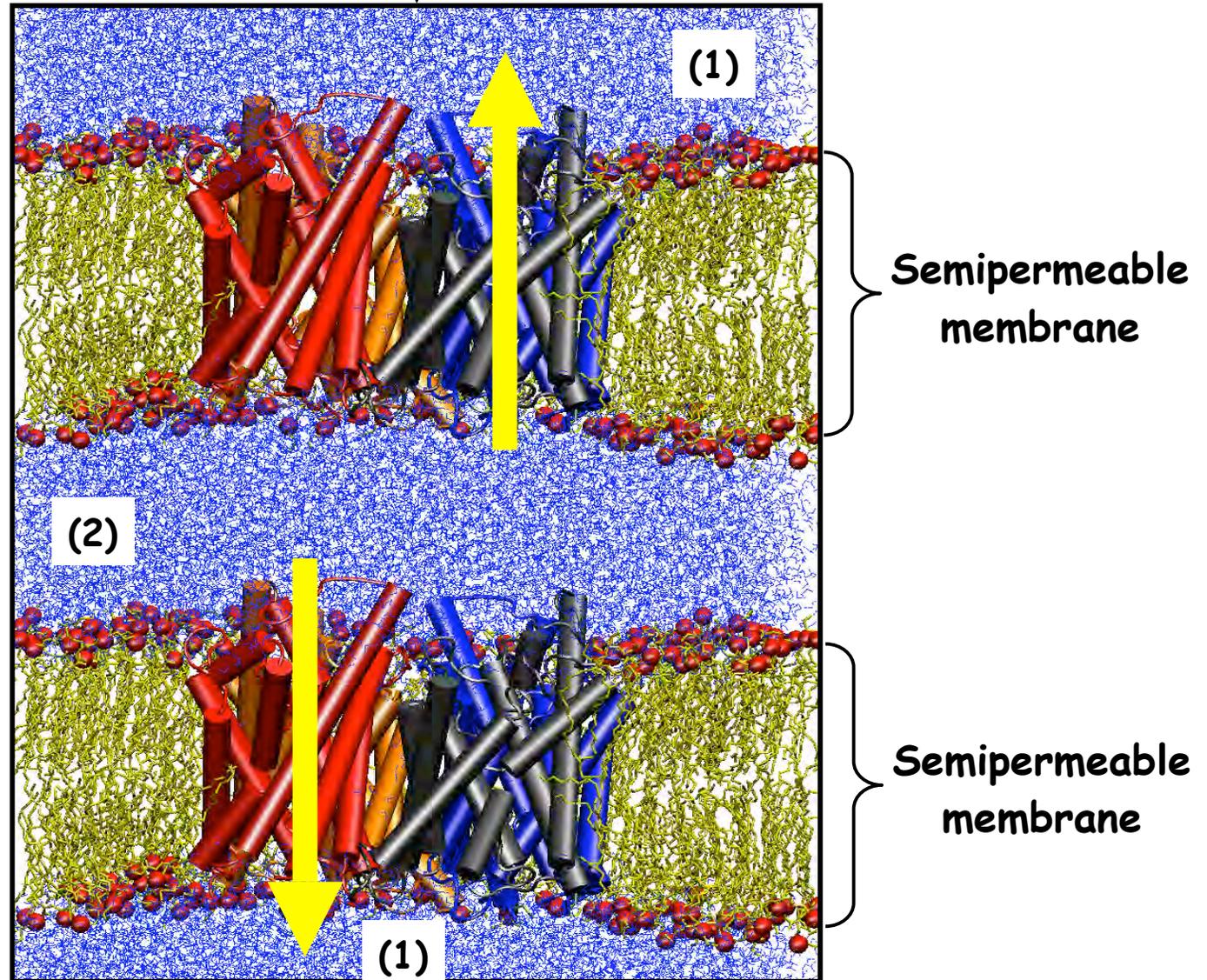
There is a small problem with this setup!

Problem: The solvents on the two sides of a membrane in a conventional periodic system are

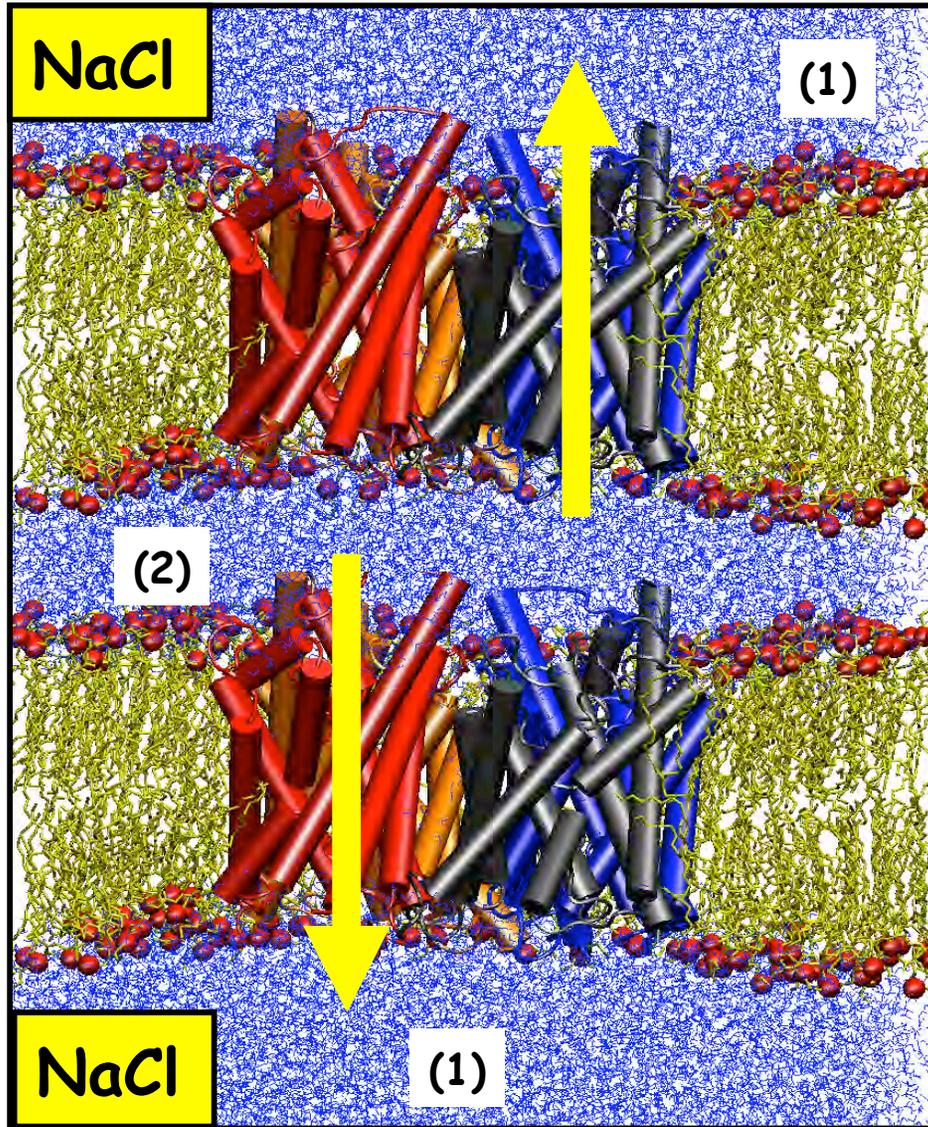


We can include more layers of membrane and water to create two compartment of water that are not in contact

NaCl



UNIT CELL



Semipermeable membrane

Semipermeable membrane

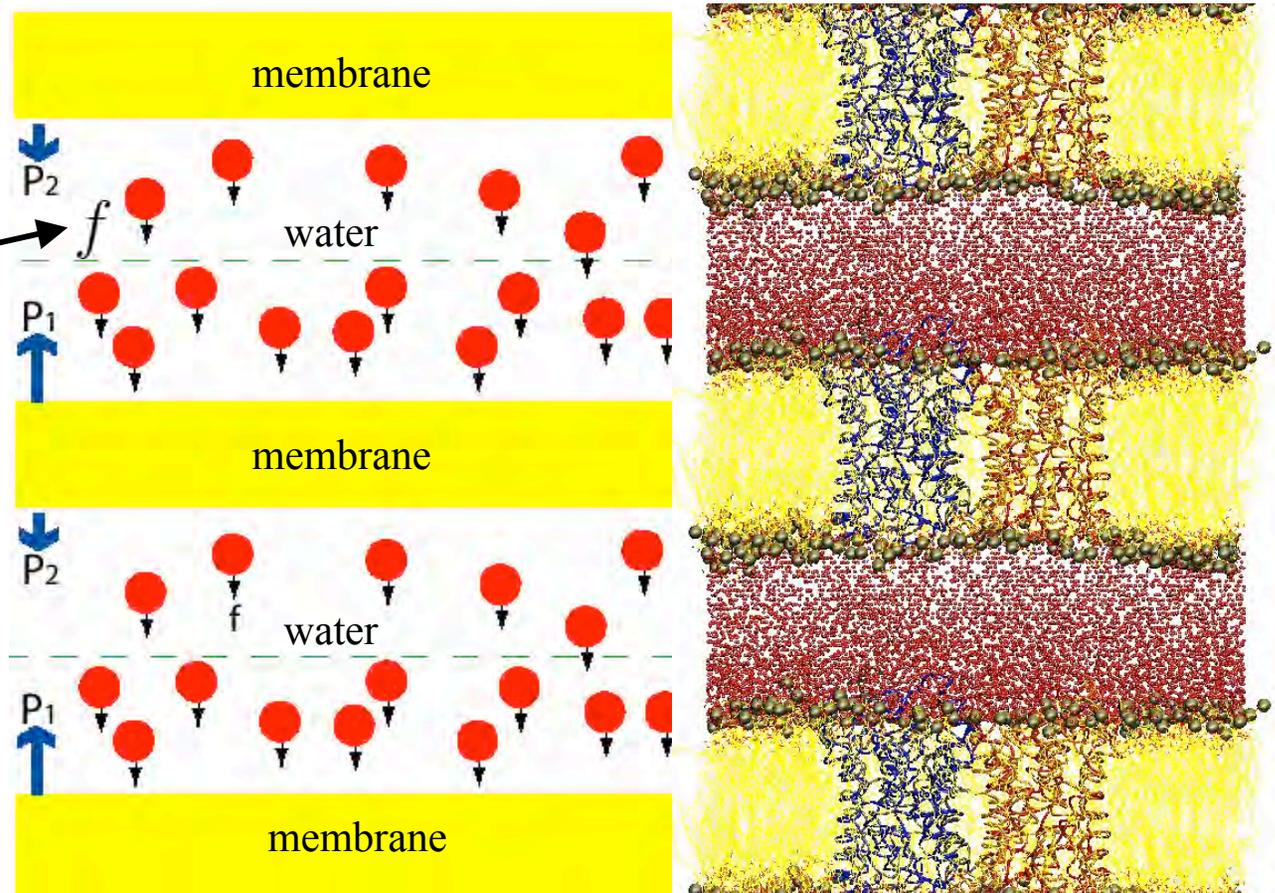
Realizing a Pressure Difference in a Periodic System

$$P_1 = P_2 + nf \Rightarrow \Delta P = nf / A$$

Fangqiang Zhu

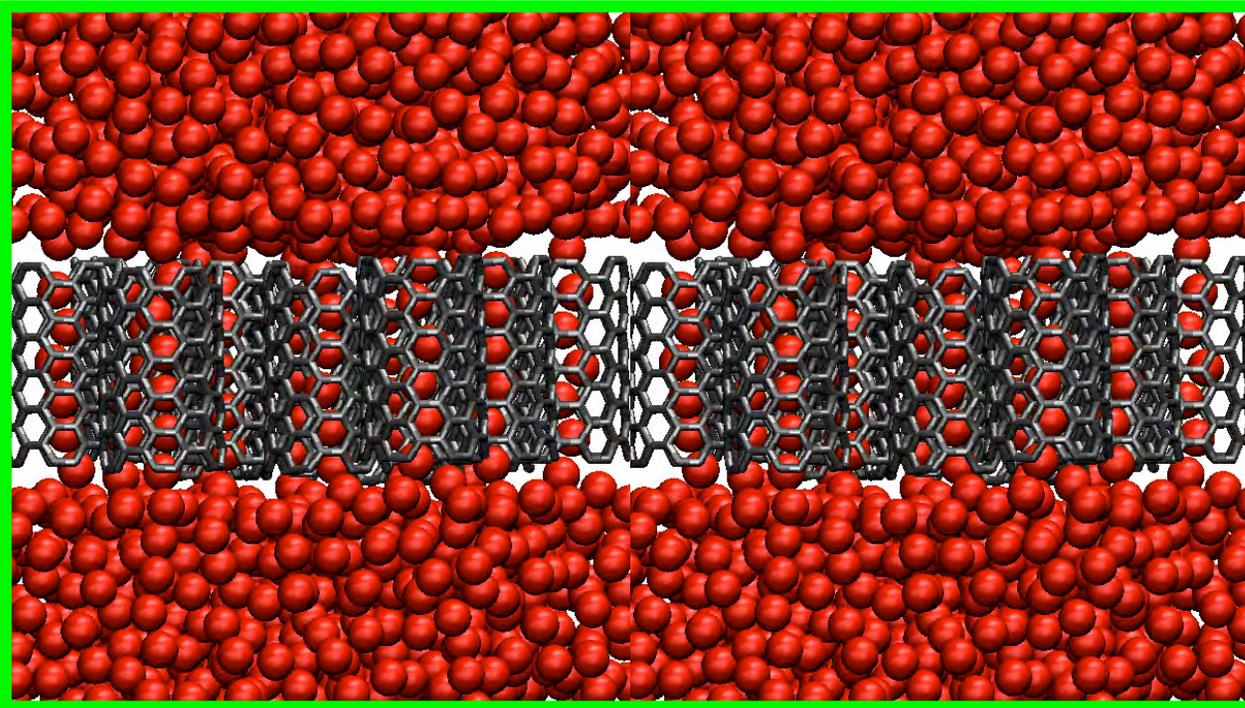
f is the force on each water molecule, for n water molecules

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



Applying a Pressure Difference Across the Membrane

$$\Delta P = nf / A$$

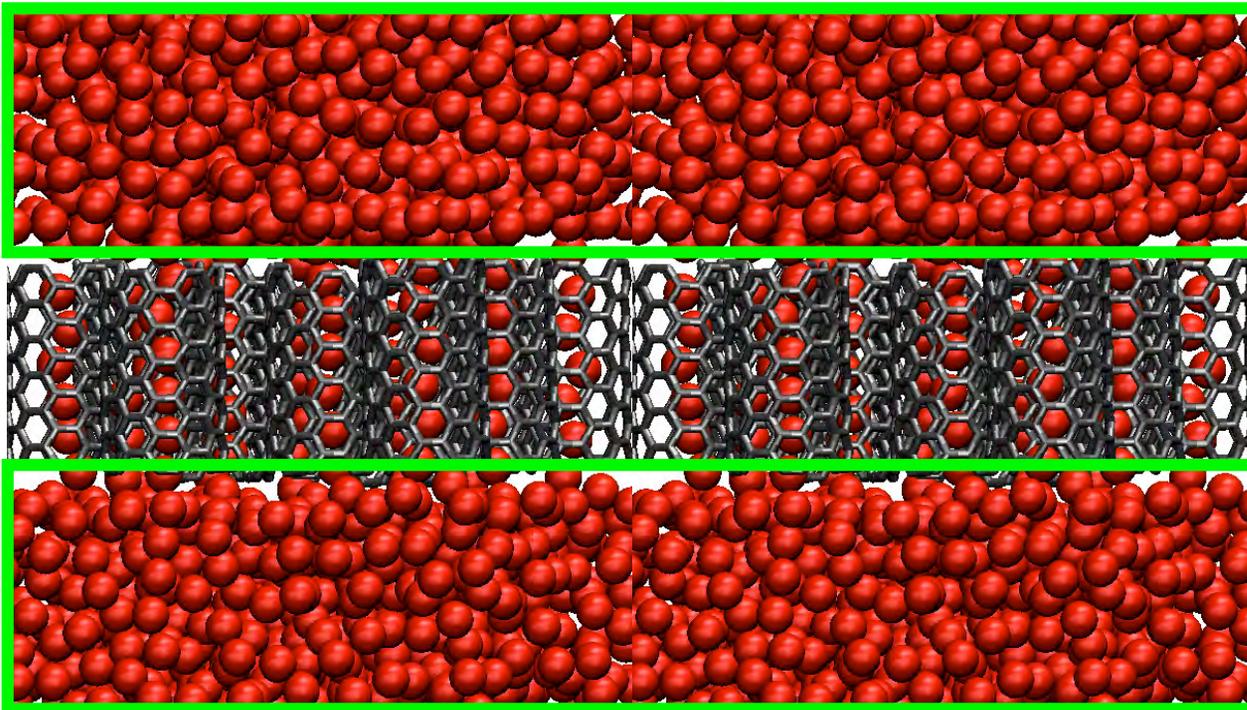


Applying
force on all
water
molecules.

Not a good
idea!

Applying a Pressure Difference Across the Membrane

$$\Delta P = nf / A$$

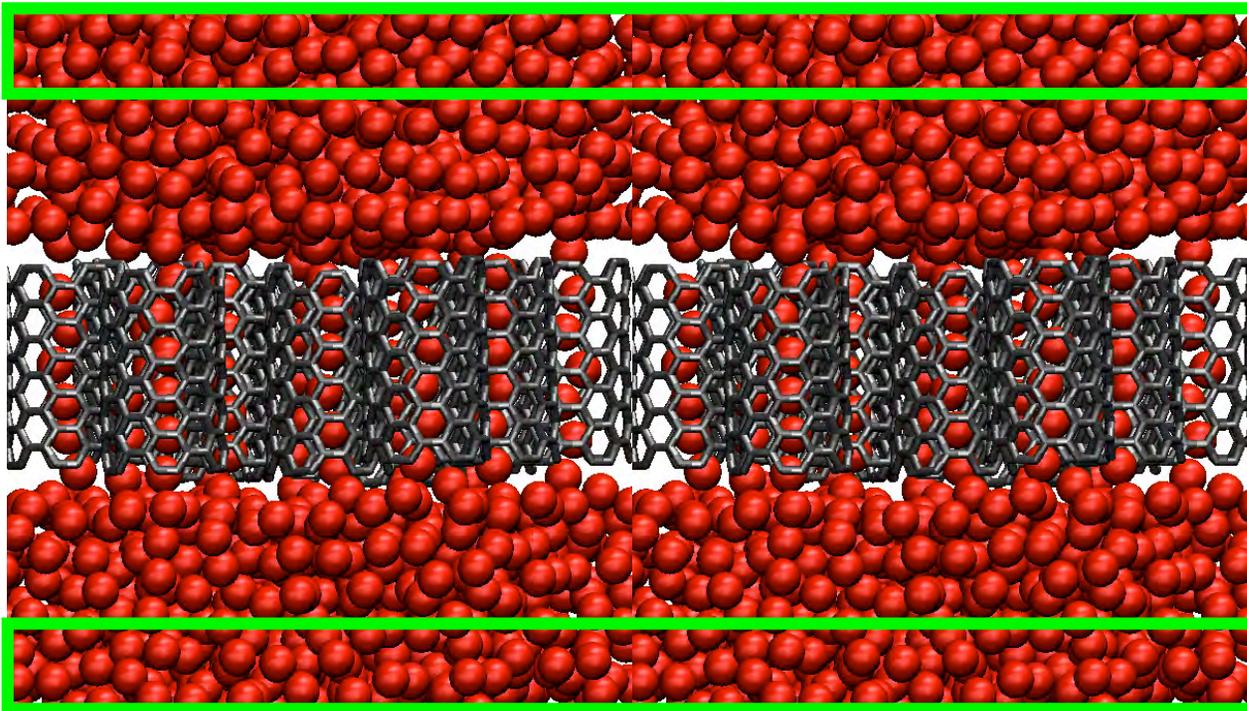


Applying
force on
bulk water
only.

Very good

Applying a Pressure Difference Across the Membrane

$$\Delta P = nf / A$$



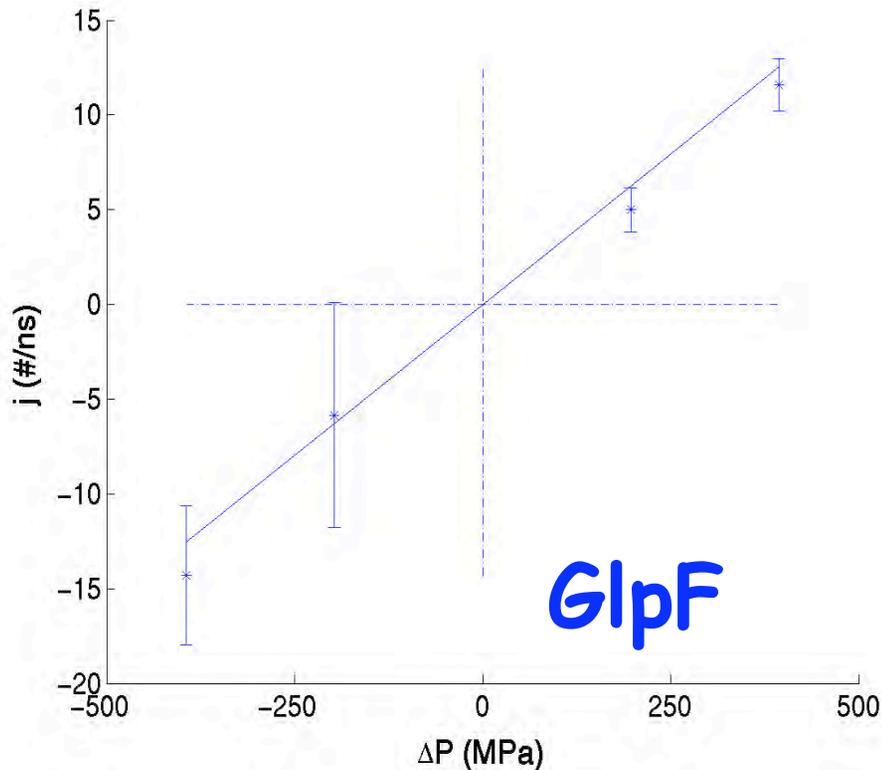
Applying
force only
on a slab of
water in
bulk.

Excellent

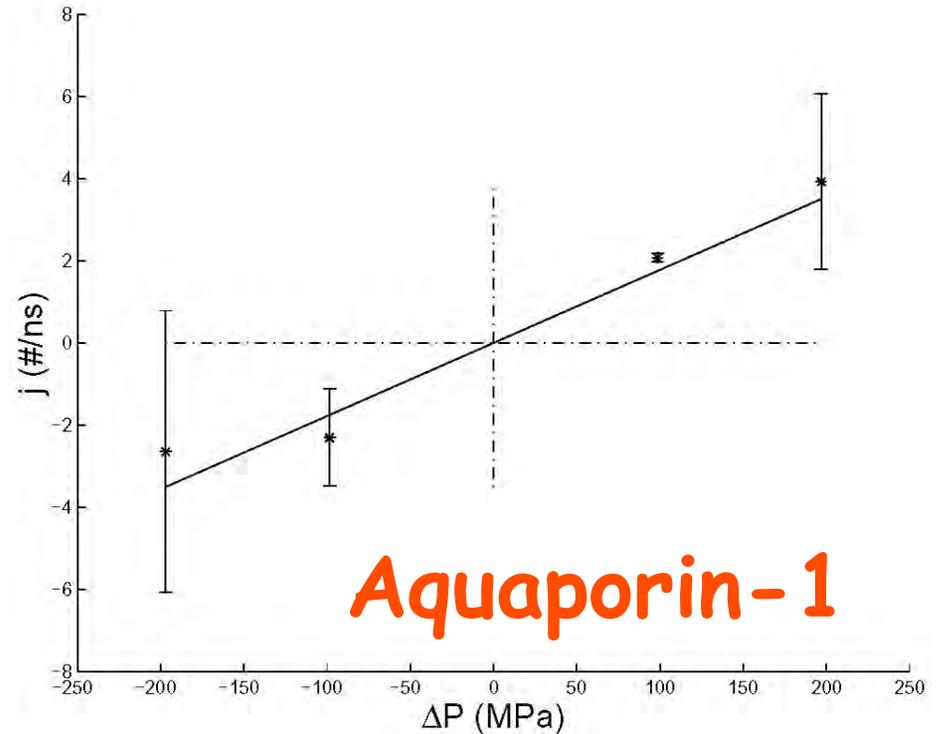
P_f can be calculated from
these simulations

$$\Phi_w = P_f A \left(\frac{\Delta P}{RT} - \Delta C_s \right)$$

Calculation of osmotic permeability of water channels



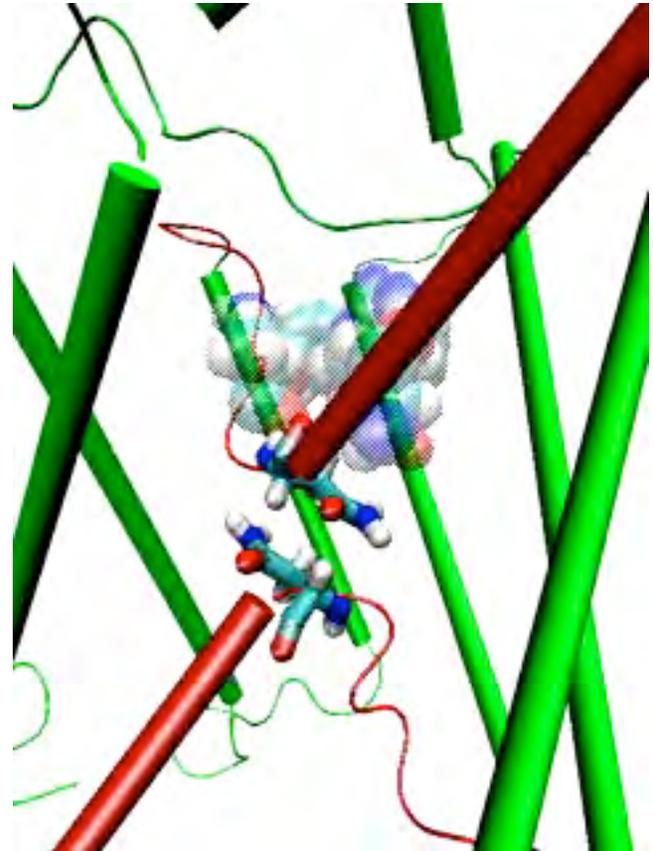
$p_f: 1.4 \times 10^{-13} \text{ cm}^3/\text{s}$



$p_f: 7.0 \pm 0.9 \times 10^{-14} \text{ cm}^3/\text{s}$
Exp: $5.4 - 11.7 \times 10^{-14} \text{ cm}^3/\text{s}$

Interactive Molecular Dynamics

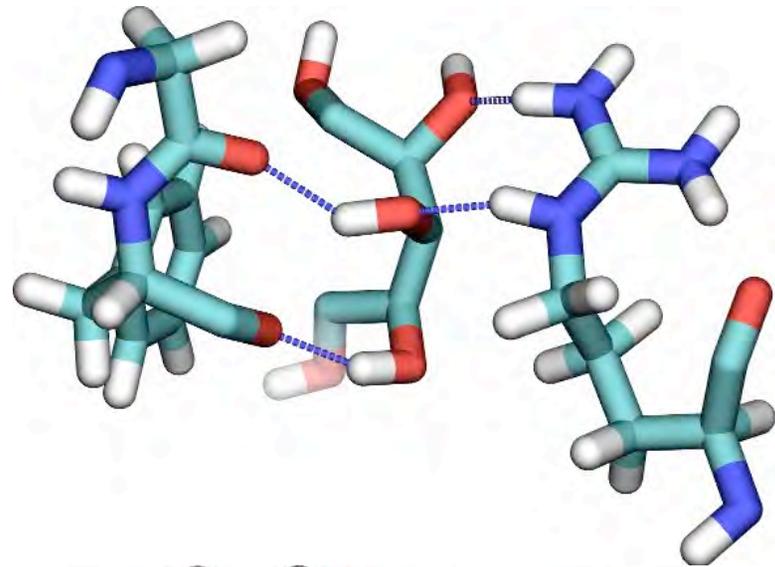
VMD \longleftrightarrow **NAMD**



Evidence for Stereoselectivity

Ribitol

Optimal hydrogen bonding
and hydrophobic matching



Arabitol

10 times slower

