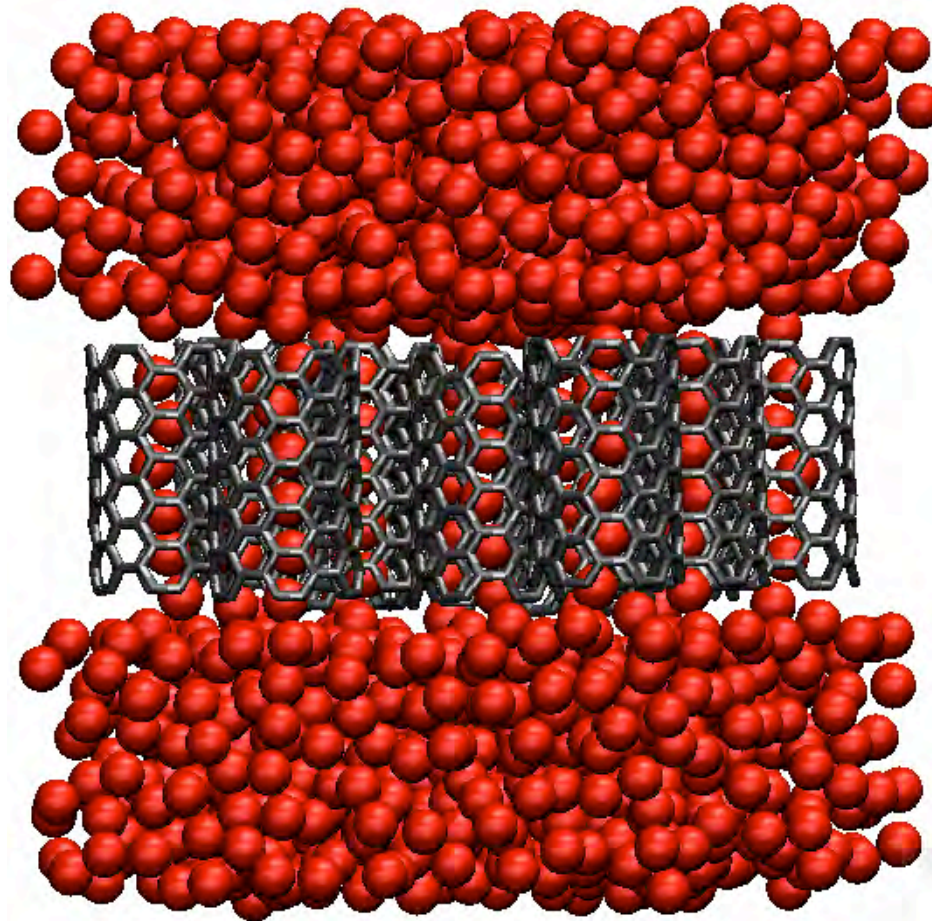


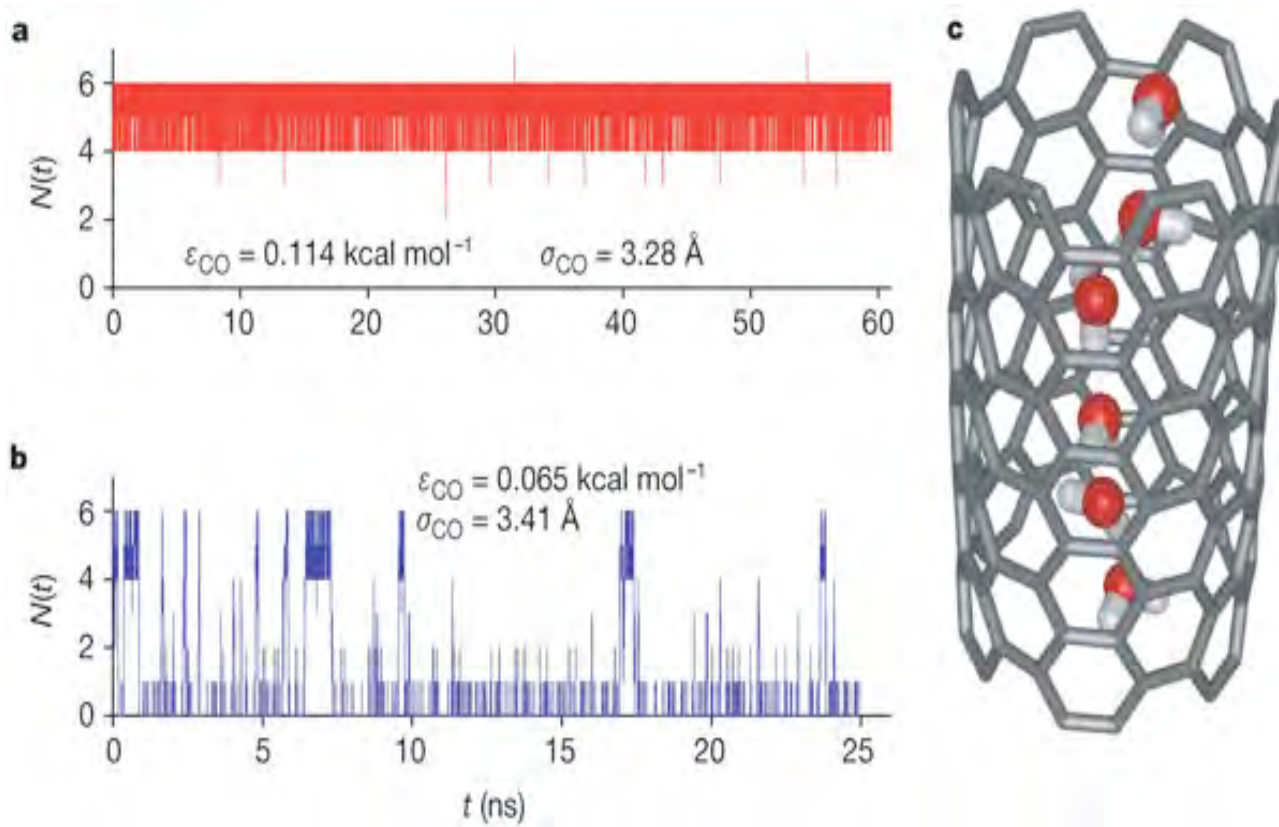
# Carbon Nanotubes

## Hydrophobic channels - Perfect Models for Membrane Water Channels



A balance between the size and hydrophobicity

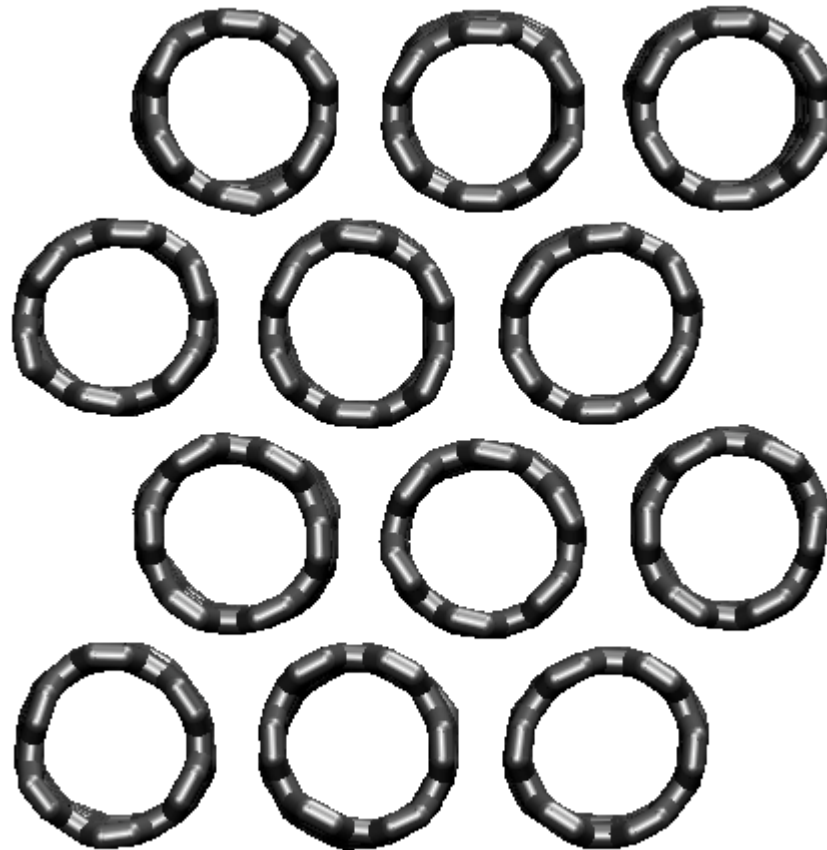
# Water-nanotube interaction can be easily modified



Modifying charges  
Modifying vdW parameters

# Carbon Nanotubes

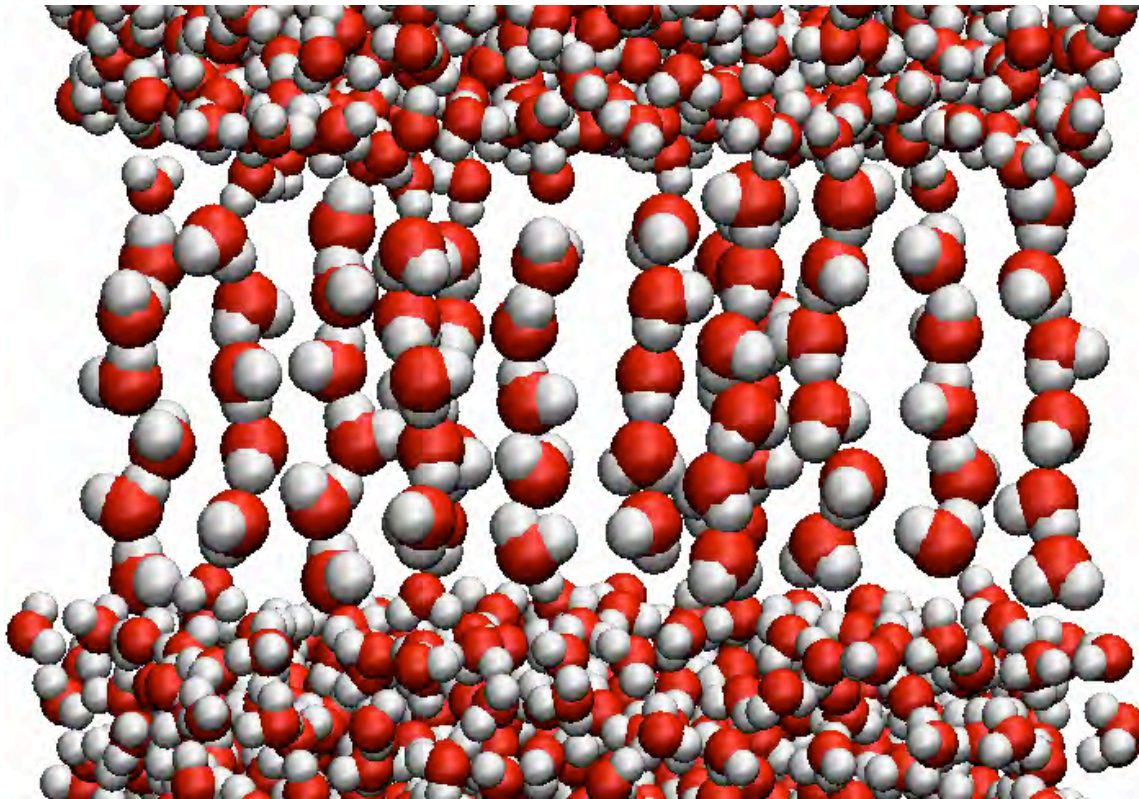
## Hydrophobic channels - Perfect Models for Membrane Water Channels



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

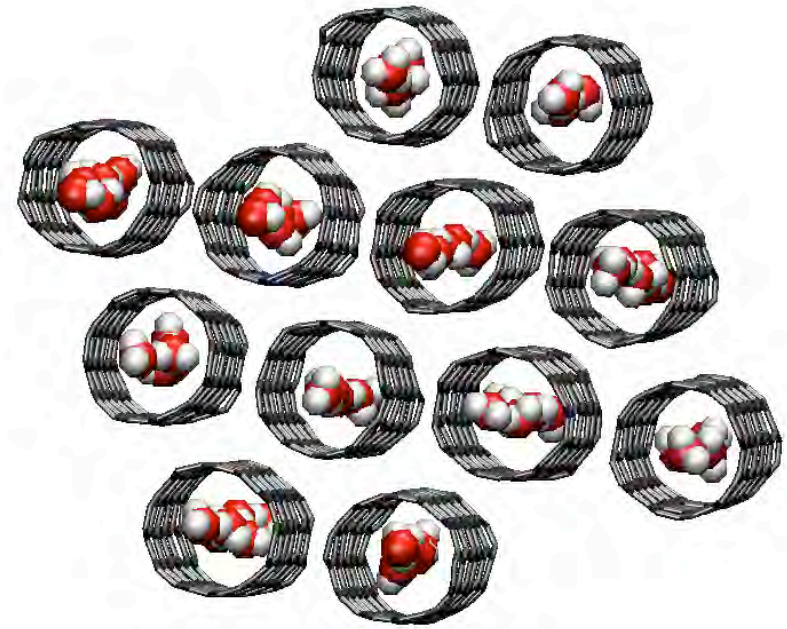
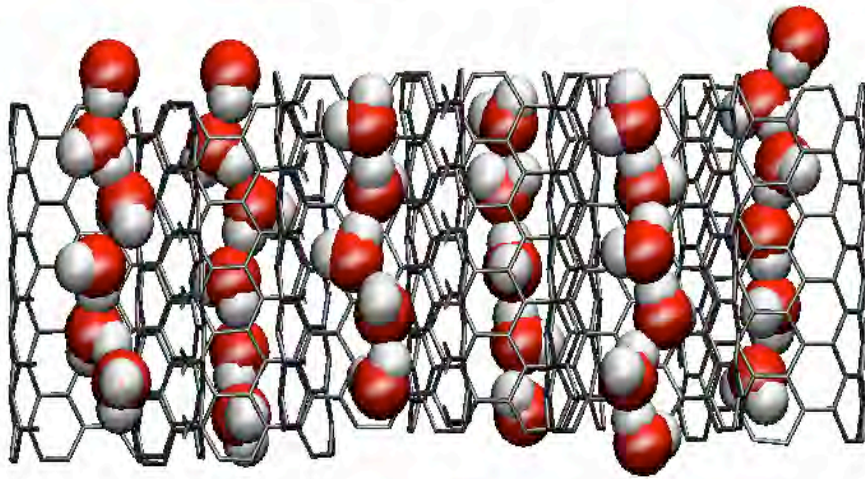
# Carbon Nanotubes

## Hydrophobic channels - Perfect Models for Membrane Water Channels



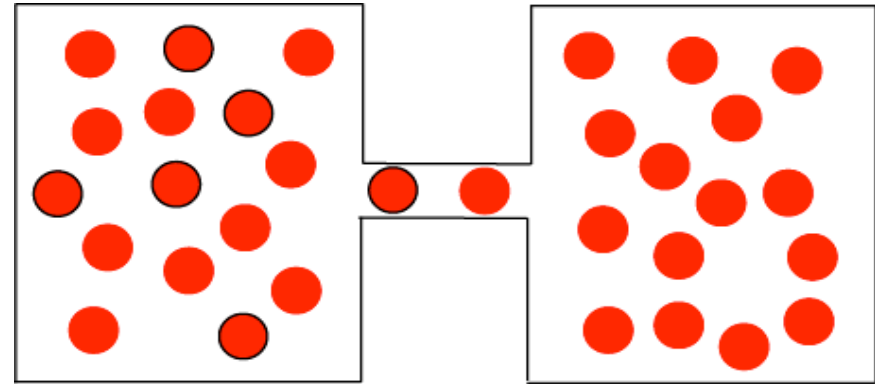
- Much better statistics
- No need for membrane and lipid molecules

# Water Single-files in Carbon Nanotubes



**Water files form polarized chains in nanotubes**

# Calculation of Diffusion Permeability from MD



$\Phi_0$ : 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

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

$\mu_w^o$  : standard chemical potential of water

$X_w$  : molar fraction of water

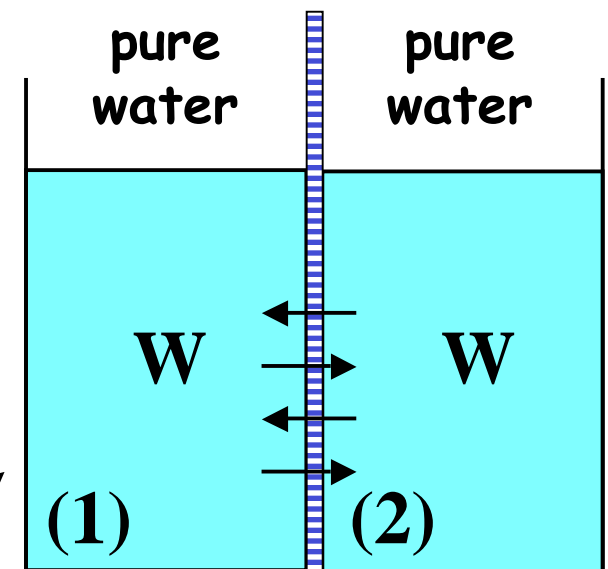
$R$  : the gas constant

$T$  : temperature

$P$  : pressure

$V_w$  : molar volume of water

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



membrane

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

# Solutes Decrease the Chemical Potential of Water

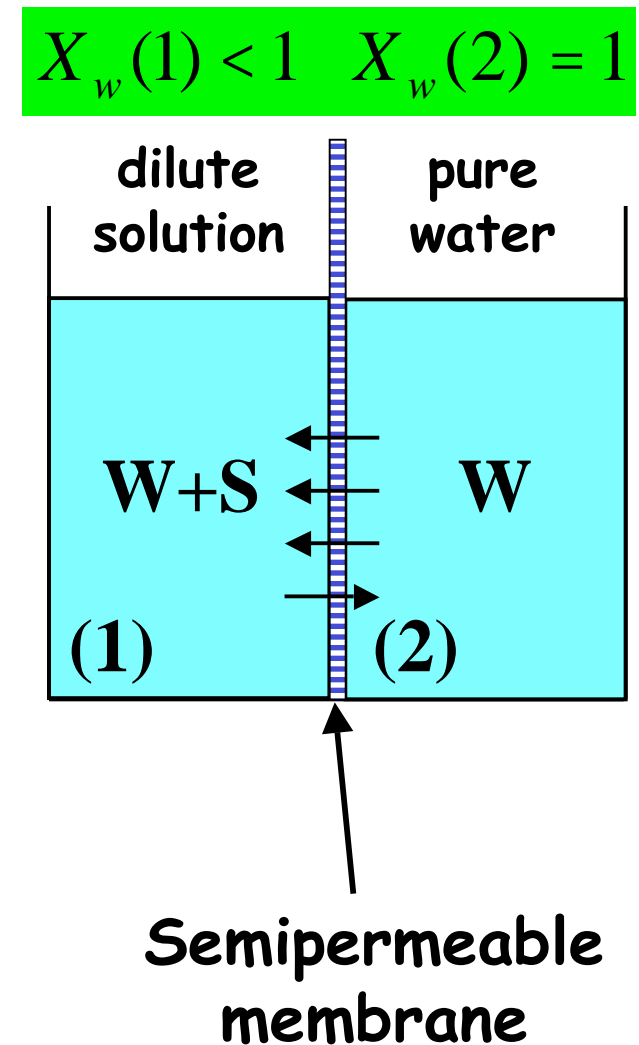
$$\mu_w = \mu_w^o + RT \ln X_w + PV_w$$

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

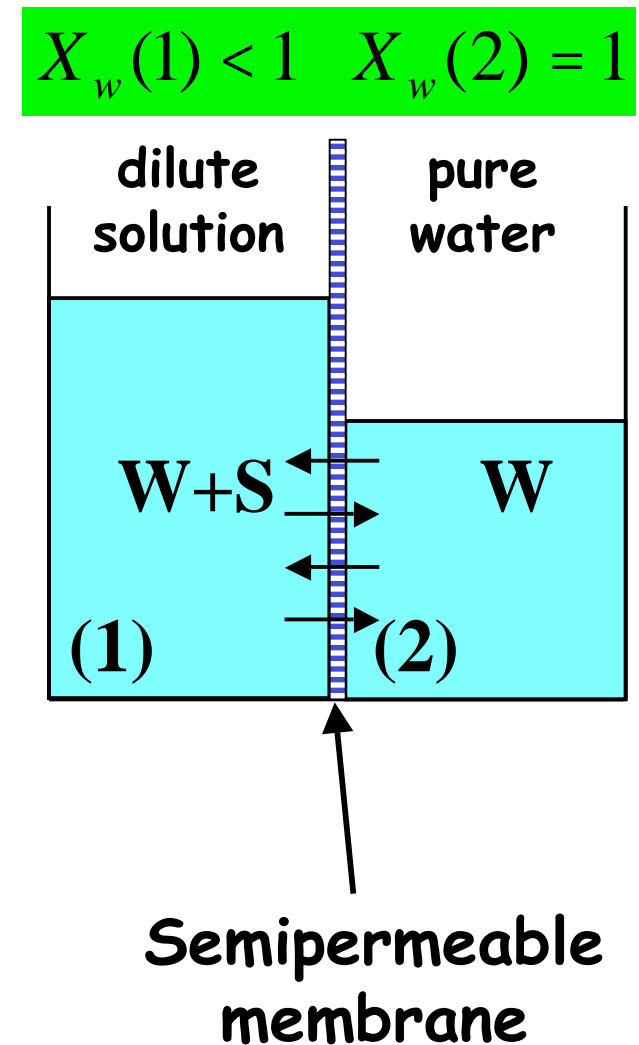
@equilibrium :  $\mu_w(1) = \mu_w(2)$

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

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

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

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



# 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.

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

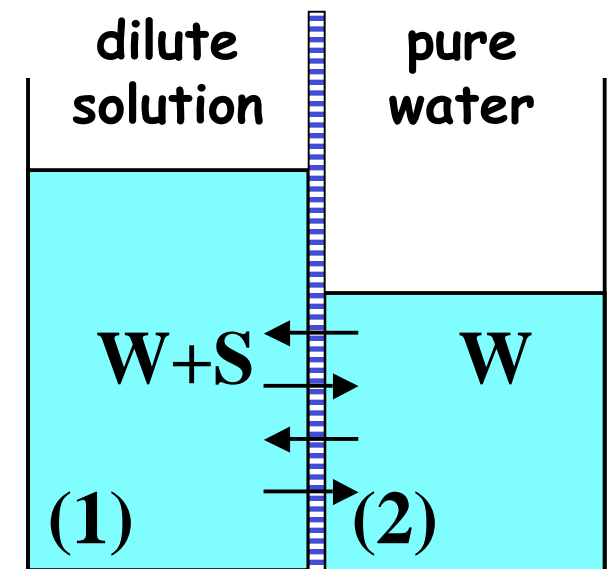
$$\Rightarrow \ln X_w = \ln(1 - X_s) \cong -X_s$$

$$\Delta PV_w = RTX_s$$

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

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 ( $55M$ ).

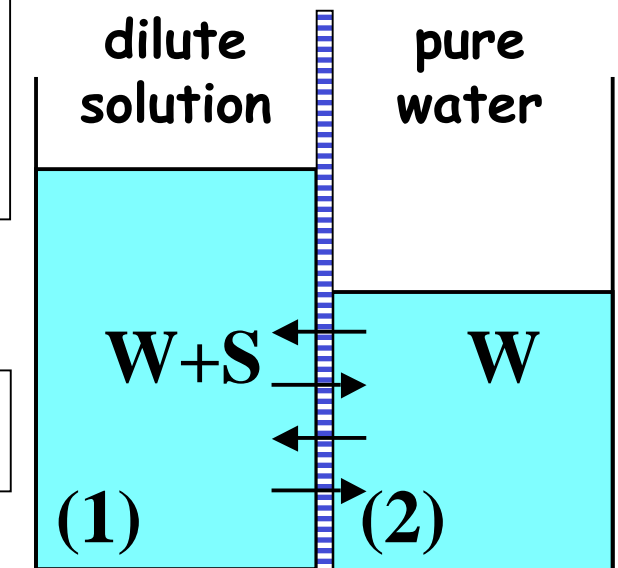
$$X_s = \frac{n_s}{n_s + n_w} \approx \frac{n_s}{n_w} = \frac{n_s}{n_w} \frac{V_w}{V_w}$$

$$n_s \ll n_w$$

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

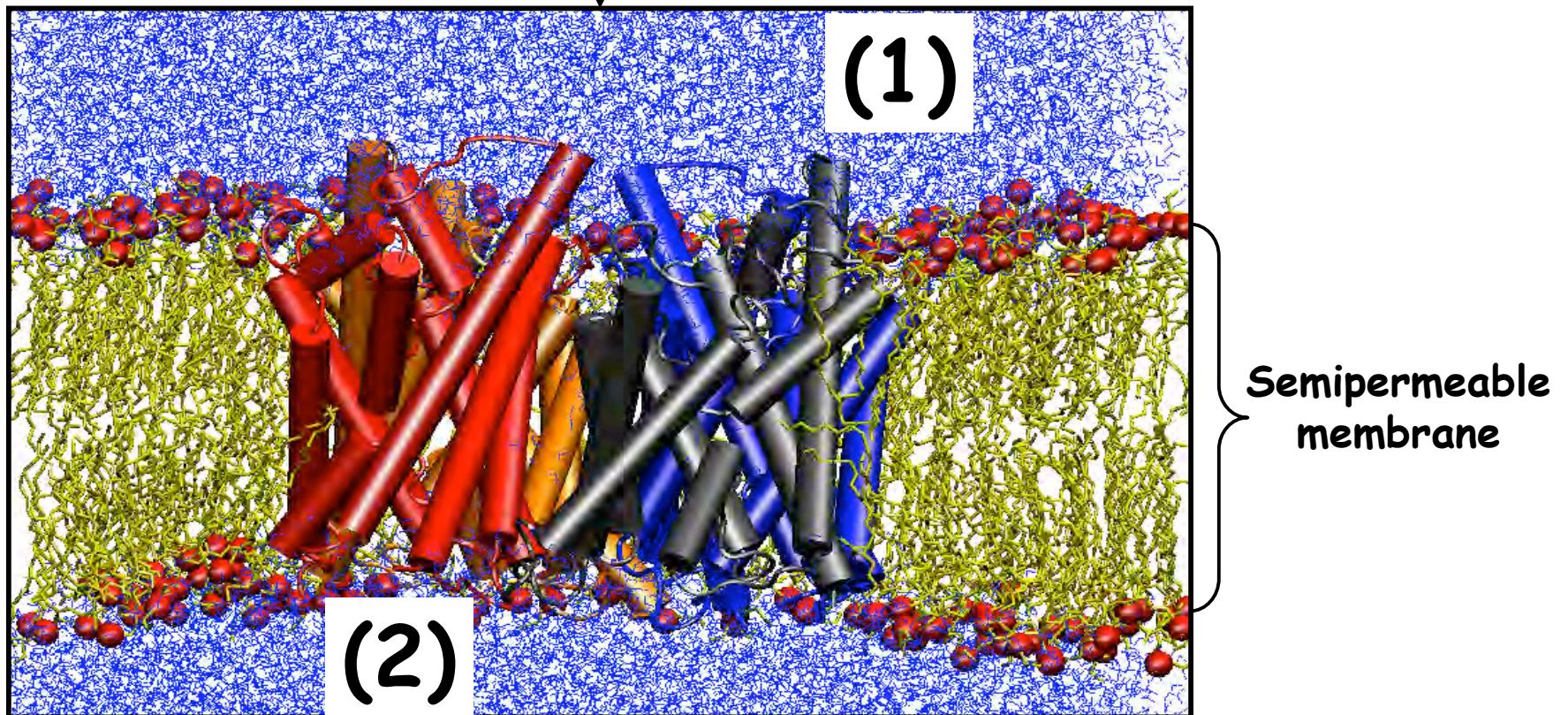
$$\Pi = \Delta P = \frac{RT}{V_w} C_s V_w = RTC_s$$

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



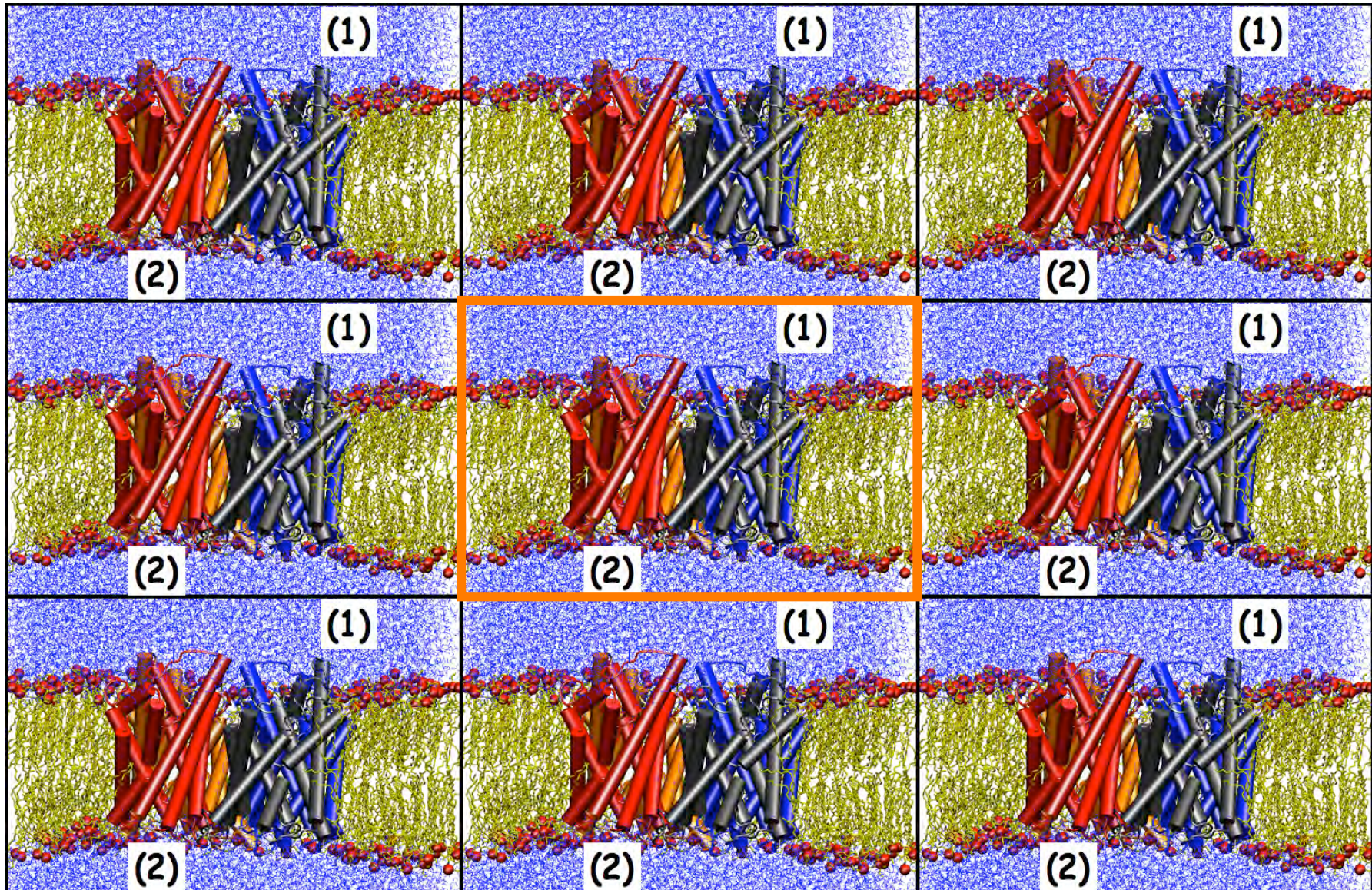
$$\Delta \Pi = \Delta P = RT \Delta C_s$$

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



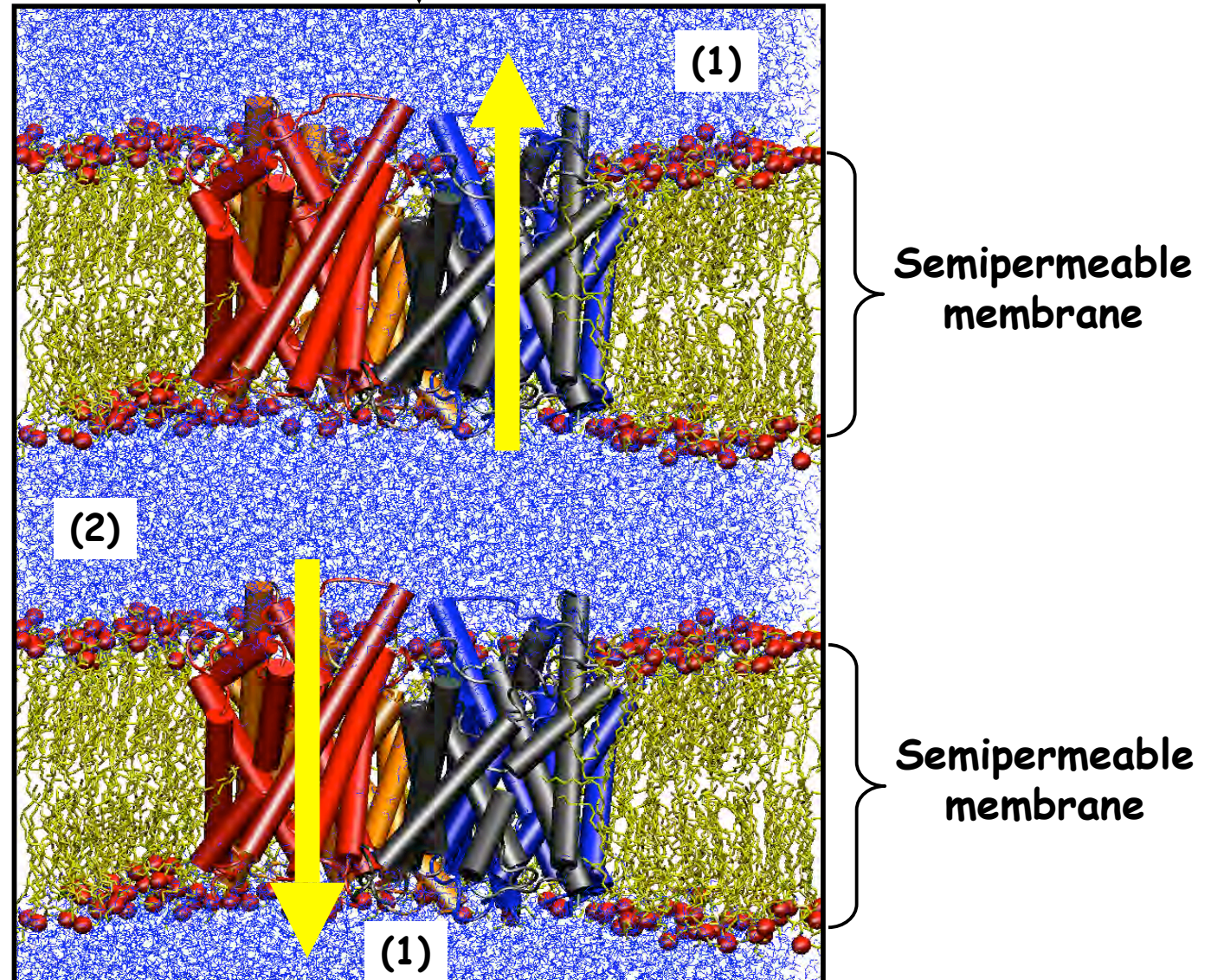
There is a small problem with this setup!

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

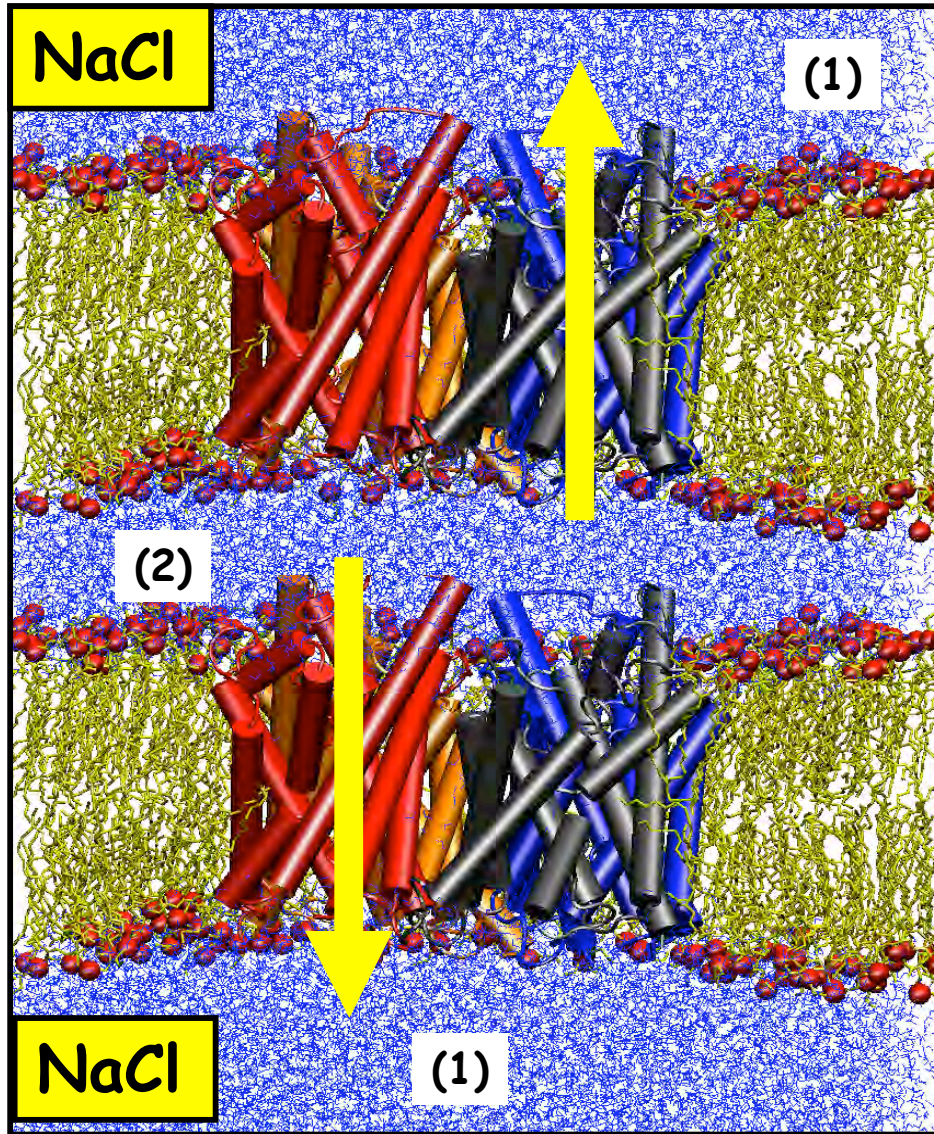
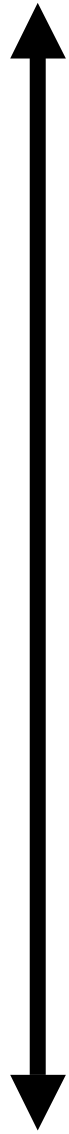


We can include more layers of membrane and water to create two compartment of water that are not in contact

NaCl



# UNIT CELL



Semipermeable membrane

Semipermeable membrane

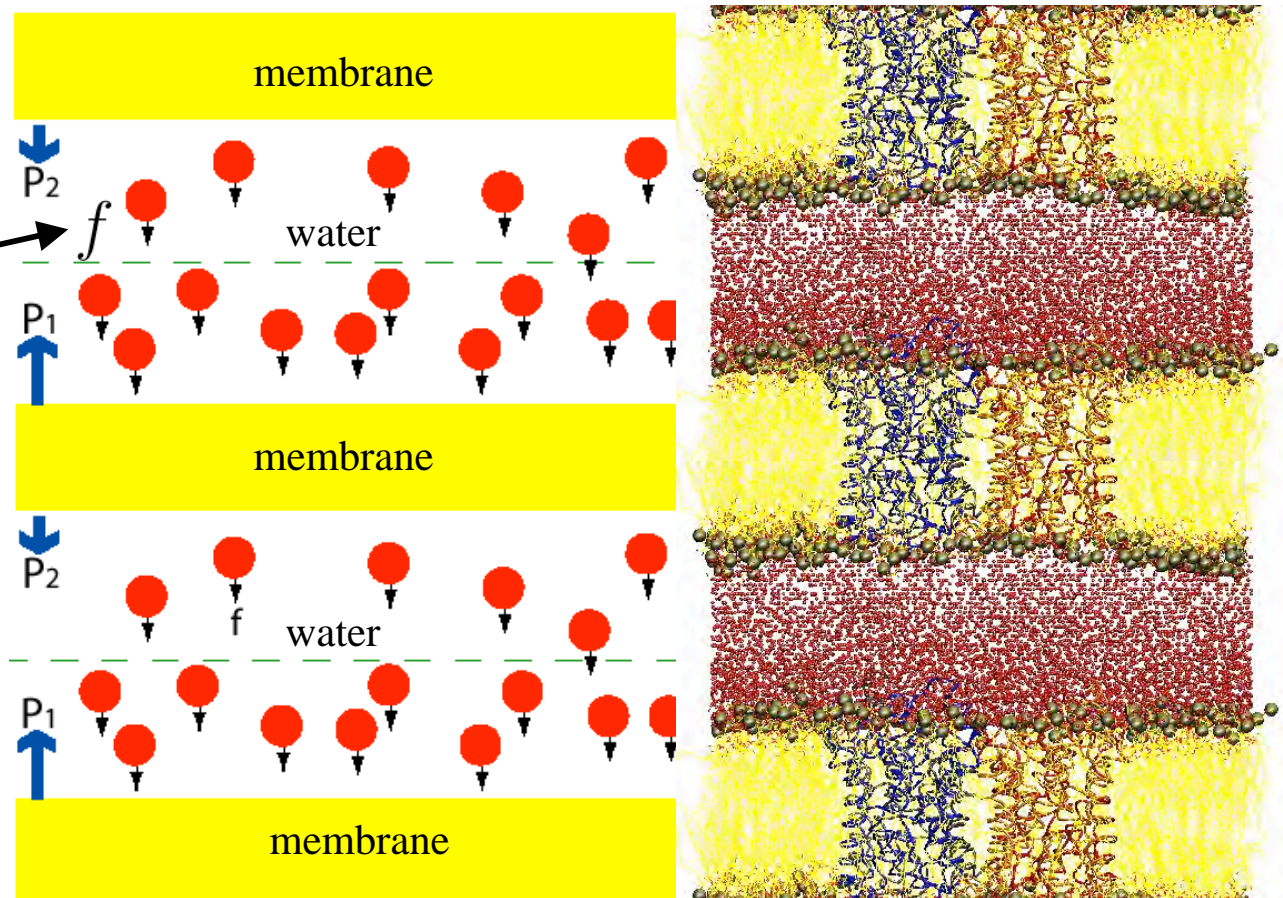
# Realizing a Pressure Difference in a Periodic System

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

Fangqiang Zhu

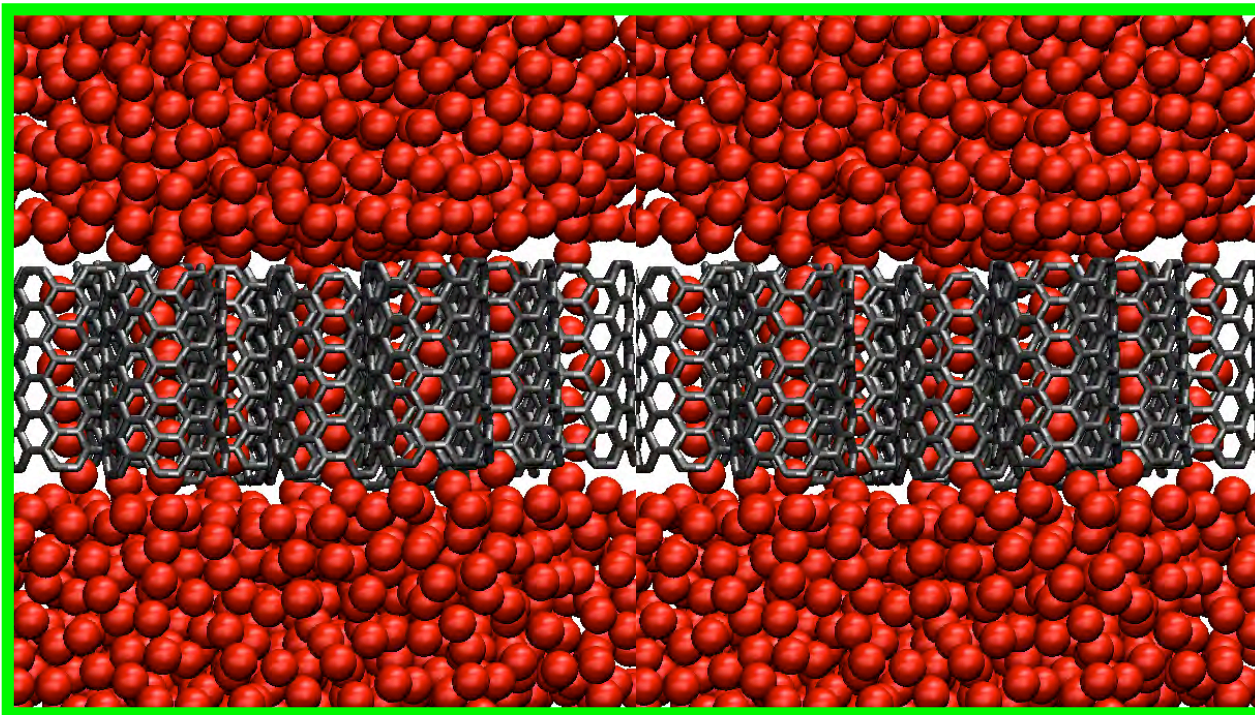
$f$  is the force on each water molecule, for  $n$  water molecules

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



# Applying a Pressure Difference Across the Membrane

$$\Delta P = nf / A$$

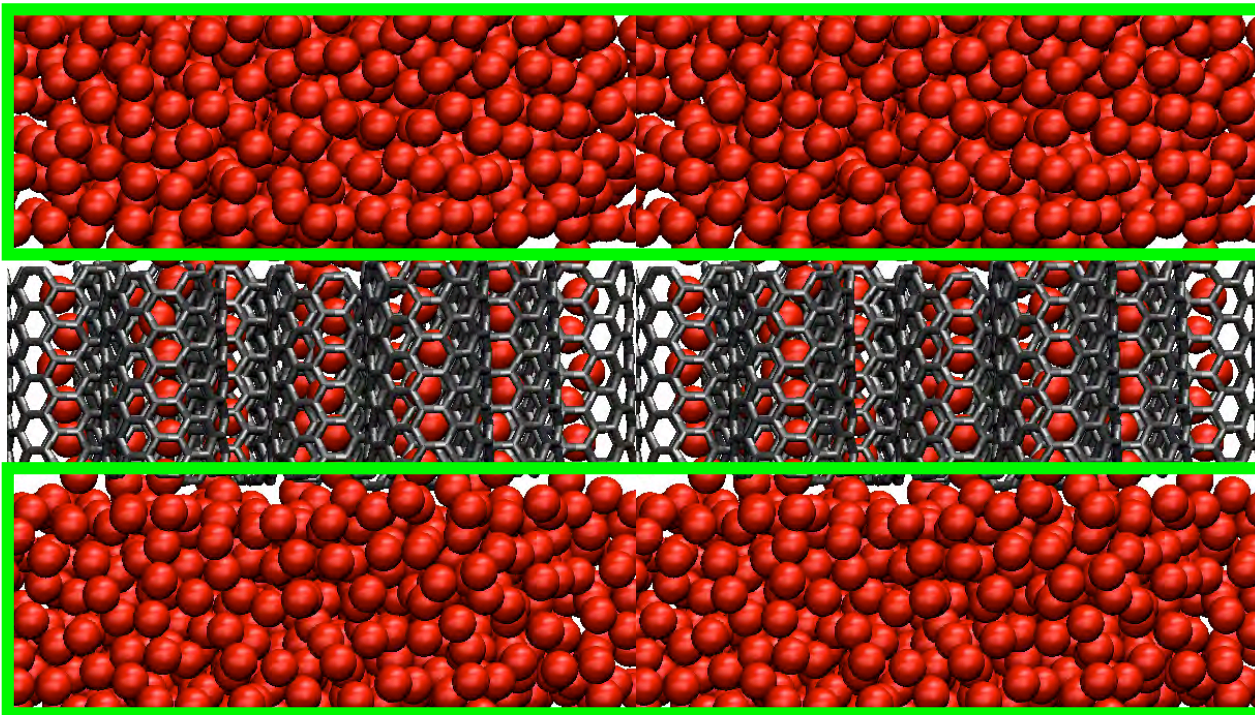


Applying  
force on all  
water  
molecules.

Not a good  
idea!

# Applying a Pressure Difference Across the Membrane

$$\Delta P = nf / A$$

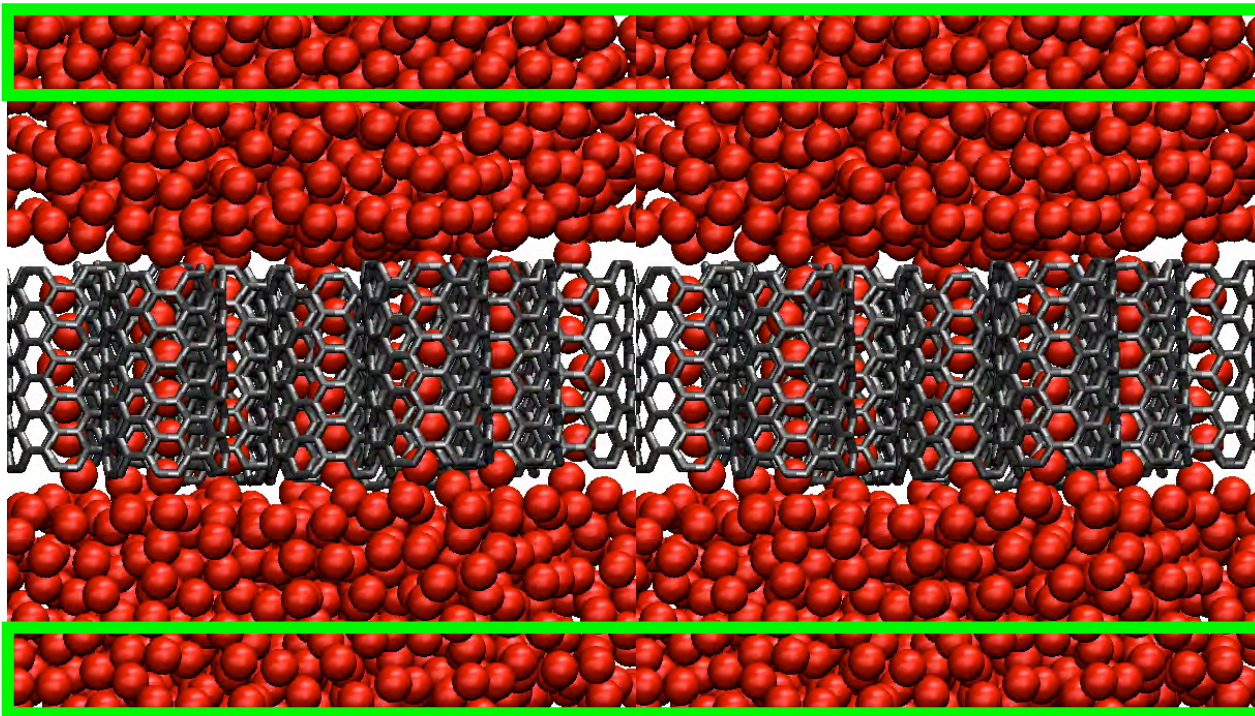


Applying  
force on  
bulk water  
only.

Very good

# Applying a Pressure Difference Across the Membrane

$$\Delta P = nf / A$$



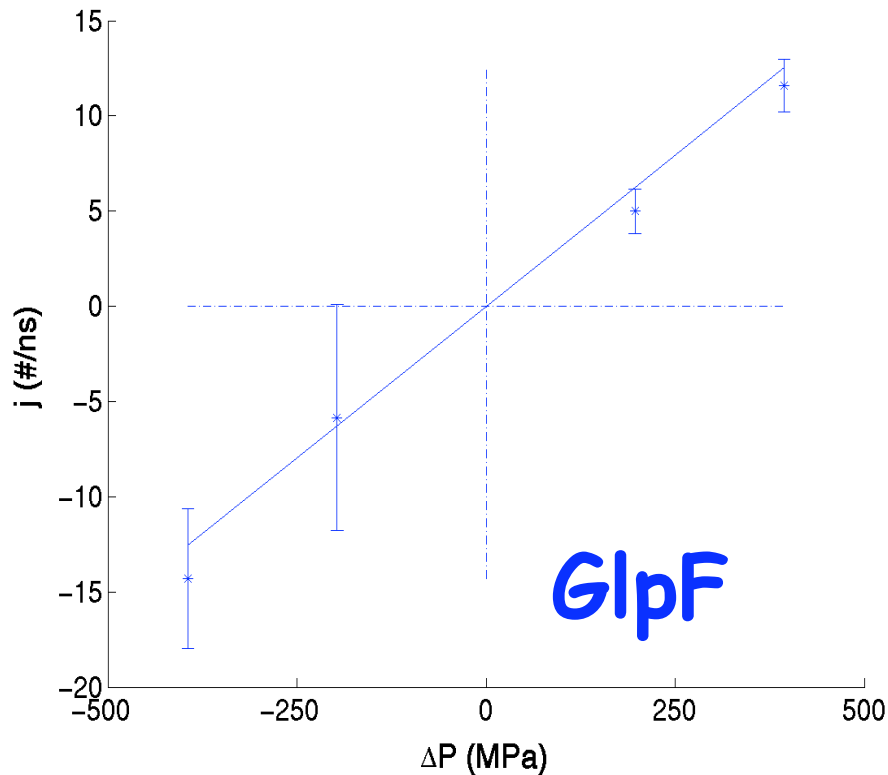
Applying force only on a slab of water in bulk.

Excellent

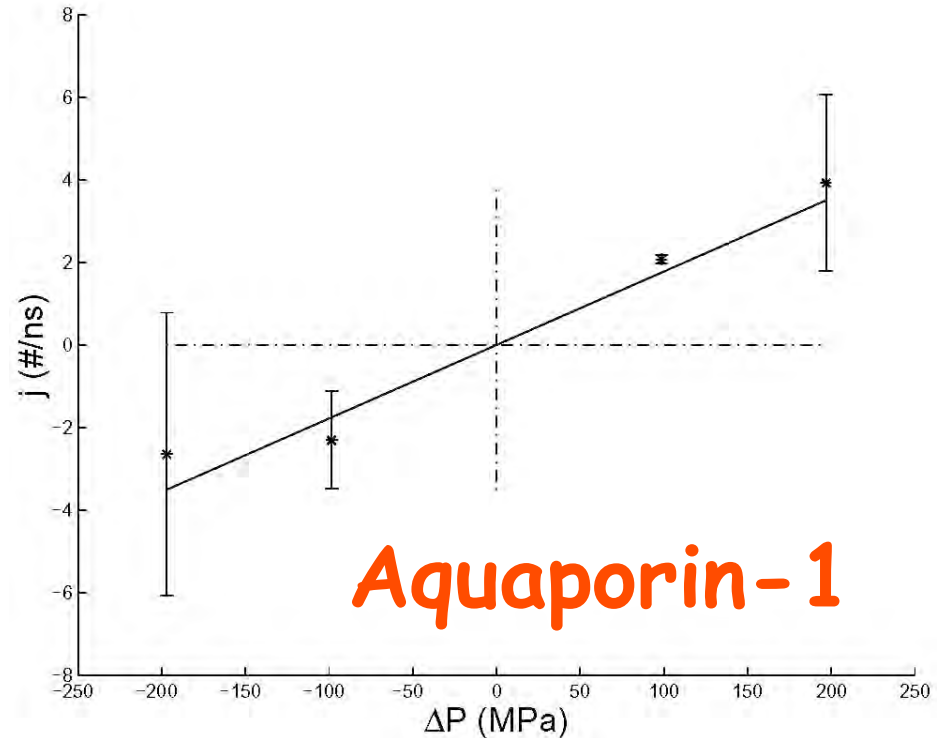
$P_f$  can be calculated from these simulations

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

# 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**

