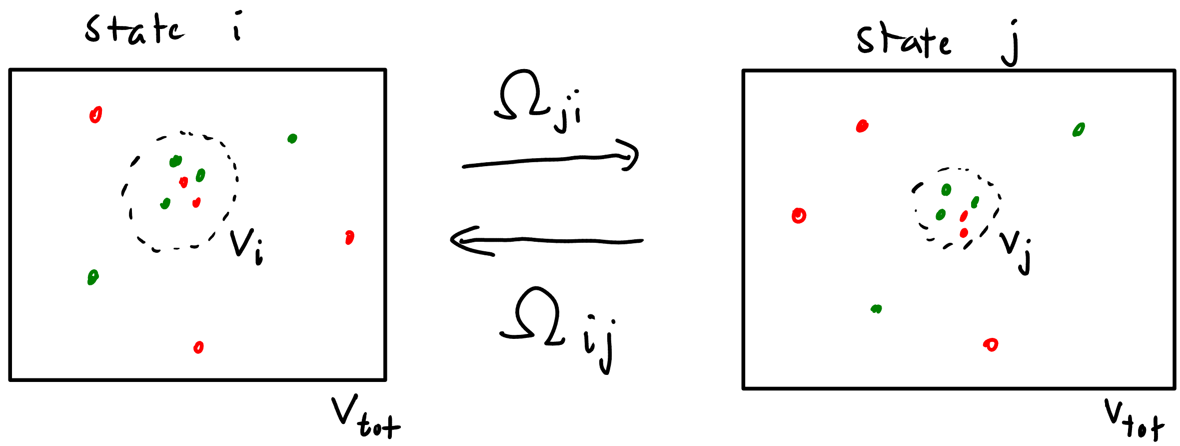
model where certain types of molecules cannot leave/enter cell (on regular timescales) but cell volume can change (b/c of water flowing in or out)



for molec. type α (all impermeable molec.) : n_α = # molec. of type α inside cell

$N_\alpha - n_\alpha$ = " " " outside cell

fixed quantities

$$\frac{\Omega_{ji}}{\Omega_{ij}} = e^{-\beta\left(-k_B T \ln \frac{6_j}{6_i}\right)}$$

$$= e^{-\beta\left(-k_B T \ln 6_j - (-k_B T \ln 6_i)\right)}$$

6_j = # microstates in state j

6_i = # " in state i

$N_{pos,\alpha}^{in,i} \equiv$ # positions available to molec. of type α on inside of cell in state i

$$= \frac{V_i}{V_{mol,\alpha}}$$

vol. of type α molec.

$$N_{pos,\alpha}^{out,i} = \frac{V_{tot} - V_i}{V_{mol,\alpha}}$$

$$\sigma_i \cong \binom{N_{pos,\alpha}^{in,i}}{n_\alpha}\binom{N_{pos,\alpha}^{out,i}}{N_\alpha - n_\alpha} \cdot \underbrace{\Big(\quad\Big)\Big(\quad\Big)\cdots}_{\text{similar factors for all other molec. types } \alpha}$$

$$\ln \binom{M}{m} \approx -m \ln \frac{m}{M}$$

$m \gg 1$, $M \gg 1$

$M \gg m$

$\uparrow$ dilute limit

$$\Rightarrow \ln \sigma_i \approx - \sum_{\alpha \in \text{types}} \Big[n_\alpha \ln \frac{n_\alpha v_{mol,\alpha}}{V_i} + (N - n_\alpha) \ln \frac{(N_\alpha - n_\alpha) v_{mol,\alpha}}{V_{tot} - V_i} \Big]$$

recall:
$$\frac{\Omega_{ji}}{\Omega_{ij}} = e^{-\beta(E_j - E_i)} \underset{t\to\infty}{\Rightarrow} p_i^s = \frac{e^{-\beta E_i}}{Z}$$

here:
$$\overset{t\to\infty}{p_i^s} = \frac{e^{-\beta(-k_B T \ln \sigma_i)}}{Z} = \frac{e^{\ln \sigma_i}}{Z}$$

Z ensures $\sum_i p_i^s = 1$

most likely state in equil $\Rightarrow$ largest σ_i

largest $\ln \sigma_i$

$$\frac{d}{dV_i}\ln 6_i = 0 \ \overset{\text{algebra}}{\Rightarrow}\ 0 = \sum_\alpha \left[-\underbrace{\frac{n_\alpha}{V_i}}_{C_\alpha^{in}} + \underbrace{\frac{(N_\alpha - n_\alpha)}{V_{tot} - V_i}}_{C_\alpha^{out}} \right]$$

↑ condition for max. 6_i

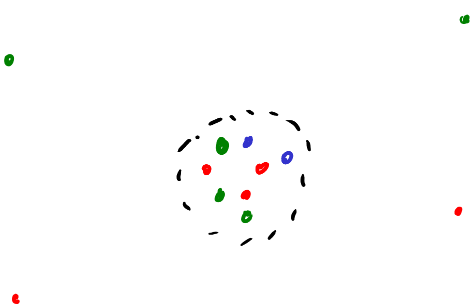
C_α^{in}: inside conc. of type α

C_α^{out}: outside conc. of type α

$$\Rightarrow \boxed{\sum_\alpha C_\alpha^{in} = \sum_\alpha C_\alpha^{out}}$$

sum of all impermeable molec. conc on inside = " " outside

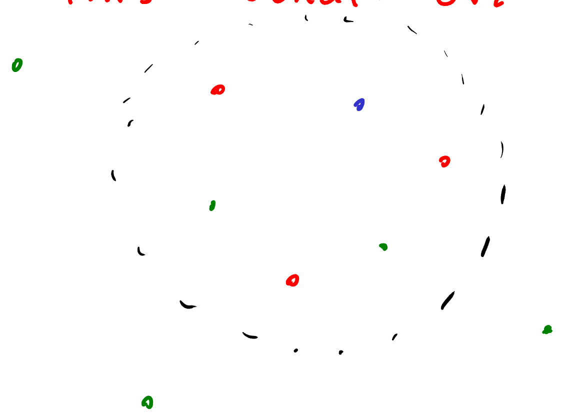
in long time limit cell will change volume (let water in/out) to approach this condition



$\Longrightarrow$

$t \to \infty$

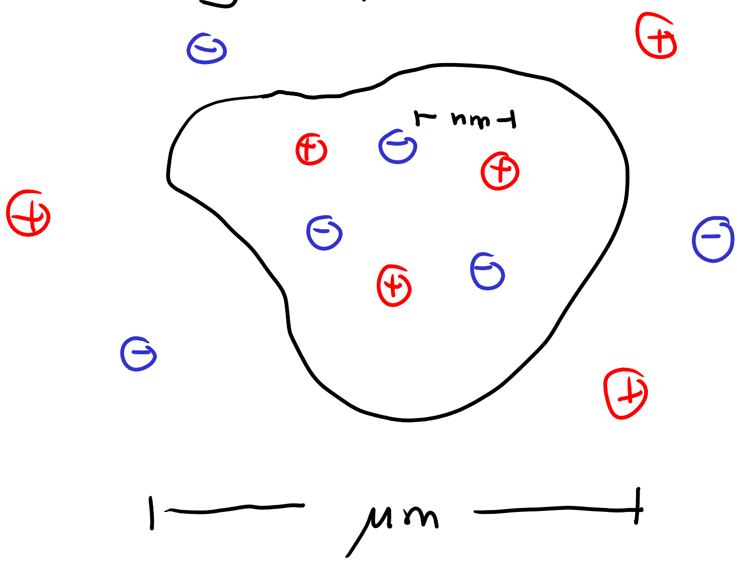
water will flow in until sys. reaches equil



all cells with flexible membranes must have transporters and/or rigid cell walls, etc. to regulate osmotic stress

II. Charged particles + transport across membranes

Starting point:



in biology:
approximate balance of neg. + pos. charges inside + outside

≈ electroneutral

typical dist. b/t charges ~ nm

pair of +e + −e ions:

Coulomb energy of attraction $= \dfrac{e^2}{4\pi \varepsilon r}$

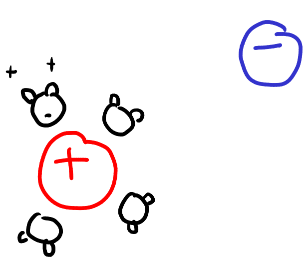
$\varepsilon = \varepsilon_r \varepsilon_0$

ε ↓ perm. of medium

ε_r → rel. perm.

ε_0 → vacuum perm.

$$\varepsilon_r = \begin{cases} 1 & \text{air} \\ \approx 80 & \text{water} \end{cases}$$



water dipoles arrange to weaken attraction

$r = 1$ nm

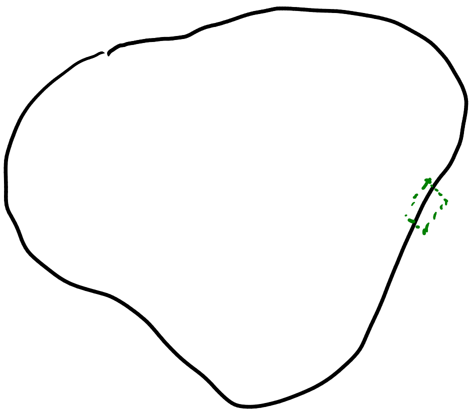
$\varepsilon_r = 80$

$\Rightarrow$

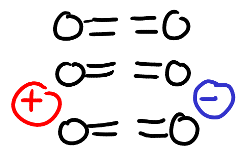
energy $\sim 0.7\ k_B T$

weak attraction easily broken by thermal fluctuations of order $\sim k_B T$

$\Rightarrow$ keeps ions dispersed in solution



zoom in



$\leftarrow 4\,\text{nm} \rightarrow$

$\varepsilon_r \approx 2$ inside membrane

Coulomb energy $= 8\ k_B T$

stable against thermal fluctuations