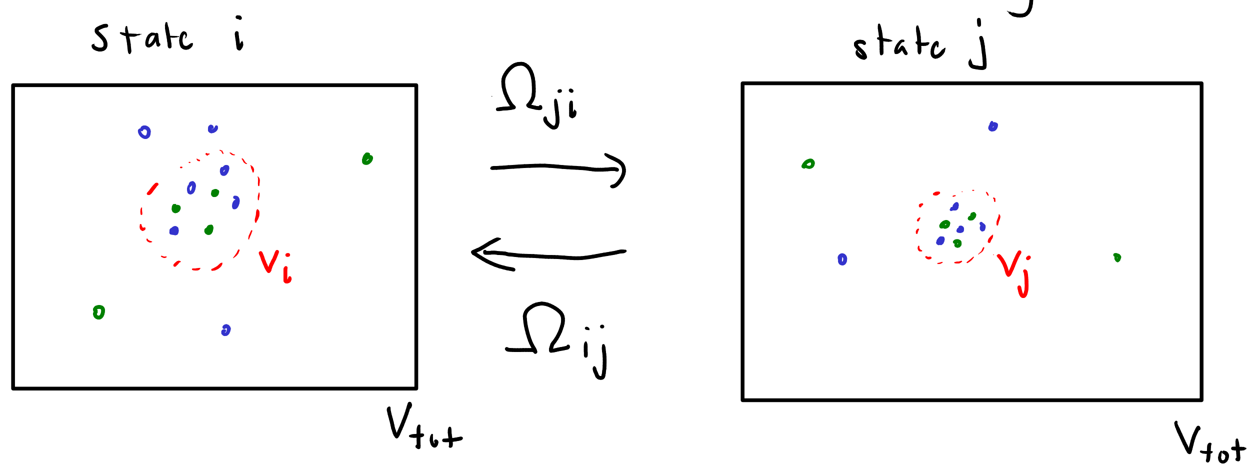
model where certain types of molecules cannot leave / enter cell (on regular timescales) but cell volume <u>can</u> change (b/c of water moving in / out)



n_α = # molec. of type α inside cell

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

focus on impermeable molec. here
n_α doesn't change

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

σ_j = # microstates in state j

σ_i = # microstates in state i

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

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

↑ vol. of type α molec.

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

$$\Omega_i \approx \underbrace{\binom{N^{in,i}_{pos,\alpha}}{n_\alpha}\binom{N^{out,i}_{pos,\alpha}}{N_\alpha - n_\alpha}}_{\text{type } \alpha \text{ configs}} \underbrace{\left(\quad\right)\left(\quad\right)}_{\text{similar factors for all other types}} \circ \circ \circ$$

"dilute approx." : ignore volume of other types when calc. config's of type α

$$\ln \binom{M}{m} \approx -m \ln \frac{m}{M} \qquad m \gg 1,\ M \gg 1$$

$$M \gg m$$

$$\Rightarrow \ln \Omega_i \approx -\sum_{\substack{\alpha \\ \in \text{types}}} \left[n_\alpha \ln \frac{n_\alpha V_{mol,\alpha}}{V_i} + (N_\alpha - n_\alpha) \cdot \ln \frac{(N_\alpha - n_\alpha) V_{mol,\alpha}}{V_{tot} - V_i} \right]$$

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

here: $$\frac{\Omega_{ji}}{\Omega_{ij}} = e^{-\beta\left(-k_B T \ln \Omega_j - (-k_B T \ln \Omega_i)\right)}$$

$$\underset{t\to\infty}{\Longrightarrow} p_i^s = \frac{e^{-\beta(-k_B T \ln \Omega_i)}}{Z} = \frac{e^{\ln \Omega_i}}{Z}$$

Z ensures $\sum_i p_i^s = 1$

most likely state i (highest p_i^s)

$\Rightarrow$ need largest $\ln \Omega_i$

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

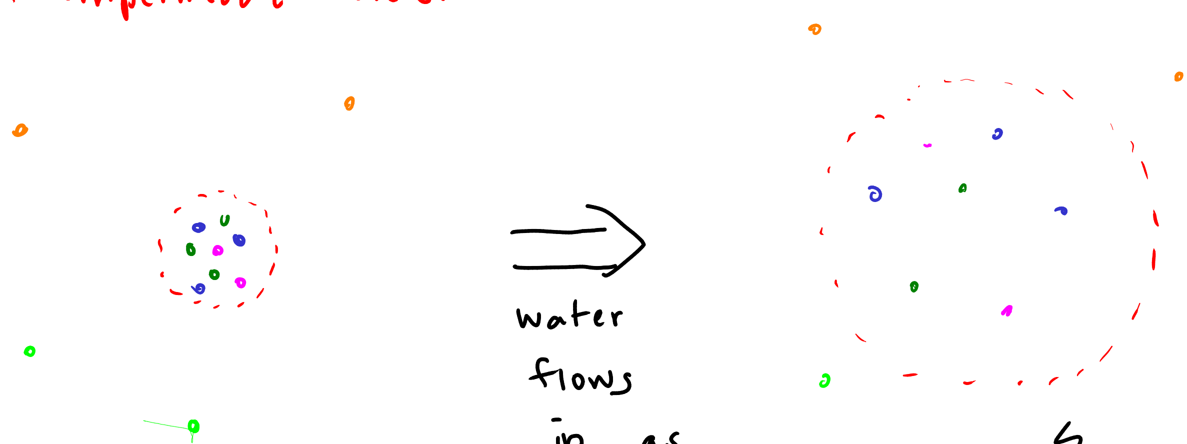
c_α^{in}: inside conc. of α molec.

c_α^{out}: outside conc. of α molec.

most likely state characterized by:

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

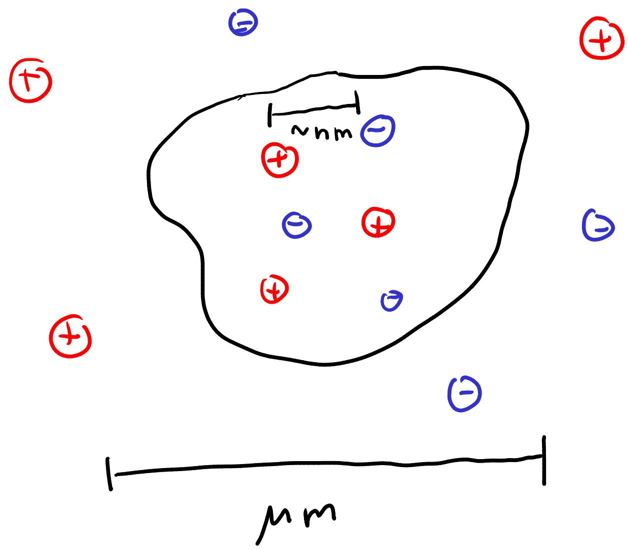
sum of all inside conc. of impermeable molec. = " " outside conc. "



all cells w/ flexible membranes <u>must</u> have transporters or other mechanisms to regulate osmotic stress

II. Charged particles + transport across membranes

Starting point:



in a cell many molecules are charged but there is an approx. balance of pos. + neg. charges on inside + outside

≈ electroneutrality

typically: few nm b/t charges

pair of +e + −e ions: Coulomb energy of attraction

r = separation ~ 1 nm

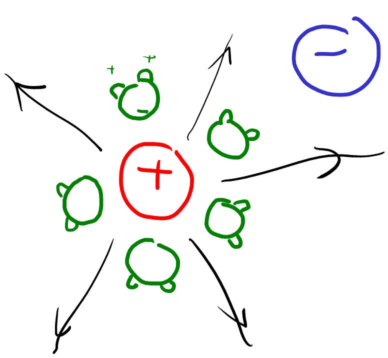
$$= \frac{e^2}{4\pi \varepsilon r}$$

$\varepsilon = \varepsilon_r \varepsilon_0$

↳ vacuum permittivity

↳ relative permittivity $\begin{cases} \approx 1 & \text{air} \\ \approx 80 & \text{water} \end{cases}$

↓ perm. of surrounding material



water reorientation weakens overall field seen by −e charge ⇒ large ε_r

$r = 1$ nm, $\varepsilon_r = 80 \Rightarrow$ energy $\sim -0.7\, k_B T$

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

$\Rightarrow$ keeps ions dispersed in solution