L32 : review

diffusion, drift, and flux

$F_{random} \Rightarrow \langle \delta x(t)^2 \rangle = 6Dt$ (in 3-D)

$D = \dfrac{\langle \Delta x^2 \rangle}{2\Delta t}$; D : diffusion coefficient $\left(\frac{m^2}{s}\right)$

$F_{applied} + F_{friction} + F_{random} = ma \approx 0$

$\Rightarrow \dfrac{\partial \mu}{\partial x} = \underbrace{-\gamma}_{\text{friction coefficient}} v + F_{random}$; $\gamma = \dfrac{k_B T}{D}$

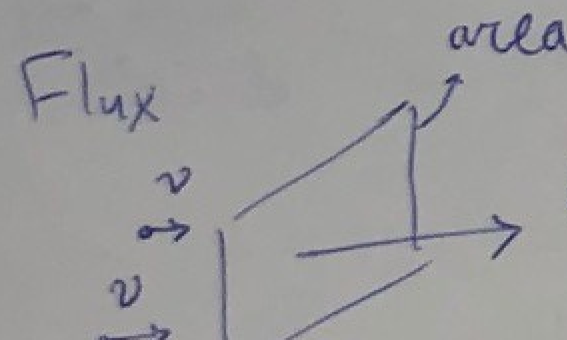
example: Protein moving on a gel reaches a terminal drift velocity

$v_{drift} = \dfrac{q}{\gamma} \mathcal{E}$

q → charge (coulomb)

$\mathcal{E}$ → electric field $\left(\frac{V}{m}\right)$

Flux



$\text{flux } J \left(\frac{mol}{m^2 \cdot s}\right) = \underset{\text{velocity}}{v} \cdot \underset{\text{concentration}}{C} = -\dfrac{1}{\gamma} \dfrac{\partial \mu}{\partial x} \cdot C = -u\,C \dfrac{\partial \mu}{\partial x}$

$u = \frac{1}{\gamma}$; $\frac{\partial \mu}{\partial x}$: driving force

Today: Transport and kinetics using the "physicochemical potential"

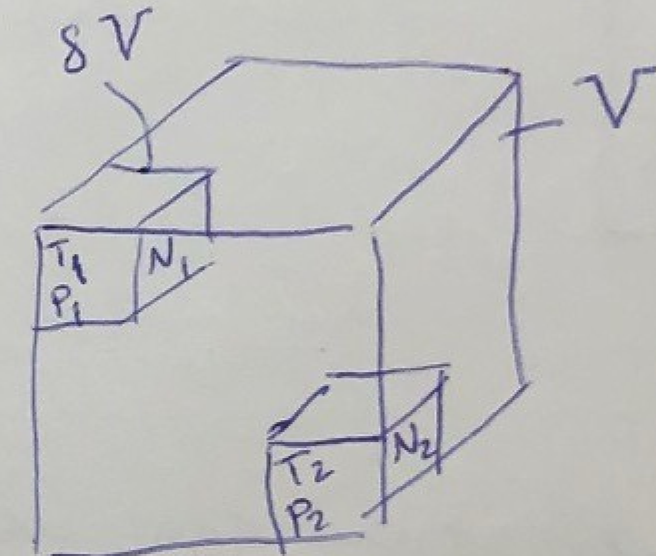
Postulates : 1) $\mu_{gi}(x) = \mu_i(T, P, x) + \mu_{fi}$

μ_{gi} : physicochemical potential: contains info about driving forces.

μ_{fi} : chemical potential due to applied forces e.g. $-q \cdot \mathcal{E}$

2) $J_i = -u_i C_i \dfrac{\partial \mu_{gi}}{\partial x}$

1)



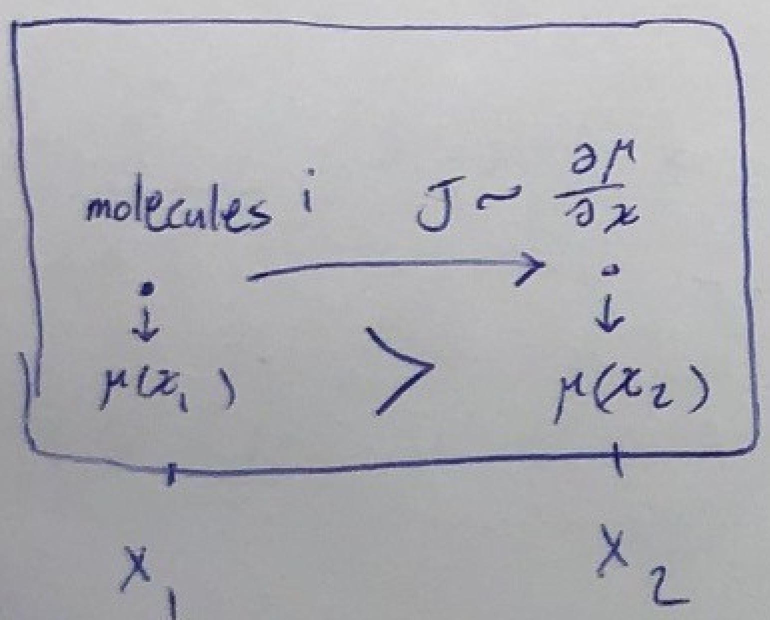
* δV is large enough that the fluctuations in N due to brownian motion are small.

C.L.T : fluctuations $\sim \dfrac{1}{\sqrt{N}}$

μ as the "driving force"

$$dE = \left(\frac{\partial E}{\partial S}\right) dS + \left(\frac{\partial E}{\partial V}\right) dV + \sum_i \frac{\partial E}{\partial n_i} dn_i + dq \cdot \underset{e}{\overset{\frac{\partial E}{\partial q}\uparrow}{\psi}} + \cdots$$

$$= T\,dS - P\,dV + \sum_i \mu_i\, dn_i + \cdots$$



Another example: concentration can act as a driving force

$$\mu(x) = \mu^0 + RT \ln\{c(x)\}$$

if $c(x_1) > c(x_2) \Rightarrow \frac{\partial \mu}{\partial x} \neq 0$

$J = -\mu\, c(x) \frac{\partial \mu(x)}{\partial x} \neq 0 \Rightarrow$ molecules will flow from high to low concentration

in order to get the "driving force" tha tells us the flux of where particles are going to move, we need $\frac{\partial \mu_{g_i}}{\partial x} \rightarrow$ molecule "i"

$$\mu_{g_i}(x) = \mu_i(T, P, x) + \underset{\substack{\downarrow \\ \text{e.g. } -q \cdot \mathcal{E}}}{\mu_{f_i}}$$

$\mathcal{E} \rightarrow$ external electric field

reminder: $\frac{\partial^2 z}{\partial x \partial y} = \frac{\partial^2 z}{\partial y \partial x}$; for example: $z = xy^2$

$\Rightarrow \frac{\partial z}{\partial y} = 2xy$, $\frac{\partial z}{\partial x} = y^2$

$\Downarrow$ $\Downarrow$

$\frac{\partial^2 z}{\partial y \partial x} = 2y$ $\frac{\partial^2 z}{\partial x \partial y} = 2y$

example: $\frac{\partial G}{\partial T} = -S$; $\frac{\partial S}{\partial n_i} = \underset{\substack{\downarrow \\ \text{molar entropy of "i"}}}{S_i}$

$\Rightarrow \frac{\partial^2 G}{\partial T \partial n_i} = -S_i \Rightarrow \frac{\partial}{\partial T}\left(\frac{\partial G}{\partial n_i}\right) = -S_i$

$\Rightarrow \frac{\partial \mu_i}{\partial T} = -S_i$

$\left.\begin{array}{l} \\ \mu_{g_i} = \mu_i(T, P, x) + \mu_{f_i} \end{array}\right\} \Longrightarrow$ (next page)

$$\frac{d\mu_{gi}}{\partial x} = \frac{\partial \mu_i}{\partial x} + \frac{\partial \mu_i}{\partial T}\frac{\partial T}{\partial x} + \frac{\partial \mu_i}{\partial p}\frac{\partial p}{\partial x} + \frac{\partial \mu_{fi}}{\partial x}$$

$$\xRightarrow{\mu_i = \mu_i^\circ + RT\ln c_i} \frac{d\mu_{gi}}{\partial x} = \left(\frac{\partial \mu_i^\circ}{\partial x} + RT\frac{\partial \ln c_i}{\partial x}\right) - s_i\frac{\partial T}{\partial x} + v_i\frac{\partial p}{\partial x} + \frac{\partial \mu_{fi}}{\partial x}$$