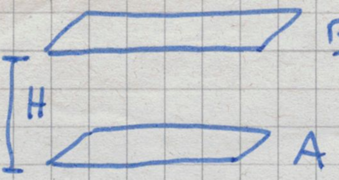


two plates at positions $x=0$ and $x=H$

number of adsorbed particles $N_A(t)=\sum_{i=1}^{N} n_A^i(t)$

$$N_B(t)=\sum_{i=1}^{N} n_B^i(t)$$

number of desorbed particles $N_D(t)=N-N_A(t)-N_B(t)$

$$\cancel{\langle N_A(0)N_A(t)\rangle=\sum_{i,j}\langle n_A^i(0)\, n_A^j(t)\rangle = N\langle n_A(0)\, n_A(t)\rangle \text{ etc.}}$$

see LB1b

$$\cancel{\langle N_D(0)N_D(t)\rangle=\sum_{i,j}\langle(1-n_A^i(0)-n_B^i(0))(1-n_A^j(t)-n_B^j(t))\rangle}$$

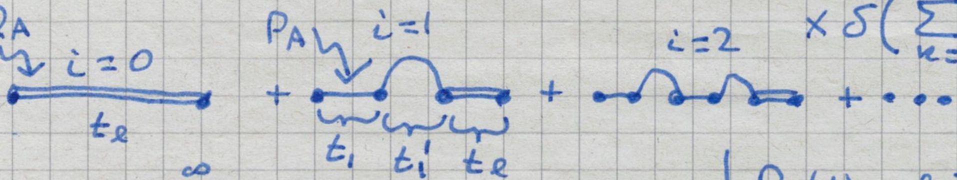
$$\cancel{=N^2(1-2\phi_A-2\phi_B)+N(C_{AA}(t)+C_{AB}(t)+C_{BA}(t)+C_{BB}}$$

$C_{AA}(t)=\langle n_A(0)\, n_A(t)\rangle$ etc.

we first consider a single surface (Levitz)

$$C_{AA}(t)=\sum_{i=0}^{\infty}\left\{\int_0^\infty dt_e\, Q_A(t_e)\prod_{j=1}^{i}\left[\int_0^\infty dt_j\, P_A(t_j)\int_0^\infty dt_j'\, J_{AA}(t_j')\right]\right.$$

$$\left.\times\,\delta\left(\sum_{k=1}^{i}(t_k+t_k')+t_e-t\right)\right.$$



$$C_{AA}(\omega)=\int_0^\infty dt\, e^{-\omega t}C_{AA}(t)$$

$$=\sum_{i=0}^{\infty}\int dt_e\, Q_A(t_e)\, e^{-\omega t_e}$$

$$\times\prod_{j=1}^{i}\int dt_j\, P_A(t_j)\, e^{-\omega t_j}\int dt_j'\, J_{AA}(t_j')\, e^{-\omega t_j'}$$

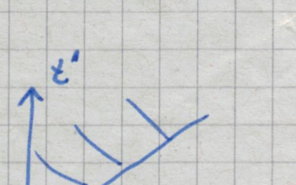
$$=\sum_{i=0}^{\infty}\left[P_A(\omega)J_{AA}(\omega)\right]^i Q_A(\omega)=\frac{Q_A(\omega)}{1-P_A(\omega)J_{AA}(\omega)}$$

$P_A(t)$: first-leavage distribution

$J_{AA}(t)$: first-re-adsorption dist.

$Q_A(t)\hat{=}\int_t^\infty dt'\, P_A(t')$ probability of being bound for entire time t

not normalized!



$$Q_A(\omega)=\int_0^\infty dt\, e^{-\omega t}Q_A(t)=\int_0^\infty dt\, e^{-\omega t}\int_t^\infty dt'\, P_A(t')$$

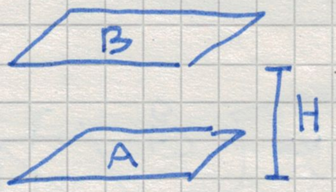
$$=\int_0^\infty dt'\, P_A(t')\int_0^{t'} dt\, e^{-\omega t}=\int_0^\infty dt'\, P_A(t')\,\frac{1-e^{-\omega t'}}{\omega}$$

$$Q_A(\omega)=\frac{P_A(\omega=0)-P_A(\omega)}{\omega}\ \longrightarrow\ C_{AA}(\omega)=\frac{P_A(0)-P_A(\omega)}{\omega(1-P_A(\omega)J_{AA}(\omega))}$$

for normalized distribution $P_A(\omega=0)=1\ \to\ C_{AA}(\omega)=\dfrac{1-P_A(\omega)}{\omega(1-P_A(\omega)J_{AA}(\omega))}$

comment: Levitz assumes particle to start in bulk, $\to$ another factor $(1-J_{AA}(\omega))/\omega$!

10.5.14 LB1b



two plates at positions $x=0$ and $x=H$

number of adsorbed particles $N_A(t) = \sum_{i=1}^{N} n_A^i(t)$

$$N_B(t) = \sum_{i=1}^{N} n_B^i(t)$$

number of desorbed particles $N_D(t) = N - N_A(t) - N_B(t)$

$$\langle N_A(0)\, N_A(t)\rangle = \sum_{i,j} \langle n_A^i(0)\, n_A^j(t)\rangle =$$

$$= \sum_{i\neq j} \langle n_A^i(0)\, n_A^j(t)\rangle + \sum_i \langle n_A^i(0)\, n_A^i(t)\rangle$$

$$= N(N-1)\phi_A^2 + N\, C_{AA}(t) = N^2 p_A^2 - N p_A^2 + N C_{AA}(t)$$

where $\phi_A = \langle n_A^i(t)\rangle$ and $C_{AA}(t) = \langle n_A^i(0)\, n_A^i(t)\rangle$

similarly $\langle N_B(0)\, N_B(t)\rangle = N(N-1)\phi_B^2 + N\, C_{BB}(t)$

$$\langle N_D(0)\, N_D(t)\rangle = \sum_{i,j} \langle (1 - n_A^i(0) - n_B^i(0))(1 - n_A^j(t) - n_B^j(t))\rangle$$

$$= N(N-1)(1-\phi_A-\phi_B)^2 + N(1 - 2\phi_A - 2\phi_B)$$

$$+ N\left(C_{AA}(t) + C_{BB}(t) + C_{AB}(t) + C_{BA}(t)\right)$$

$$= N^2(1-\phi_A-\phi_B)^2 + N\left(1 - 2\phi_A - 2\phi_B - (1-\phi_A-\phi_B)^2\right)$$

$$+ N\left(C_{AA}(t) + C_{BB}(t) + C_{AB}(t) + C_{BA}(t)\right)$$

$$= N^2(1-\phi_A-\phi_B)^2 - N(\phi_A+\phi_B)^2 + N\left[C_{AA}(t) + C_{BB}(t) + C_{AB}(t) + C_{BA}(t)\right]$$

$$\langle |N_A(0) - N_B(t)|^2\rangle = \sum_{i,j} \langle (n_A^i(0) - n_B^i(0))(n_A^j(t) - n_B^j(t))\rangle$$

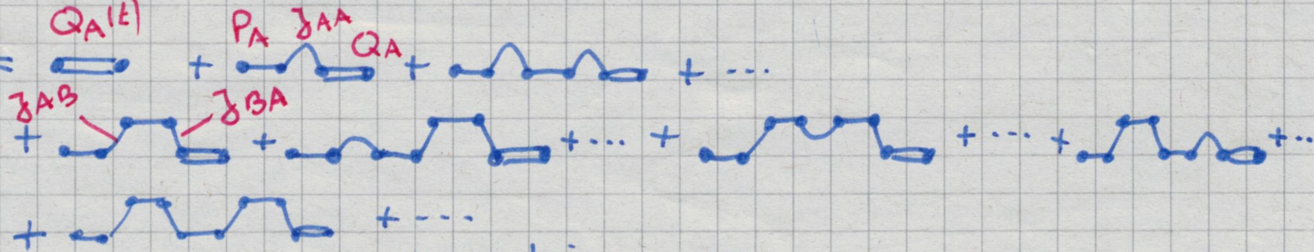
$$= N(N-1)(\phi_A - \phi_B)^2 + N\left(C_{AA}(t) + C_{BB}(t) - C_{AB}(t) - C_{BA}(t)\right)$$

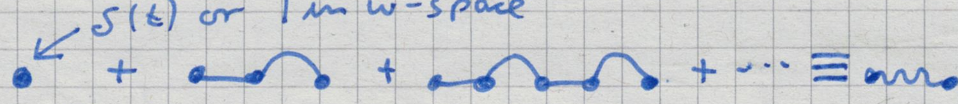
---

law of mass action: $\boxed{\dfrac{p_A}{p_B} = \dfrac{\tau_A k_A}{\tau_B k_B}}$ and $\boxed{\dfrac{p_A}{(1-p_A-p_B)/H} = \tau_A k_A}$

two surfaces

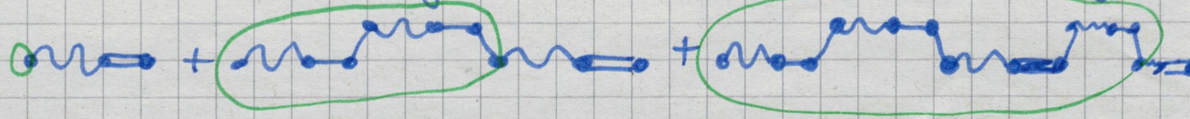
$C_{AA}(t) =$



define $\bar{C}_{AA}(t) =$ 

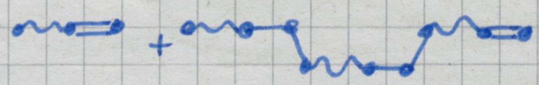
and similarly $\bar{C}_{BB}(t)$: leavage distribution without ever adsorbing on the other surface

$$\bar{C}_{AA}(w) = \frac{1}{1 - P_A(w) J_{AA}(w)}, \quad \bar{C}_{BB}(w) = \frac{1}{1 - P_B(w) J_{BB}(w)}$$

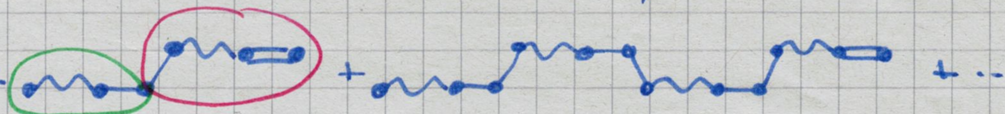
$\rightarrow C_{AA}(t) =$ 

$$= \frac{\bar{C}_{AA}(w) Q_A(w)}{1 - \bar{C}_{AA}(w) P_A(w) J_{AB}(w) \bar{C}_{BB}(w) P_B(w) J_{BA}(w)}$$

$$C_{AA}(w) = \frac{Q_A(w)\,(1 - P_B(w) J_{BB}(w))}{(1 - P_A(w) J_{AA}(w))(1 - P_B(w) J_{BB}(w)) - P_A(w) J_{AB} P_B J_{BA}}$$

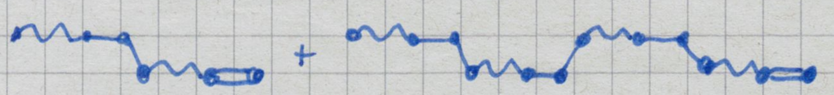
$C_{BB}(t) =$ 

$$C_{BB}(w) = \frac{Q_B\,(1 - P_A J_{AA})}{(1 - P_A J_{AA})(1 - P_B J_{BB}) - P_A J_{AB} P_B J_{BA}}$$

$C_{AB}(t) =$ 

$$C_{AB}(w) = \bar{C}_{AA}(w) P_A(w) J_{AB}(w) C_{BB}(w)$$

$$= \frac{Q_B P_A J_{AB}}{(1 - P_A J_{AA})(1 - P_B J_{BB}) - P_A J_{AB} J_{BA} P_B}$$

$C_{BA}(t) =$ 

$$C_{BA}(w) = \bar{C}_{BB}(w) P_B(w) J_{BA}(w) C_{AA}(w)$$

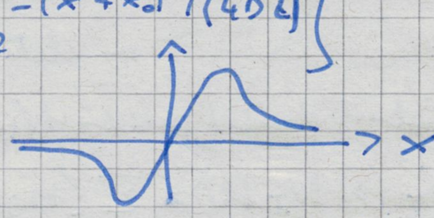
$$= \frac{Q_A P_B J_{BA}}{(1 - P_A J_{AA})(1 - P_B J_{BB}) - P_A J_{AB} J_{BA} P_B}$$

LB3

some comments on image construction on absorbing surface

$$g(x,t|x_0) = (4\pi D t)^{-1/2} e^{-\frac{(x-x_0)^2}{4Dt}}$$

$$g^{abs}(x,t|x_0) = (4\pi D t)^{-1/2}\left[e^{-(x-x_0)^2/(4Dt)} - e^{-(x+x_0)^2/(4Dt)}\right]$$



flux $j(x,t|x_0) = D\frac{\partial}{\partial x} g^{abs}(x,t|x_0) =$

(to the left!)

$$= D(4\pi D t)^{-1/2}\left[-\frac{(x-x_0)}{2Dt} e^{-\frac{(x-x_0)^2}{4Dt}} + \frac{(x+x_0)}{2Dt} e^{-\frac{(x+x_0)^2}{4Dt}}\right]$$

flux at boundary: $j(0,t|x_0) = \frac{1}{t(4\pi D t)^{1/2}}\, x_0 e^{-x_0^2/4Dt}$

integrate flux $\int_0^\infty dt\, \frac{x_0 e^{-x_0^2/4Dt}}{t(4\pi D t)^{1/2}}$, $\tilde t = 4Dt/x_0^2$

$$= \int_0^\infty \frac{d\tilde t}{\sqrt\pi}\frac{1}{\tilde t^{3/2}} e^{-1/\tilde t}, \quad x = 1/\tilde t, \quad \frac{dx}{d\tilde t} = -\frac{1}{\tilde t^2} \to d\tilde t = -\frac{dx}{x^2}.$$

$$= \int_0^\infty \frac{dx}{\sqrt\pi}\frac{e^{-x}}{\sqrt x} = 1$$ so all particles absorb, but first moment diverges!

---

exponential distribution: $P_A(t) = \frac{1}{\tau_A} e^{-t/\tau_A}$

$$\to P_A(\omega) = \int_0^\infty dt\, \frac{e^{-\omega t} e^{-t/\tau_A}}{\tau_A} = \frac{1}{\tau_A}\int_0^\infty dt\, e^{-(\omega+1/\tau_A)t}$$

$$= \frac{1}{\tau_A(\omega+1/\tau_A)} e^{-(\omega+1/\tau_A)t}\Big|_\infty^0 = \frac{1}{1+\tau_A\omega}$$

$$Q_A(\omega) = \frac{P_A(0)-P_A(\omega)}{\omega} = \frac{1-\frac{1}{1+\tau_A\omega}}{\omega} = \frac{\frac{\tau_A\omega}{1+\tau_A\omega}}{\omega}$$

$\boxed{Q_A(\omega) = \frac{\tau_A}{1+\tau_A\omega}}$ check $Q_A(\omega) = \frac{P_A(\omega=0)-P_A(\omega)}{\omega}$

$$= \frac{1-\frac{1}{1+\tau_A\omega}}{\omega}$$

$$= \frac{\tau_A\omega}{\omega(1+\tau_A\omega)} = \frac{\tau_A}{1+\tau_A\omega}$$ O.K.

Diffusion eq: $\partial_t g(x,t) = D\, \partial_x^2 g(x,t)$ LB4

$$\int_0^\infty e^{-\omega t} \partial_t g(x,t)\,dt = D\partial_x^2 \int_0^\infty dt\, e^{-\omega t} g(x,t) = D\partial_x^2 \tilde{g}(x,\omega)$$

$$= e^{-\omega t} g(x,t)\Big|_0^\infty + \omega \tilde{g}(x,\omega) = -\delta(x-x_0) + \omega\tilde{g}(x,\omega)$$

$$\rightarrow \delta(x-x_0) = (\omega - D\partial_x^2)\tilde{g}(x,\omega|x_0) \quad \text{bc2} \qquad \tilde{g}(x,\omega|x_0) = \tilde{g}(x_0,\omega \quad \text{bc1}$$

b.c.: $D\partial_x \tilde{g}(x,\omega|x_0)|_{x=x_A} = K_A\, \tilde{g}(x,\omega|x_0)|_{x=x_A} = 0$ bc3

$D\partial_x \tilde{g}(x,\omega|x_0)|_{x=x_B} = -K_B\, \tilde{g}(x,\omega|x_0)|_{x=x_B}$ bc4

general solution: $\tilde{g} = a e^{-\sqrt{\omega/D}\,x} + b e^{\sqrt{\omega/D}\,x}, \quad x < x_0$

$= c e^{-\sqrt{\omega/D}\,x} + d e^{\sqrt{\omega/D}\,x}, \quad x > x_0$

bc1 $\quad a e^{-\sqrt{\omega/D}\,x_0} + b e^{\sqrt{\omega/D}\,x_0} = c e^{-\sqrt{\omega/D}\,x_0} + d e^{\sqrt{\omega/D}\,x_0}$

bc2 $\quad D\partial_x \tilde{g}|_{x=x_0-\varepsilon} - D\partial_x \tilde{g}|_{x=x_0+\varepsilon} = 1$

$$\rightarrow D\sqrt{\omega/D}\left\{-a e^{-\sqrt{\omega/D}\,x_0} + b e^{\sqrt{\omega/D}\,x_0} + c e^{-\sqrt{\omega/D}\,x_0} - d e^{\sqrt{\omega/D}\,x_0}\right\} = 1$$

bc3 $\quad -D\sqrt{\omega/D}\,a + D\sqrt{\omega/D}\,b = K_A(a+b)$

bc4 $\quad -D\sqrt{\omega/D}\,c\, e^{-\sqrt{\omega/D}\,H} + D\sqrt{\omega/D}\,d\, e^{\sqrt{\omega/D}\,H} = -K_B c\, e^{-\sqrt{\omega/D}\,H} - K_B d\, e^{\sqrt{\omega/D}\,H}$

rescale: $Y_0 = x_0\sqrt{\omega/D}$, $\tilde{H} = H\sqrt{\omega/D}$, $\tilde{a} = a\sqrt{\omega D}$, $\tilde{K}_A = K_A/\sqrt{\omega D}$

$\rightarrow$ ① $\tilde{a} e^{-Y_0} + \tilde{b} e^{Y_0} = \tilde{c} e^{-Y_0} + \tilde{d} e^{Y_0}$

② $-\tilde{a} e^{-Y_0} + \tilde{b} e^{Y_0} + \tilde{c} e^{-Y_0} - \tilde{d} e^{Y_0} = 1$

③ $-\tilde{a} + \tilde{b} = \tilde{K}_A(\tilde{a}+\tilde{b})$

④ $-\tilde{c} e^{-\tilde{H}} + \tilde{d} e^{\tilde{H}} = -\tilde{K}_B(\tilde{c} e^{-\tilde{H}} + \tilde{d} e^{\tilde{H}})$

③ $\rightarrow \tilde{b}(1-\tilde{K}_A) = \tilde{a}(1+\tilde{K}_A) \rightarrow \tilde{b} = \tilde{a}\,\dfrac{1+\tilde{K}_A}{1-\tilde{K}_A}$

④ $\rightarrow \tilde{d} e^{\tilde{H}}(1+\tilde{K}_B) = \tilde{c} e^{-\tilde{H}}(1-\tilde{K}_B) \rightarrow \tilde{d} = \tilde{c} e^{-2\tilde{H}}\,\dfrac{(1-\tilde{K}_B)}{(1+\tilde{K}_B)}$

$1+2 \rightarrow 2\tilde{b} e^{Y_0} - 2\tilde{d} e^{Y_0} = 1 \rightarrow 2\tilde{a} e^{Y_0}\left(\dfrac{1+\tilde{K}_A}{1-\tilde{K}_A}\right) = 1 + 2\tilde{d} e^{Y_0}$

$\rightarrow \tilde{d} = \tilde{a}\left(\dfrac{1+\tilde{K}_A}{1-\tilde{K}_A}\right) - \dfrac{1}{2} e^{-Y_0}$ 5

$1-2 \rightarrow 2\tilde{a} e^{-Y_0} - 2\tilde{c} e^{-Y_0} = -1 \rightarrow \tilde{a} = \tilde{c} - \dfrac{1}{2} e^{Y_0}$

$$\tilde{a} = \tilde{d} e^{2\tilde{H}}\left(\frac{1+\tilde{K}_B}{1-\tilde{K}_B}\right) - \frac{1}{2}e^{Y_0} \overset{5}{=} \tilde{a} e^{2\tilde{H}}\left(\frac{1+\tilde{K}_B}{1-\tilde{K}_B}\right)\left(\frac{1+\tilde{K}_A}{1-\tilde{K}_A}\right)$$

$$- \frac{1}{2} e^{2\tilde{H}-Y_0}\left(\frac{1+K_B}{1-K_B}\right) - \frac{1}{2} e^{Y_0}$$

LBS

$$\rightarrow \tilde{a}\left(1-e^{2\tilde{H}}\left(\frac{1+\tilde{\kappa}_B}{1-\tilde{\kappa}_B}\right)\left(\frac{1+\tilde{\kappa}_A}{1-\tilde{\kappa}_A}\right)\right) = -\frac{1}{2}e^{y_0}\left(1+e^{2\tilde{H}-2y_0}\left(\frac{1+\kappa_B}{1-\kappa_B}\right)\right)$$

$$\rightarrow \tilde{a} = \frac{1}{2}e^{y_0}\frac{\left(1+e^{2\tilde{H}-2y_0}\left(\frac{1+\kappa_B}{1-\kappa_B}\right)\right)}{\left(e^{2\tilde{H}}\left(\frac{1+\kappa_B}{1-\tilde{\kappa}_B}\right)\left(\frac{1+\kappa_A}{1-\kappa_A}\right)-1\right)}$$

$$\tilde{b} = \tilde{a}\left(\frac{1+\tilde{\kappa}_A}{1-\tilde{\kappa}_A}\right) = \frac{1}{2}e^{y_0}\frac{\left(\frac{1+\tilde{\kappa}_A}{1-\tilde{\kappa}_A}+e^{2\tilde{H}-2y_0}\left(\frac{1+\tilde{\kappa}_B}{1-\tilde{\kappa}_B}\right)\right)}{\left(e^{2\tilde{H}}\left(\frac{1+\tilde{\kappa}_B}{1-\tilde{\kappa}_B}\right)\left(\frac{1+\tilde{\kappa}_A}{1-\tilde{\kappa}_A}\right)-1\right)}$$

flux (to the left) for $x<x_0$: $J(x,\omega|x_0) = D\partial_x\tilde{g}(x,\omega|x_0) = -a\sqrt{\omega D}\,e^{-\sqrt{\omega/D}\,x} + b\sqrt{\omega D}\,e^{+\sqrt{\omega/D}\,x}$

$$= -\tilde{a}e^{-y} + \tilde{b}e^{y}$$

flux on surface A: $\boxed{J(0,\omega|x_0) = \tilde{b}-\tilde{a}} = \tilde{a}\left(\frac{1+\tilde{\kappa}_A}{1-\tilde{\kappa}_A}-1\right) = \tilde{a}\frac{2\tilde{\kappa}_A}{1-\tilde{\kappa}_A}$

$$J(0,\omega|x_0) = \cancel{\tfrac{1}{2}}\, e^{y_0}\frac{\tilde{\kappa}_A}{1-\tilde{\kappa}_A}\frac{\left(1+e^{2\tilde{H}-2y_0}\left(\frac{1+\tilde{\kappa}_B}{1-\tilde{\kappa}_B}\right)\right)}{e^{2\tilde{H}}\left(\frac{1+\kappa_B}{1-\kappa_B}\right)\left(\frac{1+\kappa_A}{1-\kappa_A}\right)-1}$$

$$= \frac{e^{y_0}\tilde{\kappa}_A\left(1-\tilde{\kappa}_B+e^{2\tilde{H}-2y_0}(1+\tilde{\kappa}_B)\right)}{e^{2\tilde{H}}(1+\tilde{\kappa}_B)(1+\tilde{\kappa}_A)-(1-\tilde{\kappa}_B)(1-\tilde{\kappa}_A)}$$

check a few limits: $\tilde{H}\to\infty \rightarrow J(0,\omega|x_0) = \frac{\tilde{\kappa}_A(1+\tilde{\kappa}_B)e^{-y_0}}{(1+\kappa_B)(1+\tilde{\kappa}_A)} = \frac{\tilde{\kappa}_A e^{-y_0}}{1+\tilde{\kappa}_A}$

now one has in the limit $\kappa_A\to\infty$: $J(0,\omega|x_0) = e^{-y_0} = e^{-x_0\sqrt{\omega/D}}$

in the limit $y_0\to 0$ we have $J(0,\omega|0) = \frac{\tilde{\kappa}_A}{1+\tilde{\kappa}_A} = \frac{\kappa_A}{\kappa_A+\sqrt{\omega D}}$

$$J_{AA}(\omega) = J(0,\omega|0) = \frac{\tilde{\kappa}_A\left(1-\tilde{\kappa}_B+e^{2\tilde{H}}(1+\tilde{\kappa}_B)\right)}{e^{2\tilde{H}}(1+\tilde{\kappa}_B)(1+\tilde{\kappa}_A)-(1-\tilde{\kappa}_B)(1-\tilde{\kappa}_A)}$$

$$J_{BA}(\omega) = J(0,\omega|H) = \frac{e^{\tilde{H}}\tilde{\kappa}_A(1-\tilde{\kappa}_B+1+\tilde{\kappa}_B)}{e^{2\tilde{H}}(1+\tilde{\kappa}_B)(1+\tilde{\kappa}_A)-(1-\tilde{\kappa}_B)(1-\tilde{\kappa}_A)}$$

$$J_{BA}(\omega) = \frac{2e^{\tilde{H}}\tilde{\kappa}_A}{e^{2\tilde{H}}(1+\tilde{\kappa}_B)(1+\tilde{\kappa}_A)-(1-\tilde{\kappa}_B)(1-\tilde{\kappa}_A)}$$

now calculate J_{BB} and J_{AB} (as a check):

$$(5) \to \quad \tilde d = \tilde a \left(\frac{1+\tilde\kappa_A}{1-\tilde\kappa_A}\right) - \frac{1}{2} e^{-y_0}$$

$$\tilde a = \tilde d e^{2\tilde H}\left(\frac{1+\tilde\kappa_B}{1-\tilde\kappa_B}\right) - \frac{1}{2} e^{y_0} \to \tilde d = \tilde d e^{2\tilde H}\left(\frac{1+\tilde\kappa_B}{1-\tilde\kappa_B}\right)\left(\frac{1+\tilde\kappa_A}{1-\tilde\kappa_A}\right) - \frac{1}{2} e^{y_0}\left(\frac{1+\tilde\kappa_A}{1-\tilde\kappa_A}\right) - \frac{1}{2} e^{-y_0}$$

$$\tilde d\left(1 - e^{2\tilde H}\left(\frac{1+\tilde\kappa_B}{1-\tilde\kappa_B}\right)\left(\frac{1+\tilde\kappa_A}{1-\tilde\kappa_A}\right)\right) = -\frac{1}{2} e^{-y_0}\left(1 + e^{+2y_0}\left(\frac{1+\tilde\kappa_A}{1-\tilde\kappa_A}\right)\right)$$

$$\tilde d = \frac{\frac{1}{2} e^{-y_0}\left(1 + e^{2y_0}\left(\frac{1+\tilde\kappa_A}{1-\tilde\kappa_A}\right)\right)}{e^{2\tilde H}\left(\frac{1+\tilde\kappa_B}{1-\tilde\kappa_B}\right)\left(\frac{1+\tilde\kappa_A}{1-\tilde\kappa_A}\right) - 1} \qquad \tilde c = \tilde d e^{2\tilde H}\left(\frac{1+\tilde\kappa_B}{1-\tilde\kappa_B}\right)$$

$$\tilde c = \frac{1}{2} e^{2\tilde H - y_0} \frac{\left(\frac{1+\tilde\kappa_B}{1-\tilde\kappa_B}\right)\left(1 + e^{2y_0}\left(\frac{1+\tilde\kappa_A}{1-\tilde\kappa_A}\right)\right)}{e^{2\tilde H}\left(\frac{1+\tilde\kappa_B}{1-\tilde\kappa_B}\right)\left(\frac{1+\tilde\kappa_A}{1-\tilde\kappa_A}\right) - 1}$$

flux to the right ($x > x_0$): $J(x,\omega|x_0) = -D\partial_x \tilde G(x,\omega|x_0) = c\sqrt{\omega D}\, e^{-\sqrt{\omega/D}\,x} - d\sqrt{\omega D}\, e^{\sqrt{\omega/D}\,x}$

$$= \tilde c e^{-y} - \tilde d e^{y}$$

flux on surface B: $J(H,\omega|x_0) = \tilde c e^{-\tilde H} - \tilde d e^{\tilde H} = \tilde d e^{\tilde H}\left(\frac{1+\tilde\kappa_B}{1-\tilde\kappa_B} - 1\right)$

$$= \tilde d e^{\tilde H} \frac{(1+\tilde\kappa_B - 1 + \tilde\kappa_B)}{1-\tilde\kappa_B} = \frac{2\tilde\kappa_B}{1-\tilde\kappa_B} \tilde d e^{\tilde H}$$

$$= e^{\tilde H - y_0} \frac{\frac{\tilde\kappa_B}{1-\tilde\kappa_B}\left(1 + e^{2y_0}\left(\frac{1+\tilde\kappa_A}{1-\tilde\kappa_A}\right)\right)}{e^{2\tilde H}\left(\frac{1+\tilde\kappa_B}{1-\tilde\kappa_B}\right)\left(\frac{1+\tilde\kappa_A}{1-\tilde\kappa_A}\right) - 1} = \frac{e^{\tilde H - y_0}\tilde\kappa_B\left(1 - \tilde\kappa_A + e^{2y_0}(1+\tilde\kappa_A)\right)}{e^{2\tilde H}(1+\tilde\kappa_B)(1+\tilde\kappa_A) - (1-\tilde\kappa_B)(1-\tilde\kappa_A)}$$

$$J_{BB} = J(H,\omega|H) = \frac{\tilde\kappa_B\left(1 - \tilde\kappa_A + e^{2\tilde H}(1+\tilde\kappa_A)\right)}{e^{2\tilde H}(1+\tilde\kappa_B)(1+\tilde\kappa_A) - (1-\tilde\kappa_B)(1-\tilde\kappa_A)}$$

symmetry o.k.!

$$J_{AB} = J(H,\omega|0) = \frac{e^{\tilde H}\tilde\kappa_B(1 - \tilde\kappa_A + 1 + \tilde\kappa_A)}{e^{2\tilde H}(1+\tilde\kappa_B)(1+\tilde\kappa_A) - (1-\tilde\kappa_A)(1-\tilde\kappa_B)} = \frac{2e^{\tilde H}\tilde\kappa_B}{e^{2\tilde H}(1+\tilde\kappa_B)(1+\tilde\kappa_A) - (1-\tilde\kappa_A)(1-\tilde\kappa_B)}$$

for $\tilde H \gg 1$ or $H\sqrt{\omega/D} \gg 1$ or $\omega \gg D/H^2$:

$$J_{BB} \sim \frac{\tilde\kappa_B}{1+\tilde\kappa_B} \quad \text{and} \quad J_{AA} \sim \frac{\tilde\kappa_A}{1+\tilde\kappa_A} \; !$$

single-surface behavior recovered!

low-ω expansion of J_{BB}

$$J_{BB} = \frac{\tilde{\kappa}_B\left(e^{-\tilde{H}}(1-\tilde{\kappa}_A) + e^{\tilde{H}}(1+\tilde{\kappa}_A)\right)}{e^{\tilde{H}}(1+\tilde{\kappa}_B)(1+\tilde{\kappa}_A) - e^{-\tilde{H}}(1-\tilde{\kappa}_B)(1-\tilde{\kappa}_A)} = \frac{\tilde{\kappa}_B\left((e^{\tilde{H}}+e^{-\tilde{H}}) + (e^{\tilde{H}}-e^{-\tilde{H}})\tilde{\kappa}_A\right)}{(e^{\tilde{H}}+e^{-\tilde{H}})(\tilde{\kappa}_B+\tilde{\kappa}_A) + (e^{\tilde{H}}-e^{-\tilde{H}})(1+\tilde{\kappa}_A\tilde{\kappa}_B)}$$

remember $\tilde{H} = H\sqrt{\omega/D}$, $\tilde{\kappa}_A = \kappa_A/\sqrt{\omega D} \rightarrow \tilde{\kappa}_A^{-1} = \kappa_A^{-1}\sqrt{\omega D}$

$$J_{BB} = \frac{(e^{\tilde{H}}+e^{-\tilde{H}})\tilde{\kappa}_A^{-1} + (e^{\tilde{H}}-e^{-\tilde{H}})}{(e^{\tilde{H}}+e^{-\tilde{H}})(\tilde{\kappa}_A^{-1}+\tilde{\kappa}_B^{-1}) + (e^{\tilde{H}}-e^{-\tilde{H}})(1+\tilde{\kappa}_A^{-1}\tilde{\kappa}_B^{-1})}$$

$$e^{\tilde{H}}+e^{-\tilde{H}} \simeq 2 + \tilde{H}^2 + \mathcal{O}(\tilde{H}^4), \quad e^{\tilde{H}}-e^{-\tilde{H}} \simeq 2\tilde{H} + \frac{1}{3}\tilde{H}^3 + \dots$$

$$J_{BB} \simeq \frac{(2+\tilde{H}^2)\tilde{\kappa}_A^{-1} + 2\tilde{H} + \frac{1}{3}\tilde{H}^3 + \mathcal{O}(\omega^{5/2})}{(2+\tilde{H}^2)(\tilde{\kappa}_A^{-1}+\tilde{\kappa}_B^{-1}) + (2\tilde{H}+\frac{1}{3}\tilde{H}^3)(1+\tilde{\kappa}_A^{-1}\tilde{\kappa}_B^{-1}) + \mathcal{O}(\omega^{5/2})}$$

$$\simeq \frac{2\tilde{\kappa}_A^{-1} + 2\tilde{H} + \tilde{H}^2\tilde{\kappa}_A^{-1} + \frac{1}{3}\tilde{H}^3 + \mathcal{O}(\omega^{5/2})}{2\tilde{\kappa}_A^{-1} + 2\tilde{\kappa}_B^{-1} + 2\tilde{H} + \tilde{H}^2(\tilde{\kappa}_A^{-1}+\tilde{\kappa}_B^{-1}) + 2\tilde{H}\tilde{\kappa}_A^{-1}\tilde{\kappa}_B^{-1} + \frac{1}{3}\tilde{H}^3 + \mathcal{O}(\omega^{5/2})}$$

$$= \frac{1 + \tilde{H}\tilde{\kappa}_A + \frac{1}{2}\tilde{H}^2 + \frac{1}{6}\tilde{H}^3\tilde{\kappa}_A + \mathcal{O}(\omega^2)}{1 + \tilde{\kappa}_A\tilde{\kappa}_B^{-1} + \tilde{H}\tilde{\kappa}_A + \frac{1}{2}\tilde{H}^2(1+\tilde{\kappa}_A/\tilde{\kappa}_B) + \tilde{H}\tilde{\kappa}_B^{-1} + \frac{1}{6}\tilde{H}^3\tilde{\kappa}_A + \mathcal{O}(\omega^2)}$$

$$\neq \frac{1 + H\kappa_A/D + \frac{1}{2}H^2\omega/D + \frac{1}{6}H^3\kappa_A\omega/D^2}{1 + \kappa_A/\kappa_B + H\kappa_A/D + \frac{1}{2}H^2\omega(1+\kappa_A/\kappa_B)/D + H\kappa_B^{-1}\omega + \frac{1}{6}\frac{H^3\kappa_A\omega}{D^2}}$$

$$= \frac{1 + H\kappa_A/D + \omega\left(\frac{1}{2}H^2/D + \frac{1}{6}H^3\kappa_A/D^2\right)}{1 + \kappa_A/\kappa_B + H\kappa_A/D + \omega\left(\frac{1}{2}H^2(1+\kappa_A/\kappa_B)/D + H\kappa_B^{-1} + \frac{1}{6}H^3\kappa_A/D^2\right)}$$

$$= \frac{1 + H\kappa_A/D}{1 + \kappa_A/\kappa_B + H\kappa_A/D}\;\frac{\left[1 + \omega\left(\frac{1}{2}H^2/D + 1/6\,H^3\kappa_A/D^2\right)/(1+H\kappa_A/D)\right]}{\left[1 + \omega\dfrac{\left(\frac{1}{2}H^2(1+\kappa_A/\kappa_B)/D + H\kappa_B^{-1} + \frac{1}{6}H^3\kappa_A/D^2\right)}{1+\kappa_A/\kappa_B + H\kappa_A/D}\right]}$$

$$= \phi_{BB}(1 - \tau_{BB}\,\omega)$$

$[H] = m \quad [D] = \frac{m^2}{s} \quad [\kappa] = \frac{m}{s}$

$$\phi_{BB} = \frac{D + H\kappa_A}{D + D\kappa_A/\kappa_B + H\kappa_A}$$

$$\tau_{BB} = \frac{\frac{1}{2}H^2/D + 1/6\,H^3\kappa_A/D^2}{1 + H\kappa_A/D} + \frac{\frac{1}{2}H^2(1+\kappa_A/\kappa_B)/D + H/\kappa_B + \frac{1}{6}H^3\kappa_A/D^2}{1 + \kappa_A/\kappa_B + H\kappa_A/D}$$

$$\tau_{BB} = \frac{\frac{1}{2}H^2 + \frac{1}{6}H^3\kappa_A/D}{D + H\kappa_A} + \frac{\frac{1}{2}H^2(1+\kappa_A/\kappa_B) + DH/\kappa_B + \frac{1}{6}H^3\kappa_A/D}{D + D\kappa_A/\kappa_B + H\kappa_A}$$

check limits of ϕ_{BB} and τ_{BB} $\boxed{LB\ 8}$

<u>$H=\infty$</u> : all particles eventually absorb on upper plate

$\phi_{BB} = 1$, τ_{BB} divergent (as expected)

$(\tau_{BB} \simeq$

<u>$KA = 0$</u> : lower plate is reflective, all particles absorb to plate B

$$\phi_{BB} = 1 \quad , \tau_{BB} = -\frac{1}{2}\frac{H^2}{D} + \frac{\frac{1}{2}H^2 + DH/k_B}{D}$$

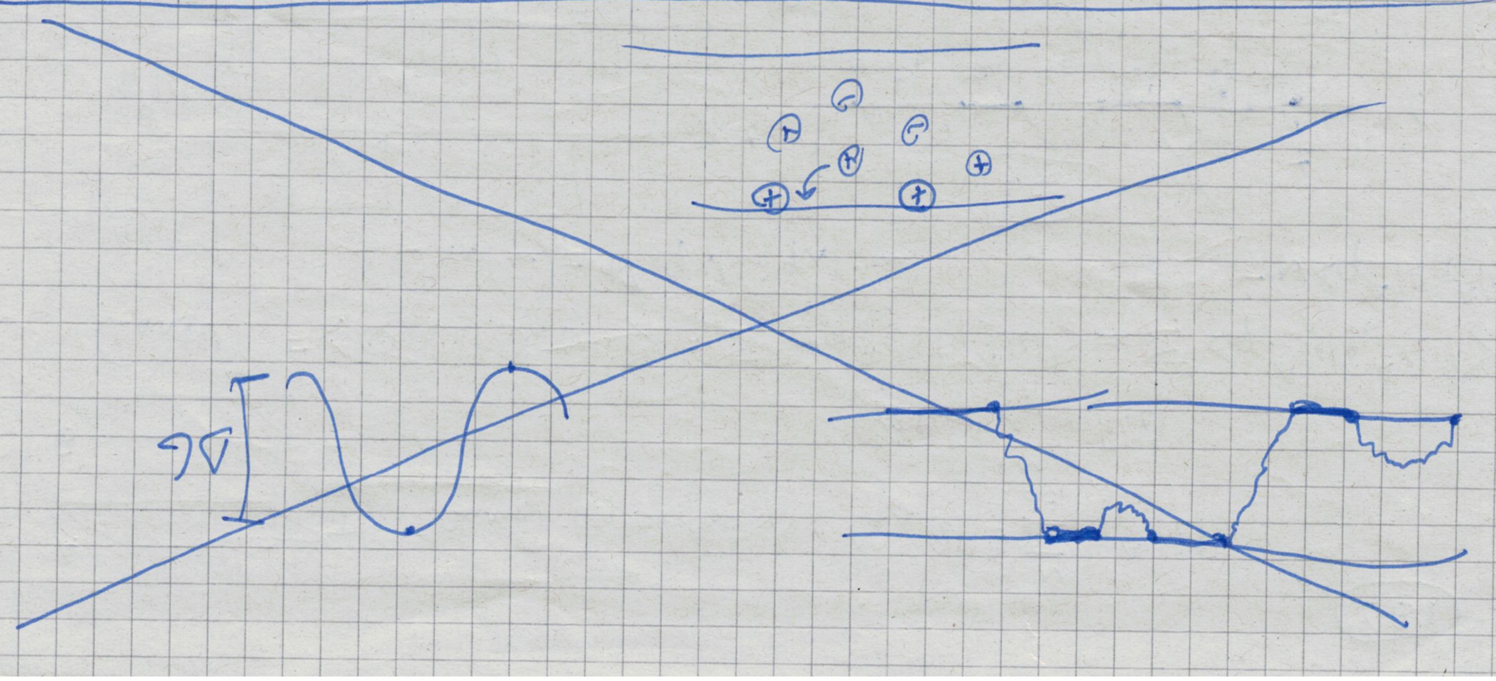
$$\tau_{BB} = H/k_B$$

<u>$k_B = 0$</u> : no particles absorb on upper plate

$\phi_{BB} = 0$,

$k_B = \infty$: all particles absorb on upper plate in zero time!

$$\phi_{BB} \equiv 1 \qquad \tau_{BB} = -\frac{\frac{1}{2}H^2 + \frac{1}{6}H^3 k_A/D}{D + Hk_A} + \frac{\frac{1}{2}H^2 + \frac{1}{6}H^3 k_A/D}{D + Hk_A} = 0$$



low-ω expansion of γ_{AB}:

$$\gamma_{AB}^{-1} = \tfrac{1}{2}\tilde{\kappa}_B^{-1}\left(e^{\tilde{H}}(1+\tilde{\kappa}_B)(1+\tilde{\kappa}_A) - e^{-\tilde{H}}\left((1-\tilde{\kappa}_A)(1-\tilde{\kappa}_B)\right)\right)$$

$$= \tfrac{1}{2}\tilde{\kappa}_A\left(e^{\tilde{H}}(1+\tilde{\kappa}_B^{-1})(1+\tilde{\kappa}_A^{-1}) - e^{-\tilde{H}}(1-\tilde{\kappa}_A^{-1})(1-\tilde{\kappa}_B^{-1})\right)$$

$$= \tfrac{1}{2}\tilde{\kappa}_A\left((e^{\tilde{H}}+e^{-\tilde{H}})(\tilde{\kappa}_A^{-1}+\tilde{\kappa}_B^{-1}) + (e^{\tilde{H}}-e^{-\tilde{H}})(1+\tilde{\kappa}_A^{-1}\tilde{\kappa}_B^{-1})\right)$$

$$= \tfrac{1}{2}\tilde{\kappa}_A\left((2+\tilde{H}^2)(\tilde{\kappa}_A^{-1}+\tilde{\kappa}_B^{-1}) + (2\tilde{H}+\tfrac{1}{3}\tilde{H}^3)(1+\tilde{\kappa}_A^{-1}\tilde{\kappa}_B^{-1})\right)$$

$$= \tfrac{1}{2}\tilde{\kappa}_A\left(2(\tilde{\kappa}_A^{-1}+\tilde{\kappa}_B^{-1}) + 2\tilde{H} + \tilde{H}^2(\tilde{\kappa}_A^{-1}+\tilde{\kappa}_B^{-1}) + 2\tilde{H}\tilde{\kappa}_A^{-1}\tilde{\kappa}_B^{-1} + \tfrac{1}{3}\tilde{H}^3\right)$$

$$= 1 + \tilde{\kappa}_A/\tilde{\kappa}_B + \tilde{H}\tilde{\kappa}_A + \tfrac{1}{2}\tilde{H}^2(1+\tilde{\kappa}_A/\tilde{\kappa}_B) + \tilde{H}\tilde{\kappa}_B^{-1} + \tfrac{1}{6}\tilde{H}^3\tilde{\kappa}_A$$

$$= 1 + \kappa_A/\kappa_B + H\kappa_A/D + \tfrac{1}{2}H^2\omega/D\,(1+\kappa_A/\kappa_B) + H\omega/\kappa_B + \tfrac{1}{6}H^3\kappa_A\omega/D^2$$

$$= (1+\kappa_A/\kappa_B+H\kappa_A/D)\left(1 + \frac{\omega\left(\tfrac{1}{2}H^2D^{-1}(1+\kappa_A/\kappa_B) + H/\kappa_B + \tfrac{1}{6}H^3\kappa_A/D^2\right)}{1+\kappa_A/\kappa_B+H\kappa_A/D}\right)$$

$$\gamma_{AB} = \phi_{AB}(1-\tau_{AB}\omega)$$

$$\phi_{AB} = \frac{1}{1+\kappa_A/\kappa_B+H\kappa_A/D} = \frac{D}{D+D\kappa_A/\kappa_B+H\kappa_A}$$

$$\tau_{AB} = \frac{\tfrac{1}{2}H^2D^{-1}(1+\kappa_A/\kappa_B) + H/\kappa_B + \tfrac{1}{6}H^3\kappa_A/D^2}{1+\kappa_A/\kappa_B+H\kappa_A/D}$$

$$\tau_{AB} = \frac{\tfrac{1}{2}H^2(\kappa_A+\kappa_B) + DH + \tfrac{1}{6}H^3\kappa_A\kappa_B/D}{\kappa_B D + D\kappa_A + H\kappa_A\kappa_B}$$

check limits of J_{AB}

LB10

$H=\infty \rightarrow \phi_{AB}=0$ and $\tau_{AB}=\infty$

$k_A=\infty \rightarrow \phi_{AB}=0$ and $\tau_{AB}=\dfrac{\frac{1}{2}H^2 + \frac{1}{6}H^3 k_B/D}{D+Hk_B}$

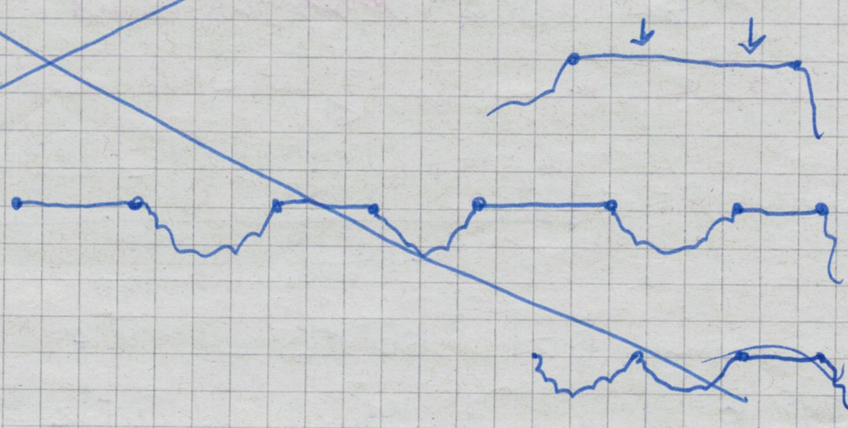
$k_A=k_B=\infty \rightarrow \phi_{AB}=0$ and $\tau_{AB}=\frac{1}{6}H^2/D$ exact transition path result!!

$k_A=0 \rightarrow \phi_{AB}=1$ and $\tau_{AB}=\underline{\frac{1}{2}H^2/D + H/k_B}$

$k_A=0$ and $k_B=\infty \rightarrow \phi_{AB}=1$ and $\tau_{AB}=\frac{1}{2}H^2/D$

exact mean-first passage result!!

$H=0 \rightarrow \phi_{AB}=\dfrac{k_B}{k_A+k_B}$ and $\tau_{AB}=0$



Summary of expressions

$$J_{AA} = \frac{\tilde{K}_A\left(1-\tilde{K}_B + e^{2\tilde{H}}\left(1+\tilde{K}_B\right)\right)}{e^{2\tilde{H}}(1+\tilde{K}_B)(1+\tilde{K}_A)-(1-\tilde{K}_B)(1-\tilde{K}_A)}$$

$$B \to A: \; J_{BA} = \cancel{e^{\tilde{H}} K_A} = \frac{2e^{\tilde{H}}\tilde{K}_A}{e^{2\tilde{H}}(1+\tilde{K}_B)(1+\tilde{K}_A)-(1-\tilde{K}_B)(1-\tilde{K}_A)}$$

$$J_{BB} = \frac{\tilde{K}_B\left(1-\tilde{K}_A + e^{2\tilde{H}}\left(1+\tilde{K}_A\right)\right)}{e^{2\tilde{H}}(1+\tilde{K}_B)(1+\tilde{K}_A)-(1-\tilde{K}_A)(1-\tilde{K}_B)}$$

$$A \to B: \; J_{AB} = \frac{2e^{\tilde{H}}\tilde{K}_B}{e^{2\tilde{H}}(1+\tilde{K}_B)(1+\tilde{K}_A)-(1-\tilde{K}_A)(1-\tilde{K}_B)}$$

$$\phi_{BB} = \frac{D + HK_A}{D + DK_A/K_B + HK_A}$$

$$\tau_{BB} = \frac{\frac{1}{2}H^2(1+K_A/K_B) + DH/K_B + \frac{1}{6}H^3K_A/D}{D + DK_A/K_B + HK_A} - \frac{\frac{1}{2}H^2 + \frac{1}{6}H^3K_A/D}{D + HK_A}$$

$$\phi_{AB} = \frac{D}{D + DK_A/K_B + HK_A}$$

$$\tau_{AB} = \frac{\frac{1}{2}H^2(K_A + K_B) + DH + \frac{1}{6}H^3K_AK_B/D}{K_BD + DK_A + HK_AK_B}$$

by symmetry (without explicit check)

$$\phi_{AA} = \frac{D + HK_B}{D + DK_B/K_A + HK_B}$$

$$\tau_{AA} = \frac{\frac{1}{2}H^2(1+K_B/K_A) + DH/K_A + \frac{1}{6}H^3K_B/D}{D + DK_B/K_A + HK_B} - \frac{\frac{1}{2}H^2 + \frac{1}{6}H^3K_B/D}{D + HK_B}$$

$$\phi_{BA} = \frac{D}{D + DK_B/K_A + HK_B}$$

$$\boxed{\tau_{BA} = \tau_{AB}}\;!$$

$$\cancel{\tau_{BA} = \frac{1}{2}H^2D^3(K_A + K_B) + DH + \frac{1}{6}H^3K_AK_B/D}$$

by symmetry: $\phi_{BA} = \dfrac{D}{D + Dk_B/k_A + Hk_B}$

$$\phi_{BA} + \phi_{BB} = \frac{D}{D + Dk_B/k_A + Hk_B} + \frac{D + Hk_A}{D + Dk_A/k_B + Hk_A}$$

$$= \frac{D(D + Dk_A/k_B + Hk_A) + (D + Hk_A)(D + Dk_B/k_A + Hk_B)}{(D + Dk_B/k_A + Hk_B)(D + Dk_A/k_B + Hk_A)}$$

$$= \frac{D^2 + D^2 k_A/k_B + DHk_A + D^2 + D^2 k_B/k_A + DHk_B + DHk_A + DHk_B + H^2 k_A k_B}{D^2 + D^2 k_A/k_B + DHk_A + D^2 k_B/k_A + D^2 + Dk_B H + DHk_B + DHk_A + H^2 k_A k_B}$$

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last and crucial check $\boxed{LB12}$

$\phi_{BA} + \phi_{BB} = 1$ (see above)

connect to thermodynamics: eq. probability LB13

time of being ~~probability to be~~ adsorbed on plate A : $C_{AA}(w=0)$

note: $Q_A(w=0)=\tau_A$, $P_A(w=0)=1$

$$C_{AA}(w=0)=\frac{\tau_A\,(1-J_{BB}(0))}{(1-J_{AA}(0))(1-J_{BB}(0))-J_{AB}(0)\,J_{BA}(0)}$$

(by construction, this equals $C_{BA}(w=0)$, as it must!)

$$\cancel{=\frac{\dfrac{\tau_A\,(Dk_A/k_B)}{D+Dk_A/k_B+Hk_A}}{\dfrac{(Dk_B/k_A)(Dk_A/k_B)-D^2}{(D+Dk_B/k_A+Hk_B)(D+Dk_A/k_B+Hk_A)}}}$$

$$\cancel{W_A=\frac{\tau_A\,Dk_A/k_B}{D+Dk_B/k_A+Hk_B}}$$ = ~~probability to be on plate A~~

$$\cancel{W_A=\frac{\tau_A D k_A^2/k_B}{D(k_A+k_B)+Hk_Ak_B}}$$

$$\cancel{=\tau_A(Dk_A/k_B)(D+Dk_B/k_A+Hk_B)}$$

≟ detailed balance

$$C_{BB}(w=0)=\frac{\tau_B\,(1-J_{AA})}{(1-J_{AA})(1-J_{BB})-J_{AB}J_{BA}}$$

$$\frac{C_{AA}(w=0)}{C_{BB}(w=0)}=\frac{\tau_A\,(1-J_{BB})}{\tau_B\,(1-J_{AA})}=\frac{\tau_A\,(Dk_A/k_B)\,(D+Dk_B/k_A+Hk_B)}{\tau_B\,(Dk_B/k_A)\,(D+Dk_A/k_B+Hk_A)}=\frac{\tau_A J_{BA}}{\tau_B J_{AB}}$$

$$=\frac{\tau_A k_A\,(Dk_A+Dk_B+Hk_Bk_A)}{\tau_B k_B\,(Dk_B+Dk_A+Hk_Ak_B)}=\boxed{\frac{\tau_A k_A}{\tau_B k_B}}$$

$\cancel{\frac{C_{AA}(w=0)}{1-C_{AA}}}$ law of mass action:

ratio of surface concentrations: $\dfrac{C_{AA}(w=0)}{C_{BB}(w=0)}=\dfrac{\tau_A k_A}{\tau_B k_B}$

generating function of

$$\frac{\partial \ln Q_{AA}(w)}{\partial P_A(w)} \neq \frac{J_{AA}(w)\left(1-P_B(w) J_{BB}(w)\right) + J_{AB}(w) P_B(w) J_{BA}(w)}{(1-P_A J_{AA})(1-P_B J_{BB}) - P_A J_{AB} P_B J_{BA}}$$

$$w \to 0 \quad = \frac{J_{AA}(1-J_{BB}) + J_{AB} J_{BA}}{(1-J_{AA})(1-J_{BB}) - J_{AB} J_{BA}}$$

$$= \frac{(D+H/K_B)^2 \cdot D K_A/K_B + D^2}{(D + D K_B/K_A + H K_B)(D + D K_A/K_B + H K_A) - (D K_B/K_A)\cdot D}$$

$$Q_{AD}(t) = \int_t^\infty dt' \left[J_{AA}(t') + J_{AB}(t') \right]$$

$J_{AA}(t)$: first re-adsorpt. distrib.

$J_{AB}(t)$: first transfer $A \to B$

$Q_{AD}(t)$: probability to be still desorbed when starting from surface A

$\hat{=}$ survival probability of ~~desorbed~~ desorbed state! $\frac{dQ_{AD}}{dt} = -J_{AA}(t) - J_{AB}(t)$

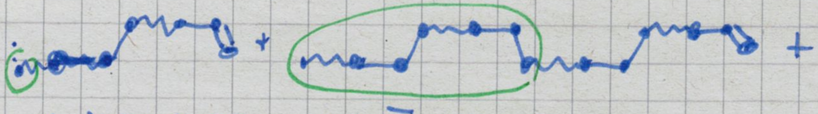
$C_{AAD}(t)$: 

$C_{AAD}(t)$: prob. dist. to start at A, and to be desorbed from surface A

$$C_{AAD}(w) = \frac{\bar{C}_{AA}(w) P_A(w) Q_{AD}(w)}{1 - \bar{C}_{AA}(w) P_A(w) J_{AB}(w) \bar{C}_{BB}(w) P_B(w) J_{BA}(w)}$$

$$= \frac{P_A(w) Q_{AD}(w)\left(1 - P_B(w) J_{BB}(w)\right)}{\left(1-P_A(w) J_{AA}(w)\right)\left(1-P_B(w) J_{BB}(w)\right) - P_A(w) J_{AB}(w) P_B(w) J_{BA}(w)}$$

$$Q_{BD}(t) = \int_t^\infty dt' \left[J_{BB}(t') + J_{BA}(t') \right]$$ prob. to be still desorbed ~~from~~ when starting from surface B

$C_{ABD}(t)$: 

$\hat{=}$ prob. dist. to start at $t=0$ at B, and to be desorbed at time t coming from surface B

$$= \frac{\bar{C}_{AA}(w) P_A(w) J_{AB}(w) \bar{C}_{BB}(w) P_B(w) Q_{BD}(w)}{1 - \bar{C}_{AA}(w) P_A(w) J_{AB}(w) \bar{C}_{BB}(w) P_B(w) J_{BA}(w)}$$

$$= \frac{P_A J_{AB} P_B Q_{BD}}{(1-P_A J_{AA})(1-P_B J_{BB}) - P_A J_{AB} P_B J_{BA}}$$

$$C_{AD}(w) = C_{AAD}(w) + C_{ABD}(w) = \frac{P_A Q_{AD}(1-P_B J_{BB}) + P_A J_{AB} P_B Q_{BD}}{(1-P_A J_{AA})(1-P_B J_{BB}) - P_A J_{AB} P_B J_{BA}}$$

$\hat{=}$ prob. dist. to start at $t=0$ at A and to be desorbed at time t

$$C_{AD}(0) = \frac{Q_{AD}(0)\left(1 - J_{BB}(0)\right) + J_{AB}(0)\, Q_{BD}(0)}{\left(1 - J_{AA}(0)\right)\left(1 - J_{BB}(0)\right) - J_{AB}(0)\, J_{BA}(0)} \qquad \left(1 - J_{AA}(0)\right)\left(1 - J_{BB}(0)\right) - J_{AB}(0)\, J_{BA}(0) = X$$

$$Q_{AD}(0) = \left.\frac{J_{AA}(0) + J_{AB}(0) - J_{AA}(\omega) - J_{AB}(\omega)}{\omega}\right|_{\omega=0} = \phi_{AA}\tau_{AA} + \phi_{AB}\tau_{AB}$$

$$Q_{BD}(0) = \phi_{BB}\tau_{BB} + \phi_{BA}\tau_{BA}$$

$$C_{AD}(0) = \frac{\left(\phi_{AA}\tau_{AA} + \phi_{AB}\tau_{AB}\right)\left(1 - \phi_{BB}\right) + \phi_{AB}\left(\phi_{BB}\tau_{BB} + \phi_{BA}\tau_{BA}\right)}{X}$$

Stream line the expressions:

$$\phi_{BB} = \frac{DK_B + HK_AK_B}{\gamma} \qquad \gamma = D(K_A + K_B) + HK_AK_B$$

$$\tau_{BB} = \frac{\frac{1}{2}H^2(K_A+K_B) + DH + \frac{1}{6}H^3K_AK_B/D}{\gamma} - \frac{\frac{1}{2}H^2 + \frac{1}{6}H^3K_A/D}{D + HK_A}$$

$$\tau_{BB} = \frac{\delta}{\gamma} - \frac{\frac{1}{2}H^2 + \frac{1}{6}H^3K_A/D}{D + HK_A} \qquad \delta = \frac{1}{2}H^2(K_A+K_B) + DH + \frac{1}{6}H^3K_AK_B/D$$

$$\phi_{AB} = \frac{DK_B}{\gamma} \qquad \tau_{AB} = \frac{\delta}{\gamma} \qquad \phi_{BA} = \frac{DK_A}{\gamma}, \quad \tau_{BA} = \tau_{AB} = \frac{\delta}{\gamma}$$

$$\phi_{AA} = \frac{DK_A + HK_AK_B}{\gamma}, \quad \tau_{AA} = \frac{\delta}{\gamma} - \frac{\frac{1}{2}H^2 + \frac{1}{6}H^3K_B/D}{D + HK_B}$$

$$\cancel{C_{AD}(0) = \left[\frac{DK_A + HK_AK_B}{\gamma}\left(\frac{\delta}{\gamma} - \frac{\frac{1}{2}H^2 + \frac{1}{6}H^3K_B/D}{D + HK_B}\right) + \frac{DK_B\delta}{\gamma^2}\right]\frac{DK_A}{\gamma}}$$

$$\cancel{+ \frac{DK_B}{\gamma}\left[\frac{DK_A}{\gamma}\frac{\delta}{\gamma} + \frac{DK_B + HK_AK_B}{\gamma}\left(\frac{\delta}{\gamma} - \frac{\frac{1}{2}H^2 + \frac{1}{6}H^3K_A/D}{D + HK_A}\right)\right]}$$

$$\cancel{= \frac{2D^2\delta K_AK_B}{\gamma^3} + \frac{\delta}{\gamma}\frac{D}{\gamma\gamma}\left(DK_A^2 + HK_A^2K_B + DK_B^2 + HK_B^2K_A\right) -}$$

$$\tau_{BB} = \Big(\tfrac{1}{2}\cancel{DH^2(K_A+K_B)} + D^2H + \tfrac{1}{6}\cancel{H^3K_AK_B} + \tfrac{1}{2}H^3K_A(K_A + \cancel{K_B}) + DH^2K_A + \tfrac{1}{6}\cancel{H^4K_A^2K_B/D}$$

$$- \tfrac{1}{2}\cancel{H^2D(K_A+K_B)} - \tfrac{1}{6}H^3K_A(K_A + \cancel{K_B}) - \tfrac{1}{2}\cancel{H^3K_AK_B} - \tfrac{1}{6}\cancel{H^4K_A^2K_B/D}\Big) \Big/ \left(\gamma(D + HK_A)\right)$$

$$= \frac{D^2H + \frac{1}{3}H^3K_A^2 + DH^2K_A}{\gamma(D + HK_A)} = \frac{DH}{\gamma} + \frac{\frac{1}{3}H^3K_A^2}{\gamma(D + HK_A)} = \frac{DH(D + HK_A) + \frac{1}{3}H^3K_A^2}{\gamma(D + HK_A)}$$

$$\tau_{AA} = \frac{DH(D + HK_B) + \frac{1}{3}H^3K_B^2}{\gamma(D + HK_B)}$$

$$\phi_{AA}\tau_{AA} = \frac{\kappa_A(D+H\kappa_B)}{\gamma}\,\frac{\left(DH(D+H\kappa_B)+\frac{1}{3}H^3\kappa_B^2\right)}{\gamma(D+H\kappa_B)}$$

$$= \frac{\kappa_A\left(DH(D+H\kappa_B)+\frac{1}{3}H^3\kappa_B^2\right)}{\gamma^2}$$

$$\phi_{AB}\tau_{AB} = \frac{D\kappa_B\delta}{\gamma^2}, \quad \phi_{BA}\tau_{BA} = \frac{D\kappa_A\delta}{\gamma^2}$$

$$\cancel{\phi_{AA}\tau_{AA}+\phi_{AB}\tau_{AB}} = \phi_{BB}\tau_{BB} = \frac{\kappa_B(D+H\kappa_A)}{\gamma}\,\frac{\left(DH(D+H\kappa_A)+\frac{1}{3}H^3\kappa_A^2\right)}{\gamma(D+H\kappa_A)}$$

$$= \frac{\kappa_B\left(DH(D+H\kappa_A)+\frac{1}{3}H^3\kappa_A^2\right)}{\gamma^2}$$

$$\gamma^3 C_{AD}(0)\,X = \left[\kappa_A\left(DH(D+H\kappa_B)+\frac{1}{3}H^3\kappa_B^2\right)+D\kappa_B\delta\right]D\kappa_A$$
$$+ D\kappa_B\left\{\kappa_B\left(DH(D+H\kappa_A)+\frac{1}{3}H^3\kappa_A^2\right)+D\kappa_A\delta\right\}$$

$$= 2D^2\delta\kappa_A\kappa_B + D\kappa_A^2\left(DH(D+H\kappa_B)\right) + \frac{1}{3}DH^3\kappa_B^2\kappa_A^2$$
$$+ D\kappa_B^2\left(DH(D+H\kappa_A)\right) + \frac{1}{3}DH^3\kappa_A^2\kappa_B^2$$

$$= 2D^2\delta\kappa_A\kappa_B + D^3H(\kappa_A^2+\kappa_B^2) + D^2H^2\kappa_A\kappa_B(\kappa_A+\kappa_B) + \frac{2}{3}DH^3\kappa_A^2\kappa_B^2\cancel{(\kappa_A+\kappa_B)}$$

$$= H^2D^2\kappa_A\kappa_B(\kappa_A+\kappa_B) + 2D^3H\kappa_A\kappa_B + \frac{1}{3}H^3D\kappa_A^2\kappa_B^2$$
$$+ D^2H^2\kappa_A\kappa_B(\kappa_A+\kappa_B) + D^3H(\kappa_A^2+\kappa_B^2) + \frac{2}{3}H^3D\kappa_A^2\kappa_B^2\cancel{(\kappa_A+\kappa_B)}$$

$$= 2H^2D^2\kappa_A\kappa_B(\kappa_A+\kappa_B) + D^3H(\kappa_A+\kappa_B)^2 + H^3D\kappa_A^2\kappa_B^2\cancel{(\kappa_A+\kappa_B+\kappa_A\kappa_B)}$$

$$= HD\left[2HD\kappa_A\kappa_B(\kappa_A+\kappa_B) + D^2(\kappa_A+\kappa_B)^2 + H^2\kappa_A^2\kappa_B^2\right]$$

$$= HD\left[D(\kappa_A+\kappa_B)+H\kappa_A\kappa_B\right]^2 = HD\gamma^2$$

$$\rightarrow C_{AD}(0) = \frac{HD}{\gamma X} = \frac{HD}{(D(\kappa_A+\kappa_B)+H\kappa_A\kappa_B)\,X}$$

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$$C_{AA}(0) = \frac{\tau_A D\kappa_A}{(D(\kappa_A+\kappa_B)+H\kappa_A\kappa_B)\,X} \rightarrow \boxed{\frac{C_{AA}(0)}{C_{AD}(0)} = \frac{\tau_A\kappa_A}{H}}$$

law of mass action: $\dfrac{C_{AA}(0)}{C_{AD}(0)/H} = \tau_A\kappa_A$

surface conc.

bulk conc.