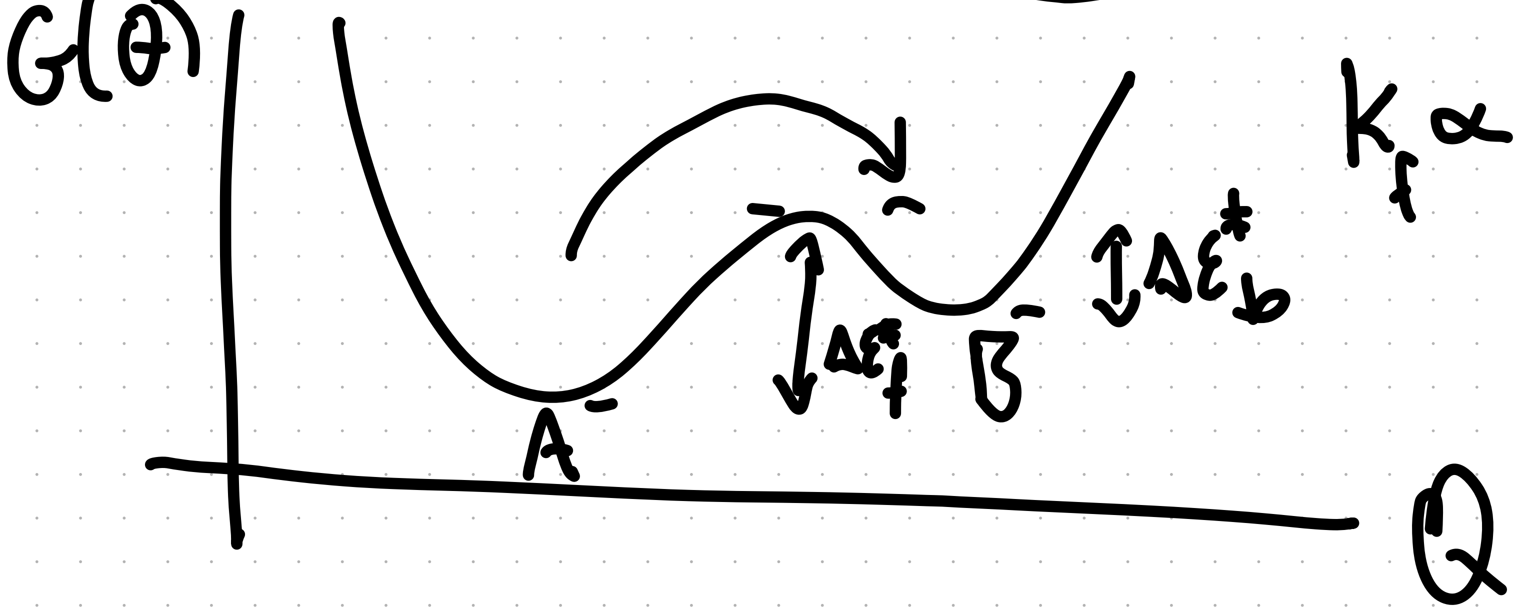
Non-equilibrium Pt 3



$$k_f \propto e^{-\Delta E_f^{\ddagger}/k_B T}$$

M - - - - N

Q

State A

MN

State B

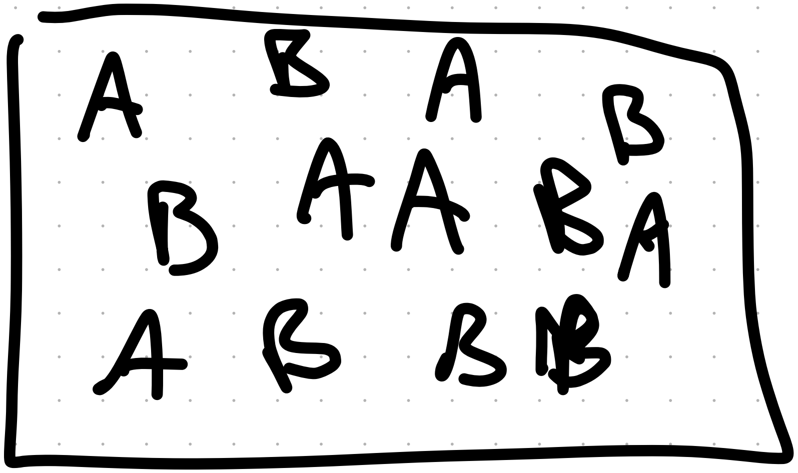
$$K_{eq} = k_f / k_b$$

$$k_f \propto e^{-(G_A - G^{\ddagger})/k_B T}$$

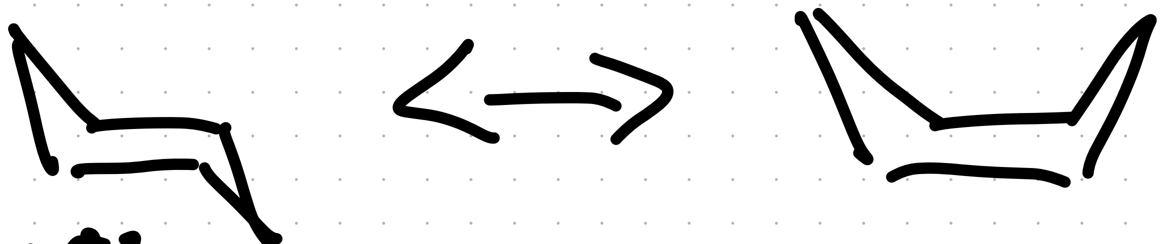
$$k_b \propto e^{-(G_B - G^{\ddagger})/k_B T}$$

$$k_f / k_B \propto e^{-\beta \Delta G}$$

$$K = -k_B T \ln \Delta G$$



$$A \underset{k_b}{\overset{k_f}{\rightleftharpoons}} B$$



99.99%

$$A+B=N$$

$$\frac{dA}{dt} = B k_b - A k_f$$

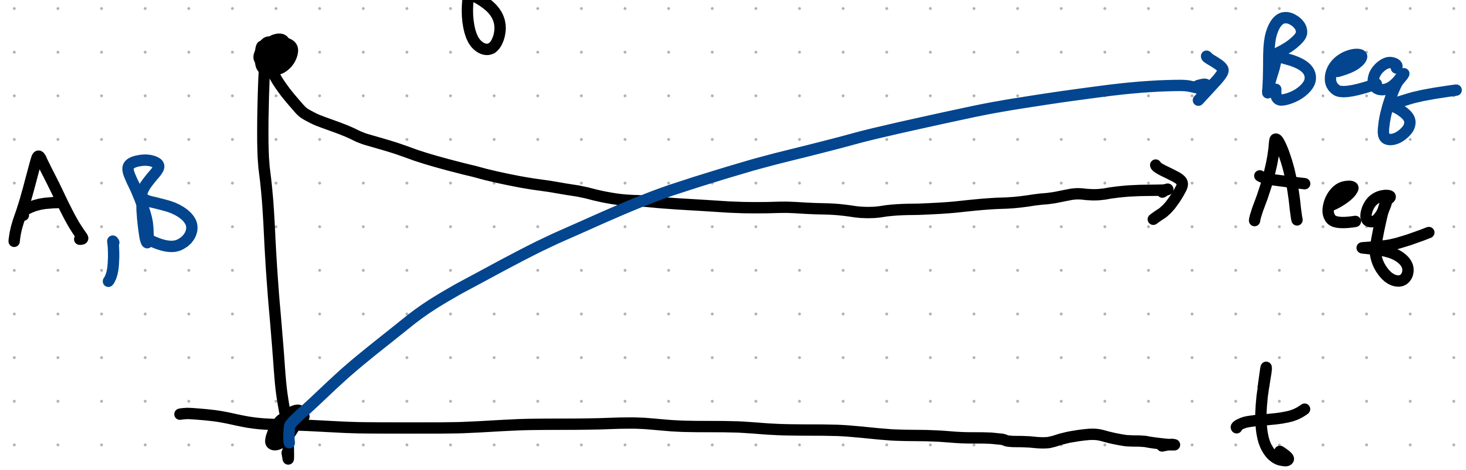
$$\frac{dB}{dt} = A k_f - B k_b$$

$$A + B = N$$

$$A_{eq} + B_{eq} = N$$

$$A = A_{eq} + C \qquad C = \delta A = -\delta B$$

$$B = B_{eq} - C$$



Detailed Balance

$$A_{eq} k_f = B_{eq} k_b$$

$$\left[\frac{dA_{eq}}{dt} = \frac{dB_{eq}}{dt} = 0 \right]$$

$$\frac{dA}{dt} = \frac{d(\cancel{A_{eq}} + c)}{dt} = -k_f(A_{eq} + c) + k_b(B_{eq} - c)$$

$$\frac{dB}{dt} = \frac{d(\cancel{B_{eq}} - c)}{dt} = k_f(A_{eq} + c) - k_b(B_{eq} - c)$$

$$2\frac{dC}{dt} = 2k_b(\underline{B_{eq}} - C)$$

$$-2k_f(\underline{A_{eq}} + C)$$

$$[\, k_b B_{eq} = k_f A_{eq} \,]$$

$$= -2(k_b + k_f)C$$

$$C(t) = C(0)\,e^{-(k_f+k_b)t}$$

$$\tau_{rxn} = \frac{1}{k_f + k_b}$$

Macrosopically, deviation from equilibrium goes away

Var(c) ?

Onsager Regression Hypothesis (1931)

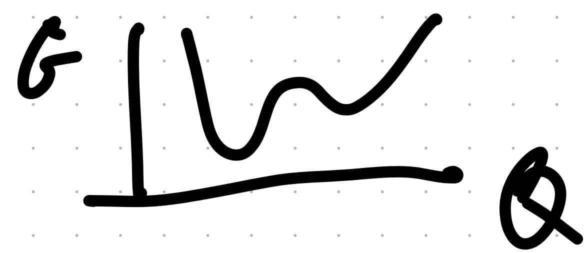
Small fluctuations at equilibrium
microscopic

decay on average the same way as

macroscopic non-equilibrium dev.

$$\langle C(t)C(t')\rangle = \underbrace{\langle C^2\rangle_{eq}}_{var(C)}\, e^{-(k_f+k_b)|t-t'|}$$

Why Var $C \neq 0$



$$\frac{dC}{dt} = -(k_1+k_2)C + \delta F(t)$$

F "force"

maybe $\sim -\partial G/\partial Q$

$$\langle \delta F(t)\,\delta F(t')\rangle = 2(k_1+k_2)\langle C^2\rangle_{eq} \times \delta(t-t')$$

A_1
A_2
A_3
$\vdots$
A_N

$A_1 \rightarrow A_2$

$A_1 \rightarrow A_j$

$\vdots$

$A_m \underset{k_b^i}{\overset{k_f^i}{\rightleftharpoons}} A_N$

$$\frac{dA_i}{dt} = -\sum k_{ij}^f A_i + \sum k_{ij}^b A_j$$

$$\frac{dA}{dt} = -k_f A + k_b B$$

$$\frac{dA}{dt} = -WA + \delta F$$

A vector concentrations

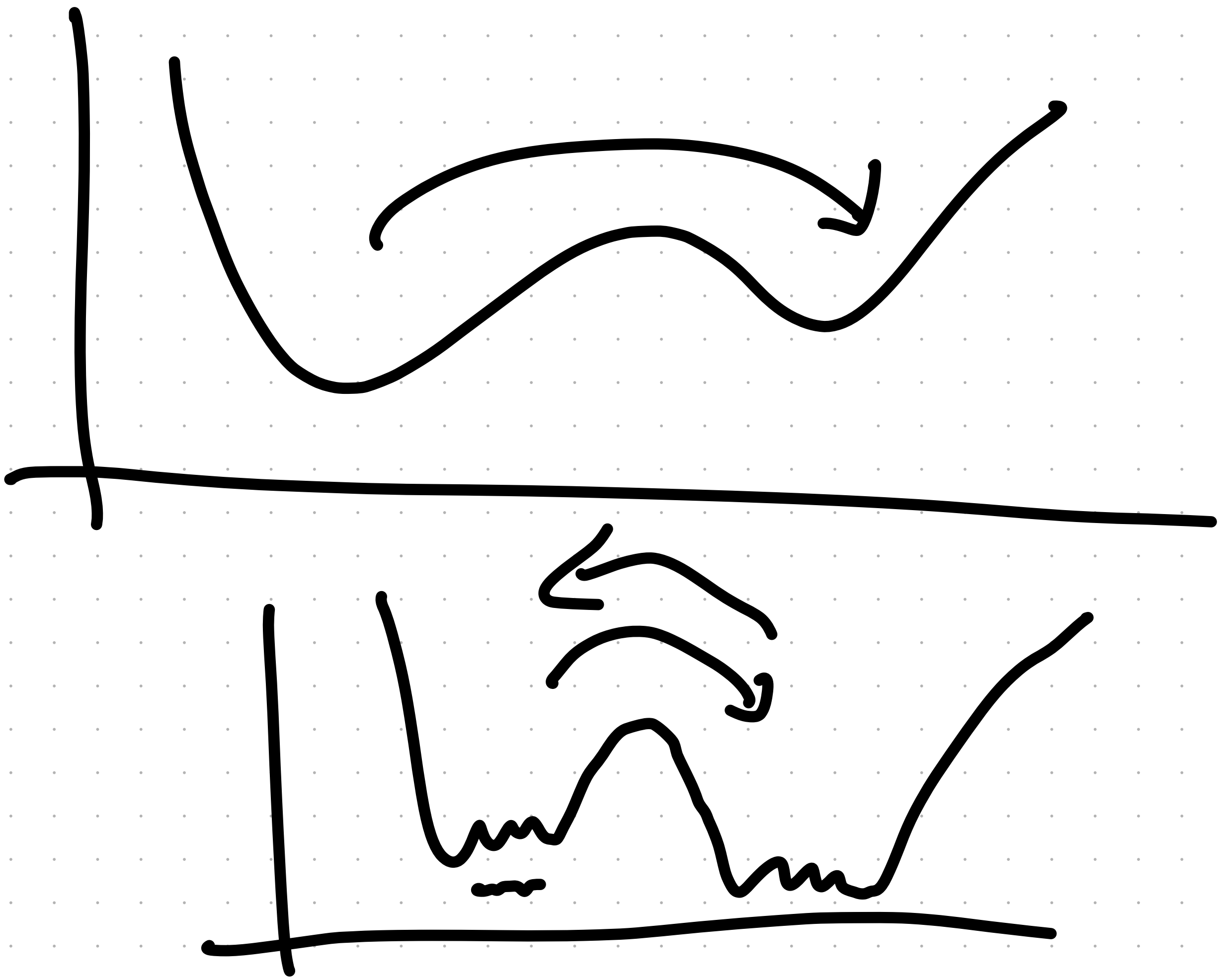
W rate matrix

condition like $\sum$ columns $= 1$

$$A(t) = \underline{e^{-Wt}} \cdot A(0)$$

dominated by largest eigen

$$A(t) \sim e^{-\lambda_1 t} A(0)$$



Van-kampen