Kinetics & Chemical Rates

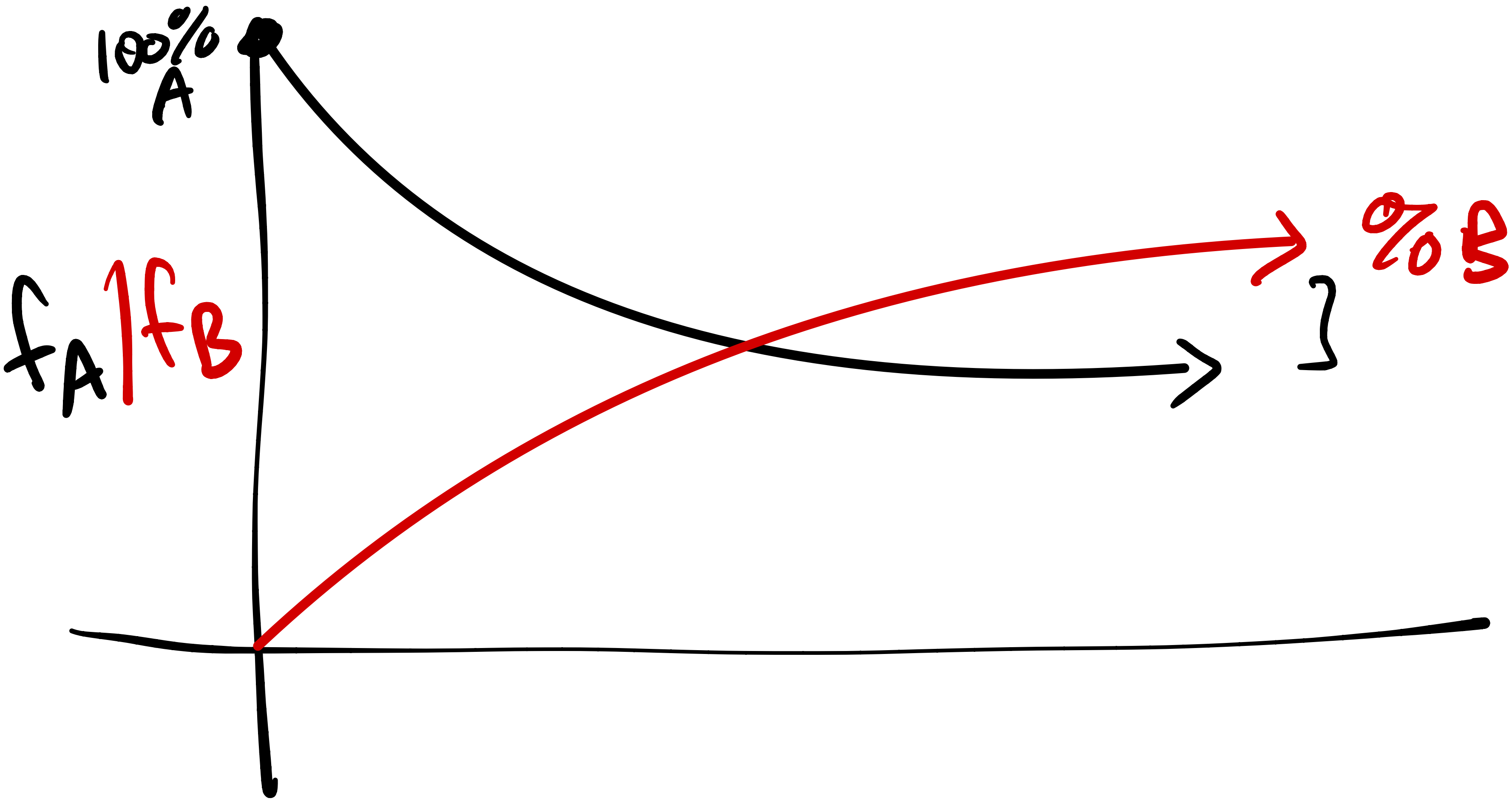
Consider

$$A \rightleftarrows B$$

Chemical equilibrium

Detailed balance:

$$\#A \cdot r_{A \to B} = \#B \, r_{B \to A}$$



$$[A]_{eq}\, k_{A\to B} = [B]_{eq}\, k_{B\to A}$$

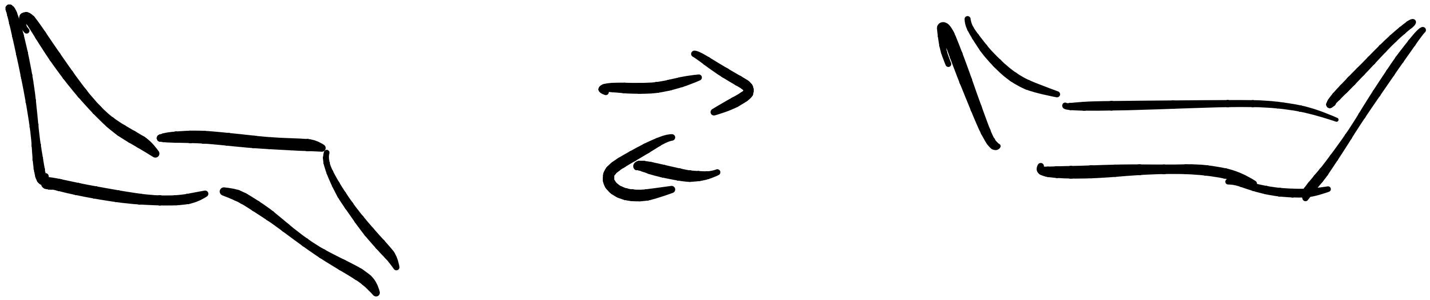
$$K_{eq} = \frac{[B]_{eq}}{[A]_{eq}} = \frac{k_{A\to B}}{k_{B\to A}}$$

$$\text{fraction } A = \frac{\# A}{\text{total MC}} = \frac{A/V}{(A+B)/V}$$

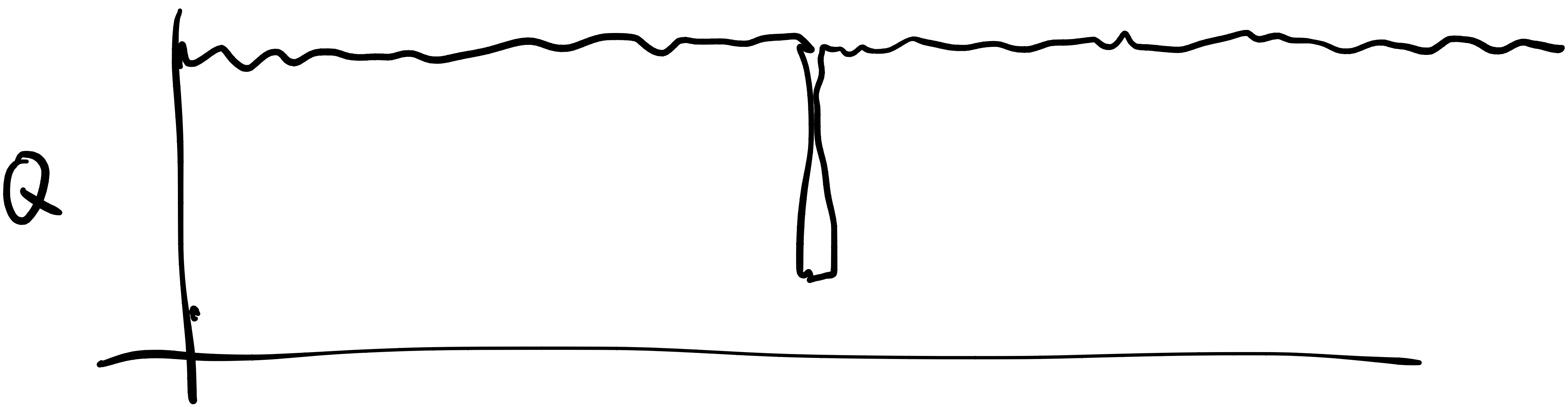
$$= \frac{[A]}{[A]+[B]} = \boxed{\frac{1}{1+\frac{[B]}{[A]}}} \underset{@eq}{=} \frac{1}{1+K_{eq}}$$

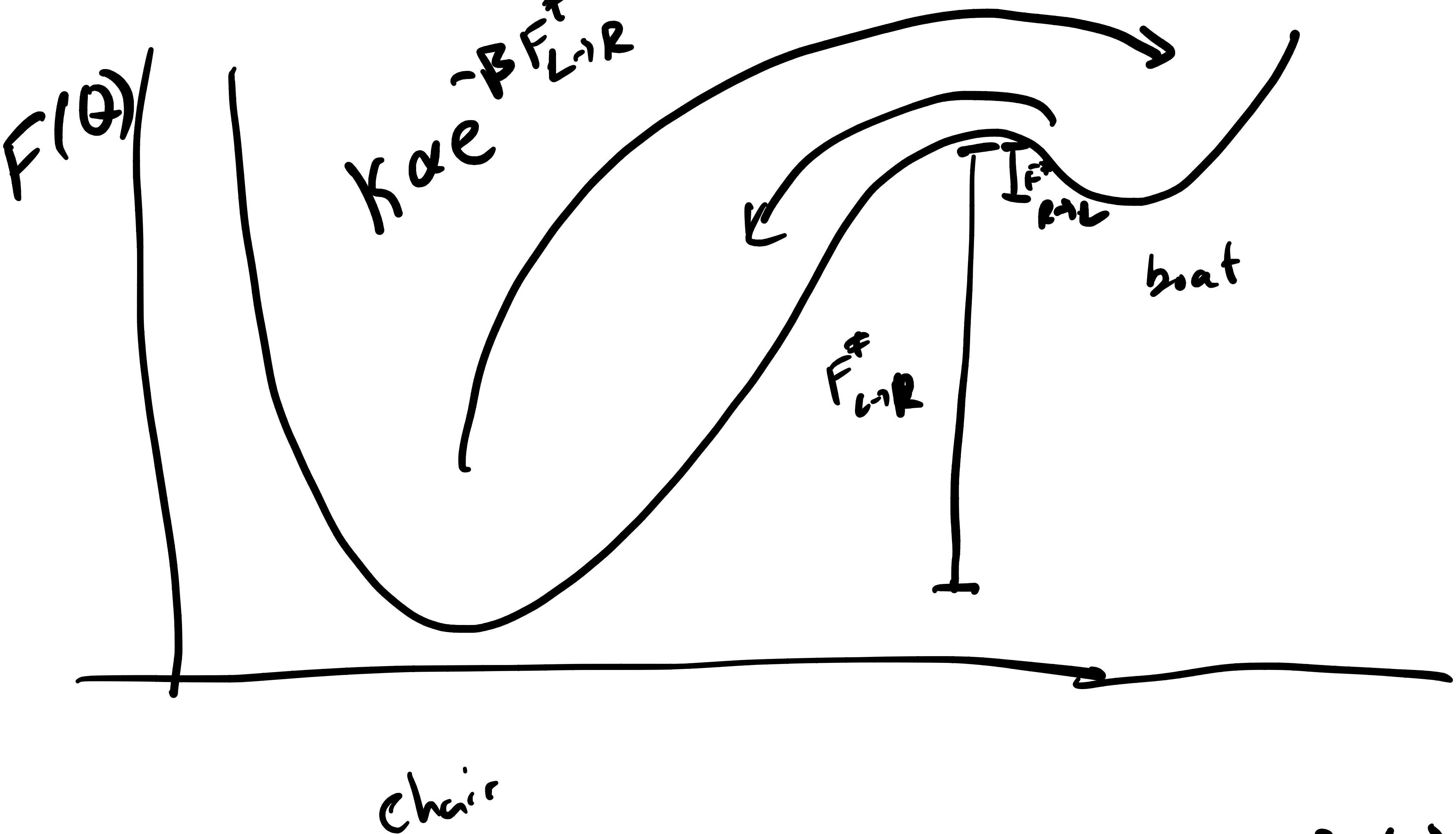
$$\text{frac } B = 1 - \frac{1}{1+K_{eq}} = \frac{K_{eq}}{1+K_{eq}} = \frac{1}{1+{}^{1}/_{K_{eq}}}$$

$$\text{frac } B(t) = \frac{1}{1+{}^{[A]}/_{[B]}}$$



99.99% @ Eq





$$F(Q') = -k_B T \log \int dx\, \delta(Q(x) - Q')\, e^{-\beta U(x)}$$

$$K_{eq} = \frac{k_f}{k_b} \propto \frac{e^{-\beta[F(Q^{\ddagger}) - F(Q_L)]}}{e^{-\beta[F(Q^{\ddagger}) - F(Q_R)]}}$$

$$= \propto e^{-\beta[\Delta F]}$$

const N, V, T

$$\Delta F = -k_B T \ln(K_{eq}) \quad + \text{const}$$

$$N, P, T \left[\Delta G = -k_B T \ln(K_{eq}) \right]$$


reaction coordinate
Q

$$A \rightleftarrows B$$

$\# A_{beg} - C$ $\quad\quad$ $\# B + C$

$$C = [A] - [A]_{eq} = \delta A = -\delta B$$

$$[A] + [B] = \text{const}$$

$$\frac{d[A]}{dt} = \frac{d[\cancel{A_{eq}} + C]}{dt} = k_{B\to A}[B] - k_{A\to B}[A]$$

$$\frac{d[B]}{dt} = \frac{d[\cancel{B_{eq}} - C]}{dt} = k_{A\to B}[A] - k_{B\to A}[B]$$

$$\frac{d[A]}{dt} = \frac{d[\cancel{A_{eq}} + C]}{dt} = k_{B\to A}[B] - k_{A\to B}[A]$$

$$\frac{d[B]}{dt} = \frac{d[\cancel{B_{eq}} - C]}{dt} = k_{A\to B}[A] - k_{B\to A}[B]$$

subtract

$$2\frac{dC}{dt} = 2\left[k_{B\to A}\underbrace{[B]}_{[B_{eq}-C]} - k_{A\to B}\underbrace{[A]}_{[A_{eq}+C]}\right]$$

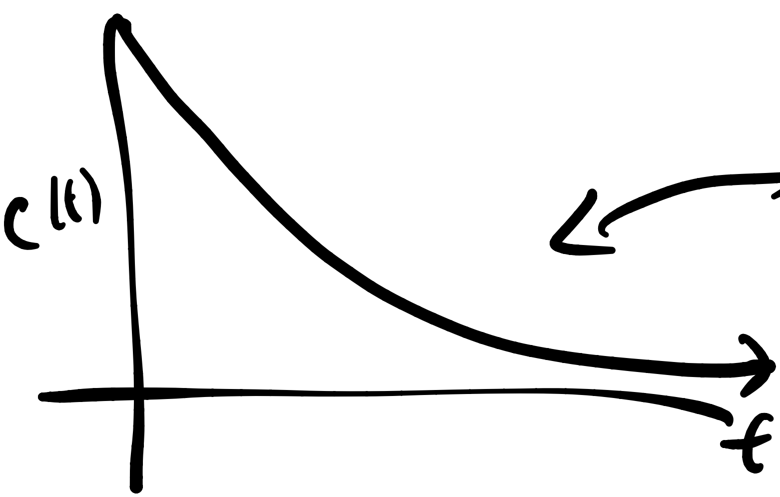
$$k_{B\to A}[B_{eq}] = k_{A\to B}[A_{eq}]$$

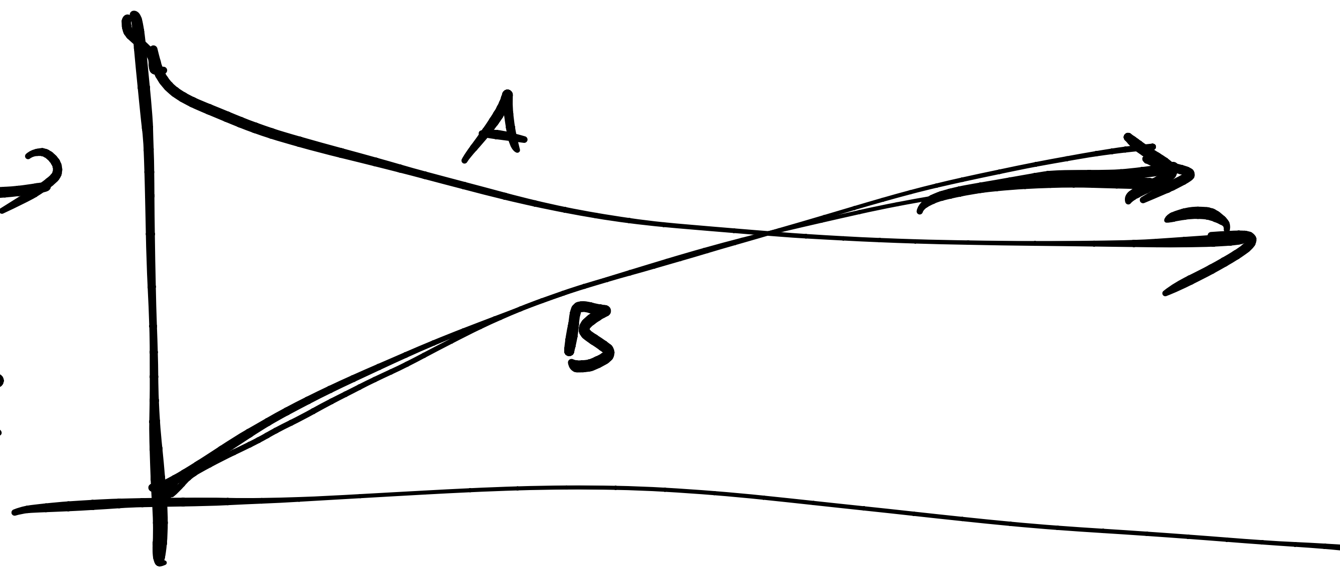
$$= -2(k_{B\to A} + k_{A\to B})C$$

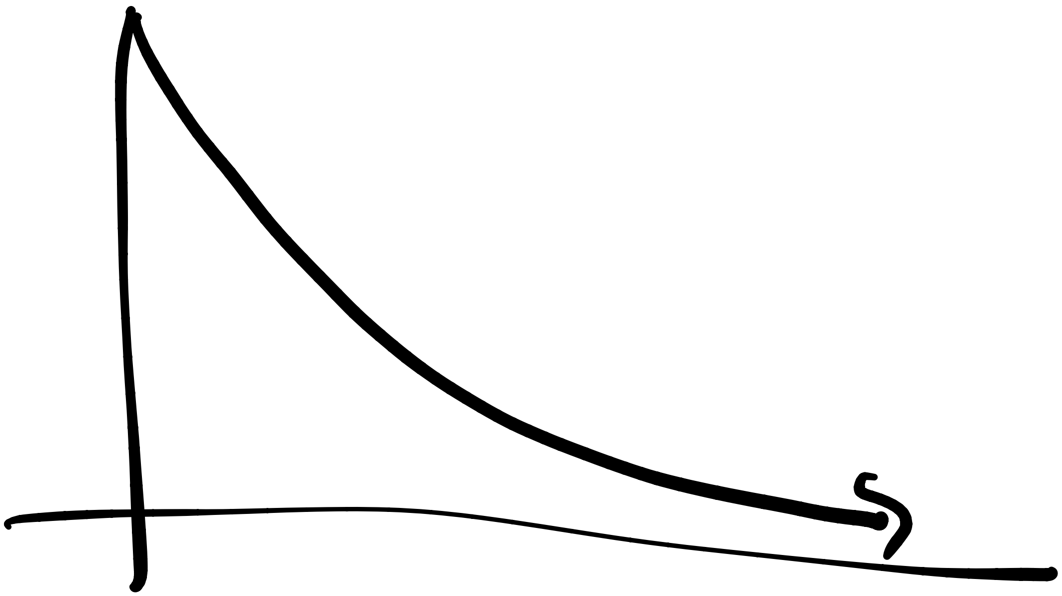
$$\frac{dC}{dt} = -(k_{A\to B} + k_{B\to A})C$$

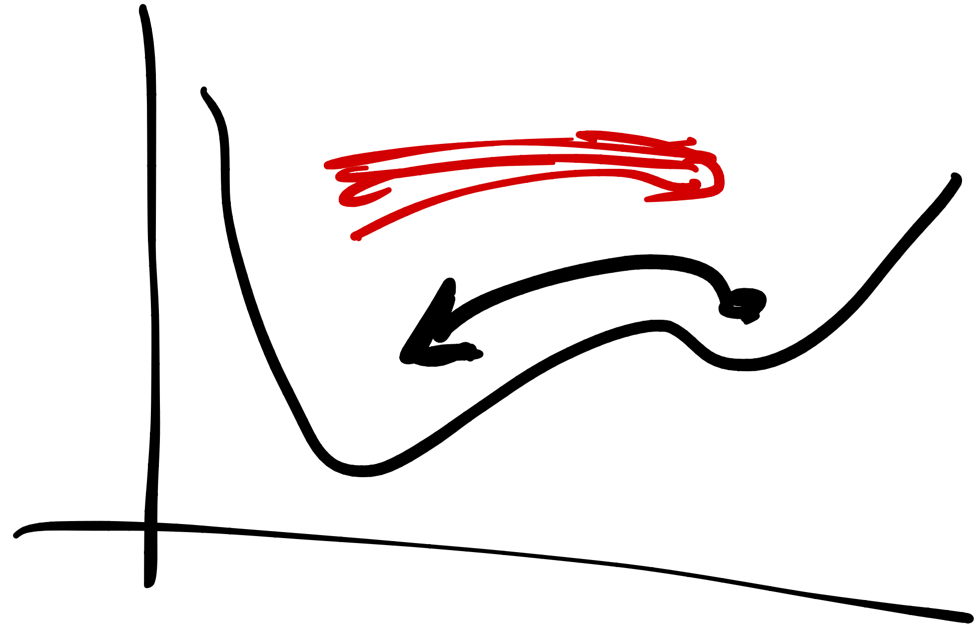
$$C(t) = C(0)\,e^{-(k_{A\to B}+k_{B\to A})t}$$

$$1/(k_{A\to B} + k_{B\to A}) = \tau_{rxn}$$

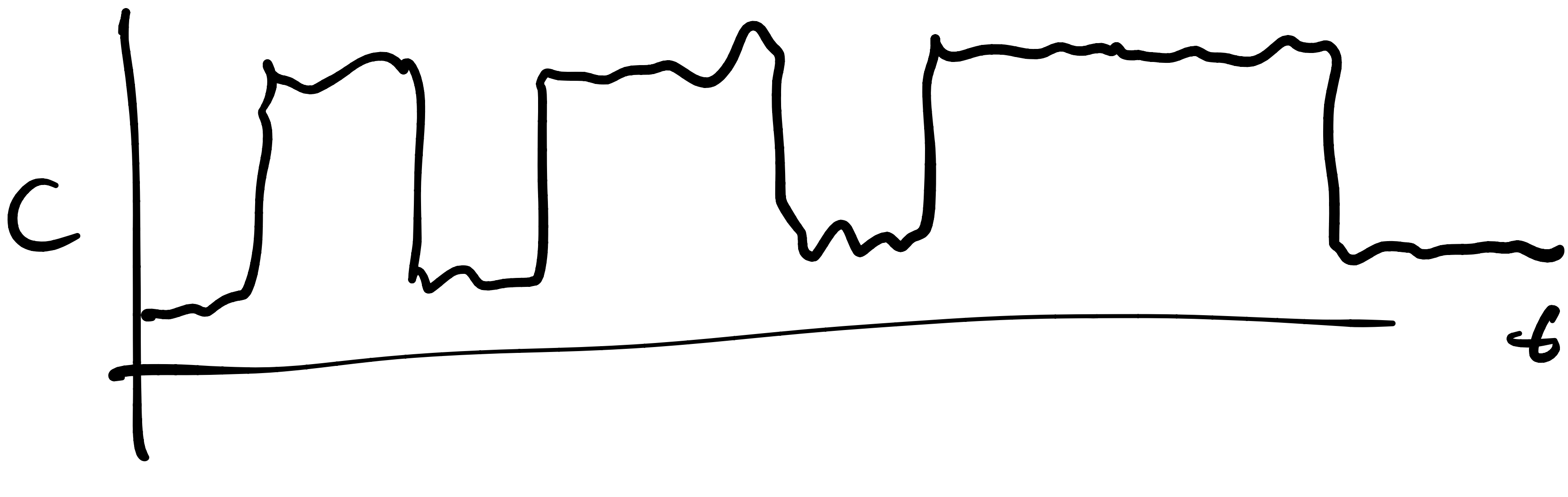






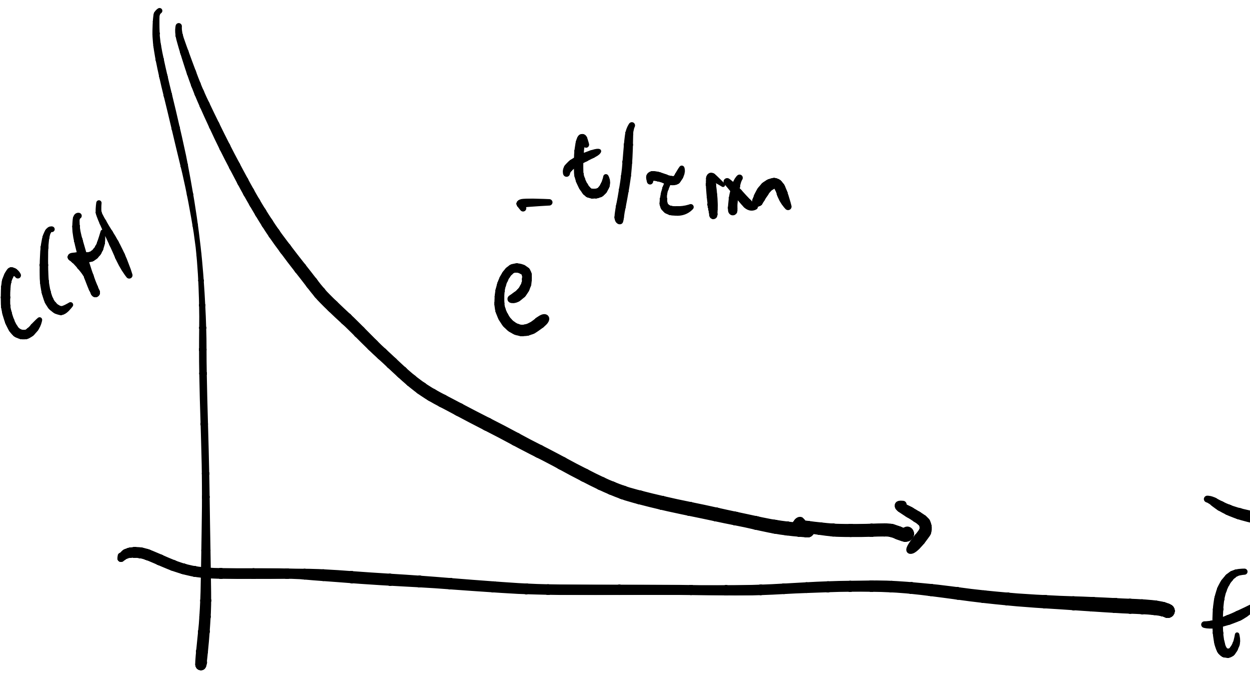


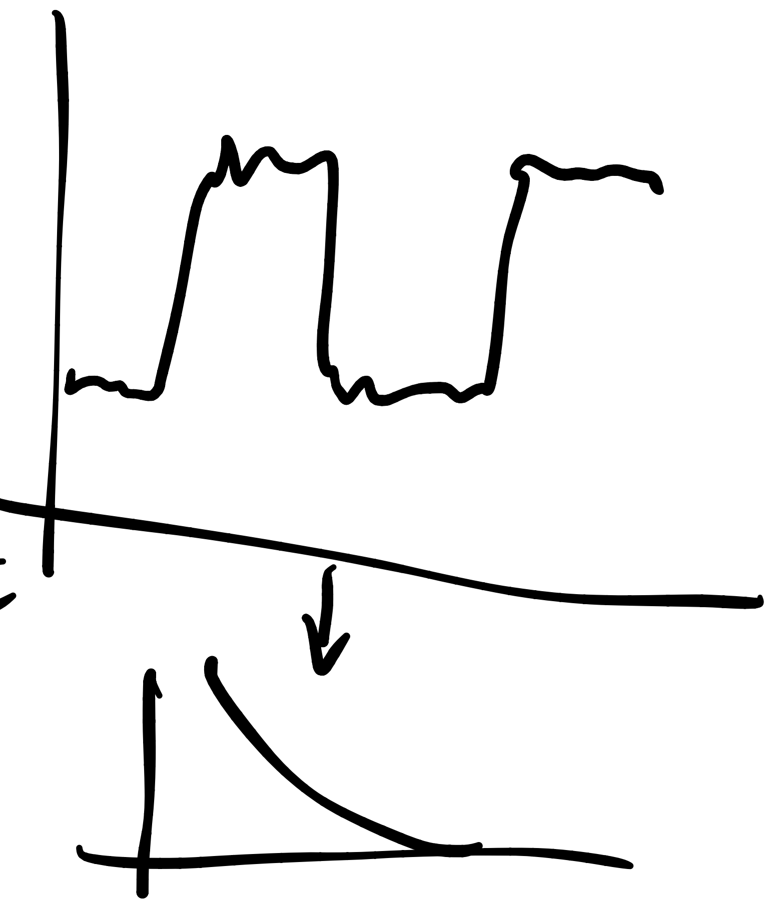
$$\langle C(t)C(t')\rangle = \langle c^2\rangle_{eq}\, e^{-|t-t'|/\tau}$$



Onsager Regression Hypothesis (1931)

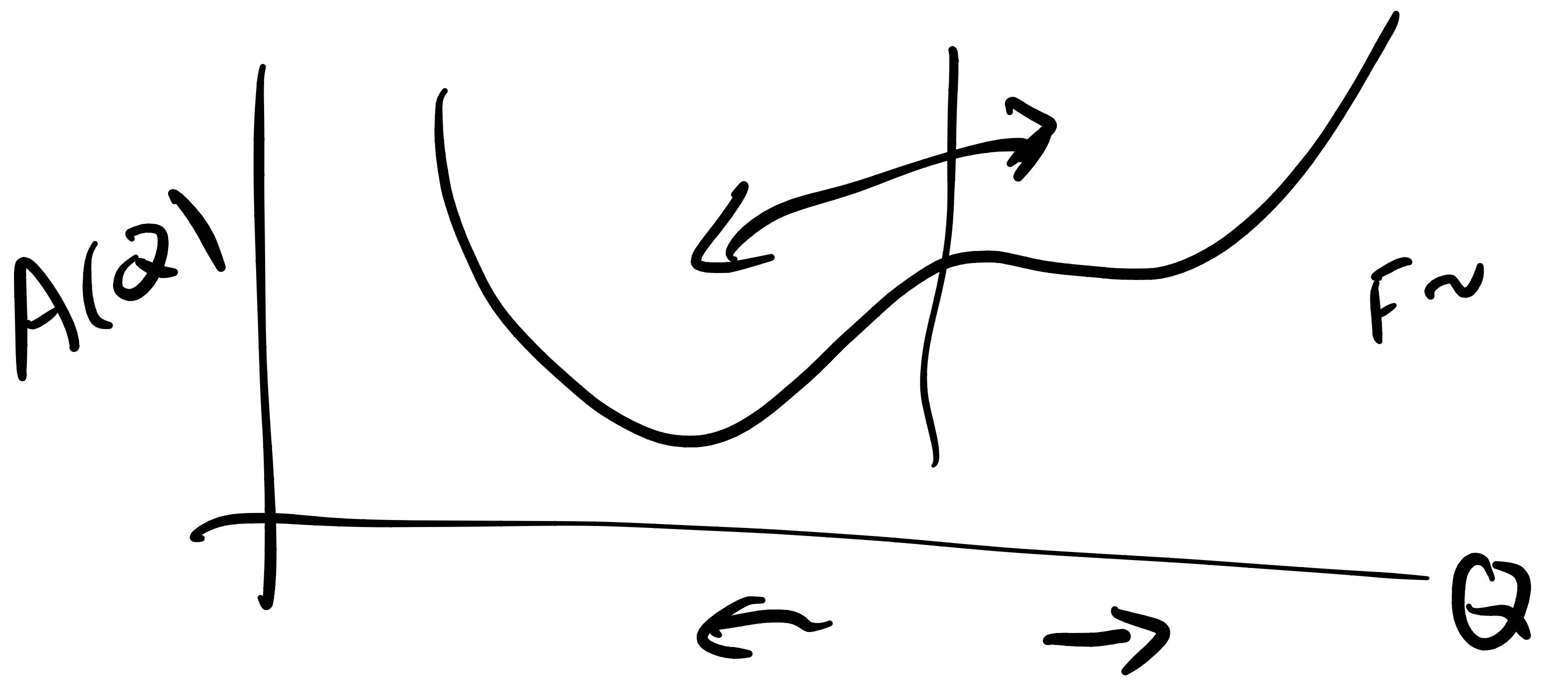
fluctuations relax at the same rate as macroscopic deviations from Eq





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

$$\frac{dC}{dt} = -(k_f + k_b)C + \text{"}\delta F_{random}\text{"}$$



$$F \sim -\frac{dA}{dQ}$$

What is C from microscopic perspective

$$H_A[Q] = \begin{cases} 1 & Q < Q^{\ddagger} \\ 0 & Q \geq Q^{\ddagger} \end{cases}$$

$$f_A = \int dQ \, \underset{\uparrow \langle H_A \rangle}{H_A[Q]} \frac{e^{-\beta F(Q)}}{Z} \equiv \chi_A$$

$$\langle H_A^2 \rangle \overset{?}{=} \langle H_A \rangle = \chi_A$$

$$\mathrm{Var}_A = \langle \delta H_A^2 \rangle = \langle H_A^2 \rangle - \langle H_A \rangle^2$$

$$= \chi_A - \chi_A^2 = \chi_A(1 - \chi_A)$$

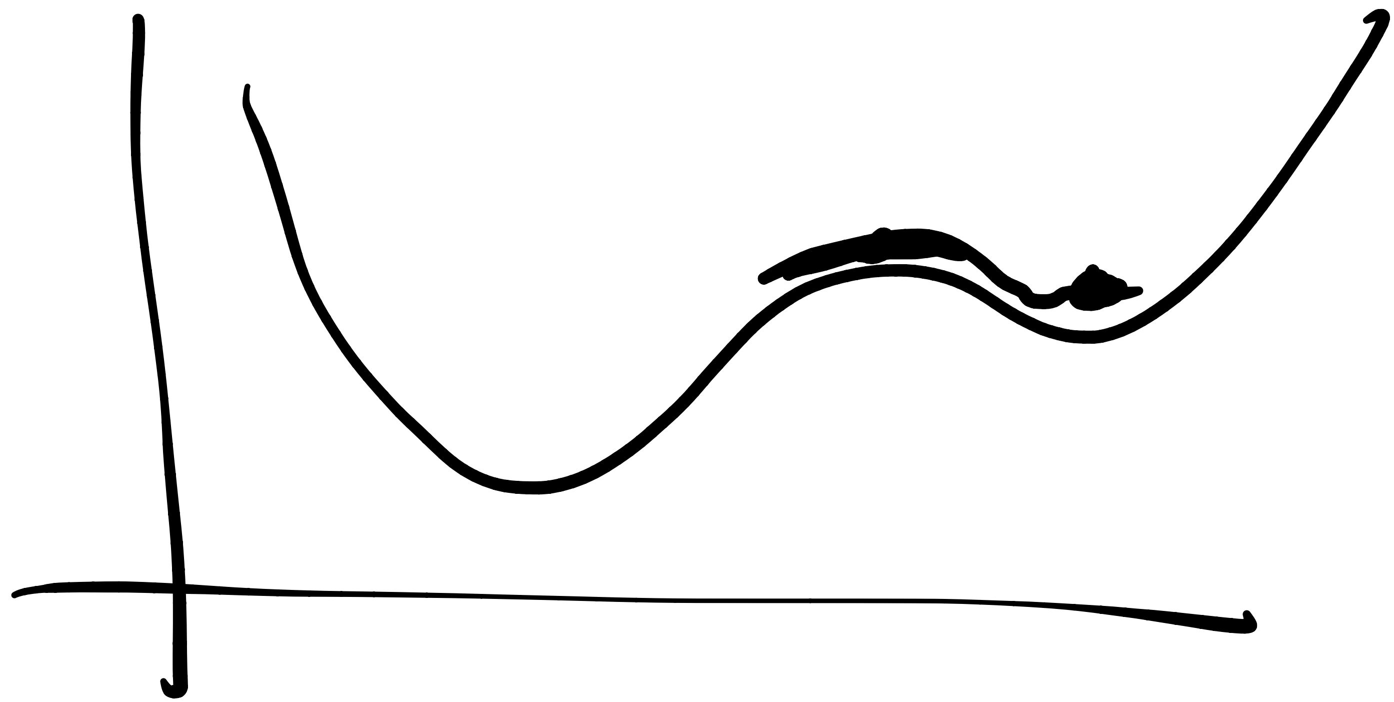
$$= \chi_A \chi_B$$

Var C

$$@\,Eq \quad = \frac{1}{1 + K_{eq}} \cdot \frac{1}{1 + 1/K_{eq}}$$

$$= K_{eq} / (1 + K_{eq})^2$$

Transition State Theory [Chandler]

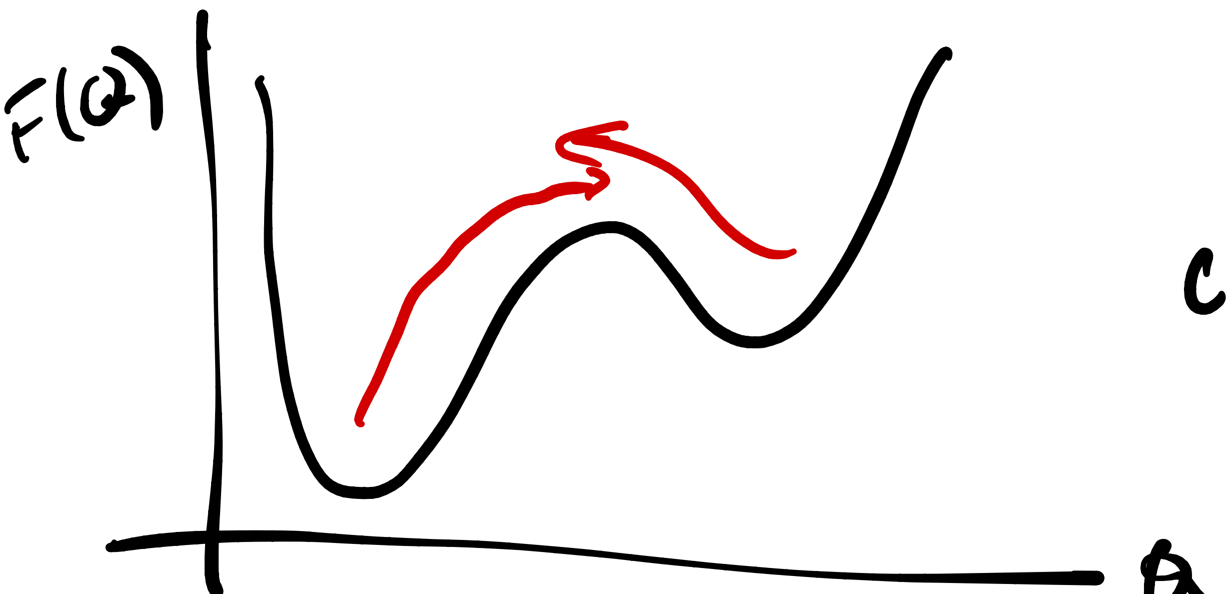


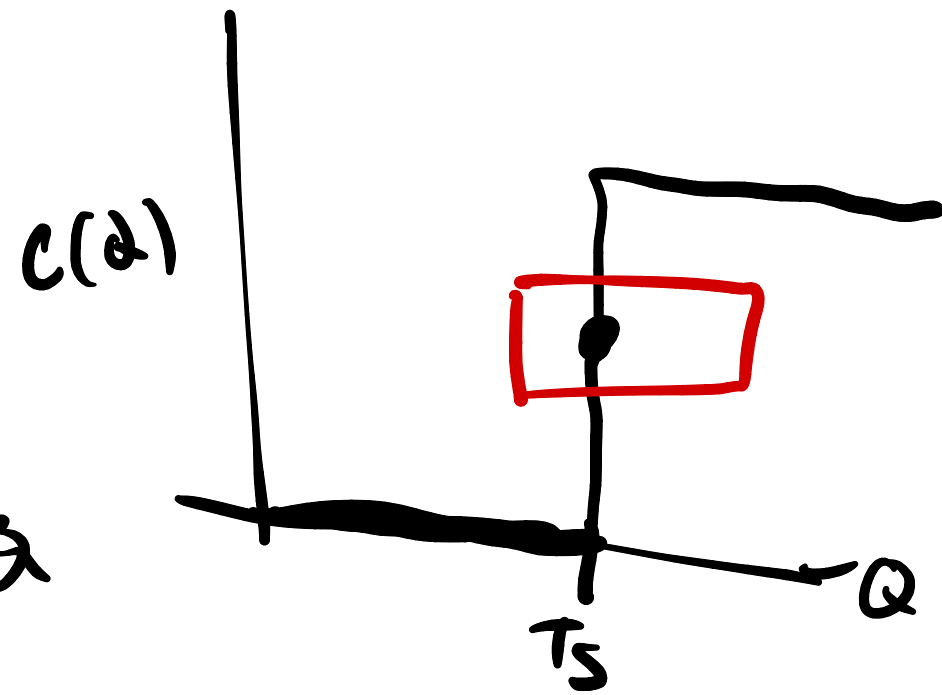
$$k_f^{TST\,A\to B} = \frac{1}{\chi_A}\langle \dot{Q}\; \delta(Q(0)-Q^{\ddagger})\; \delta H_B(Q(t))\rangle$$

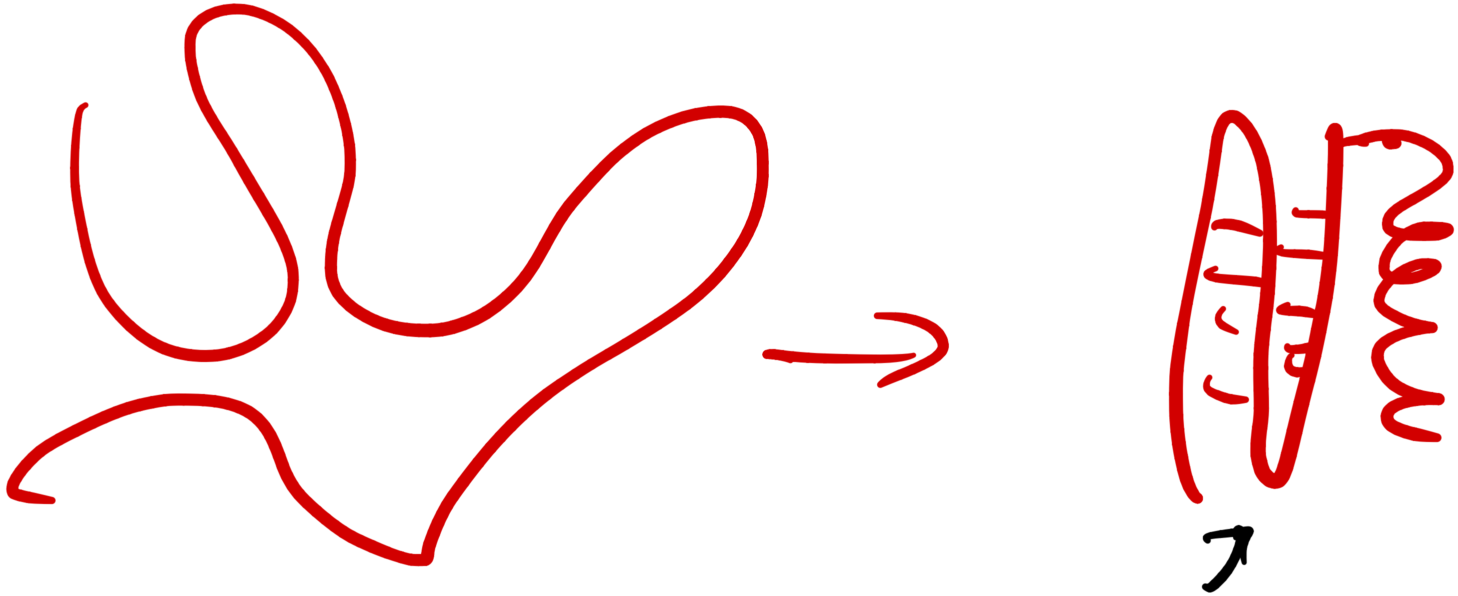
in state B after some time

fraction of trajectories that start at Q^* and end up in B before A

Committor $C(Q^*)$

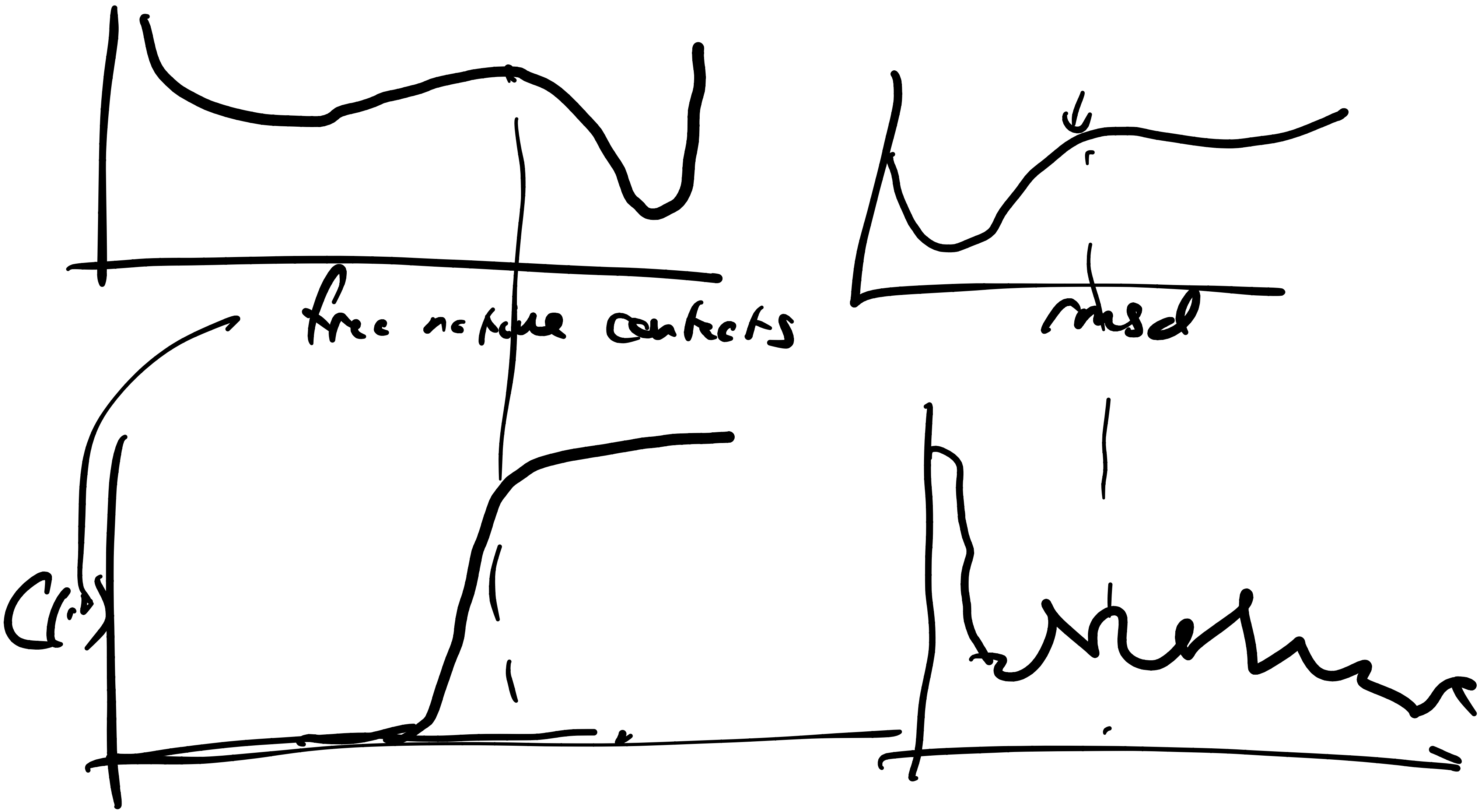


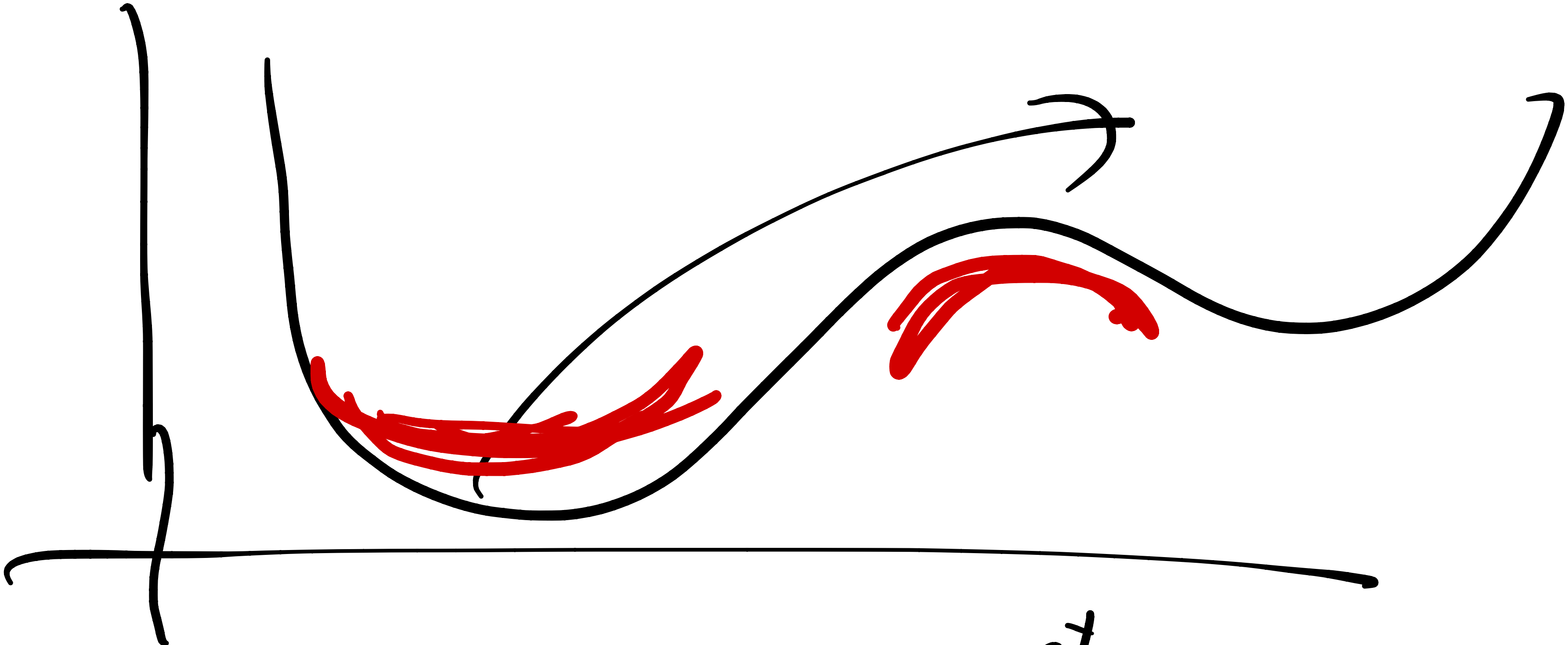




Q_1 = RMSD to native struct

Q_2 = fraction of native contacts


free native contacts
rmsd
C(r)



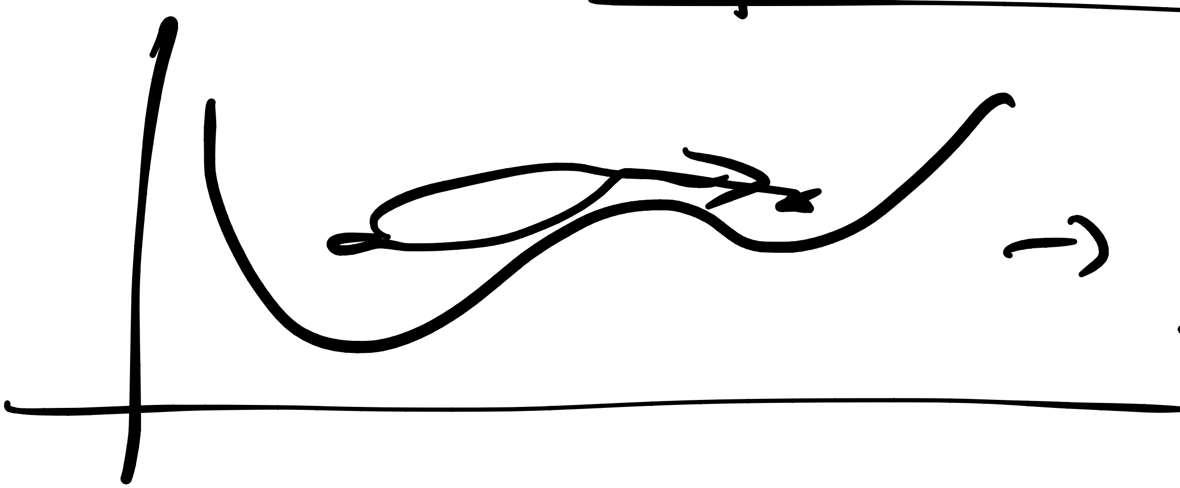
$$k_{A\to B} \propto e^{-\beta E^{\ddagger}}$$

Fokker–Planck Equation
Smoluchowski

$e^{-\beta F(Q)}$

$\uparrow$

$P(Q)$



$\rightarrow P(Q)$