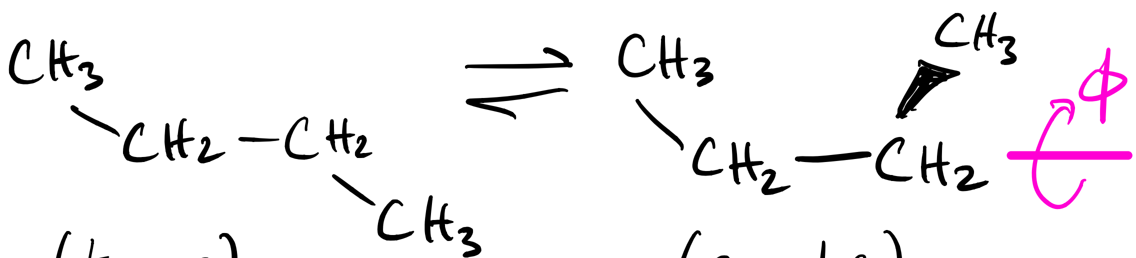
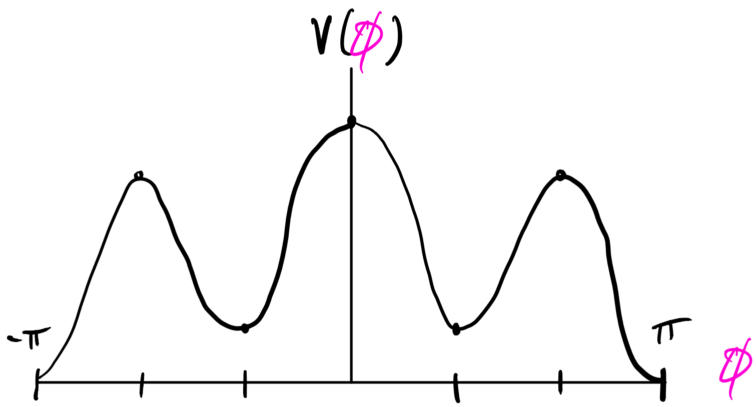
Lecture 15

Recall from last lecture...

A crash course in a few aspects of dynamics of chemical systems, i.e. kinetics.



(trans) (gauche)

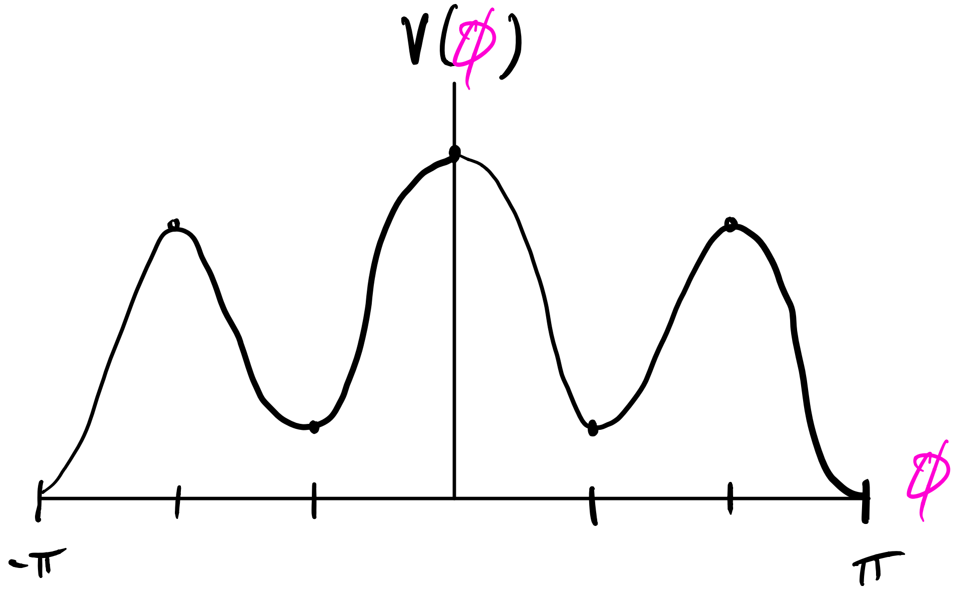


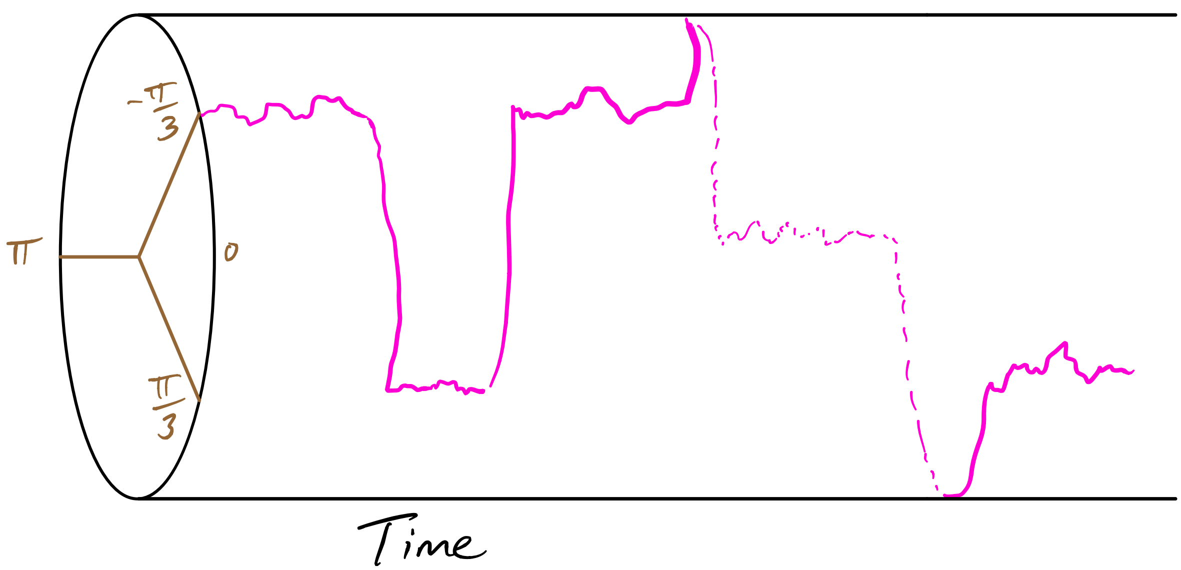
$$P(\phi) \propto e^{-\beta V(\phi)}$$

$$\Rightarrow \boxed{V(\phi) = -k_B T \ln P(\phi)}$$

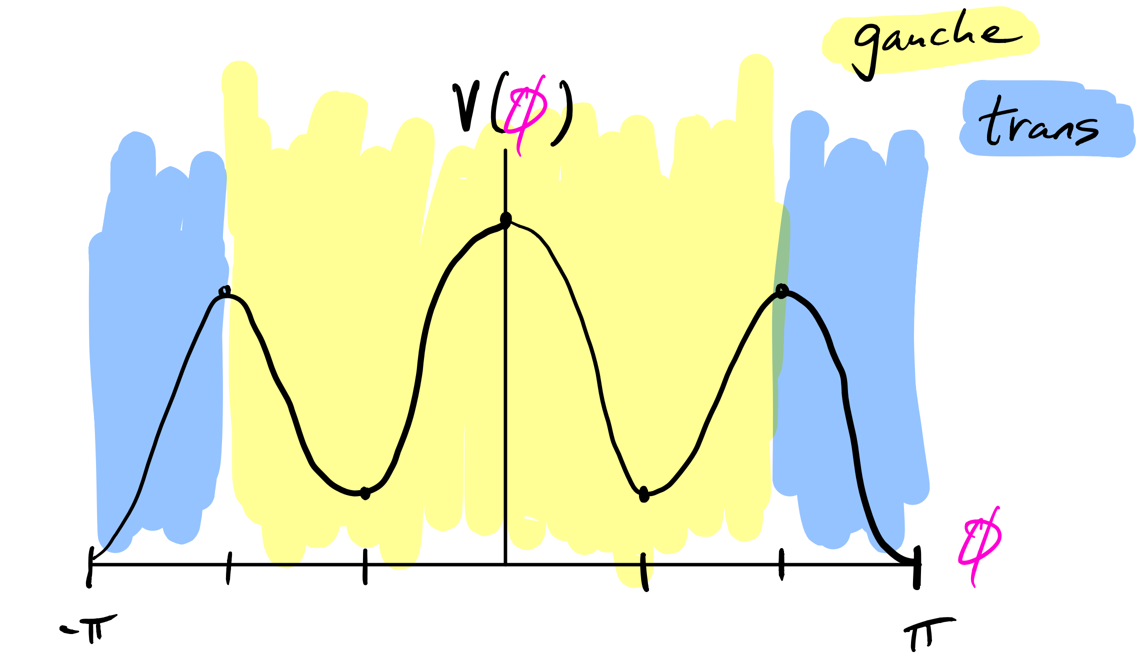
A free energy is actually a log probability for a degree of freedom you intend to measure and/or control when the other degrees of freedom will be averaged over.

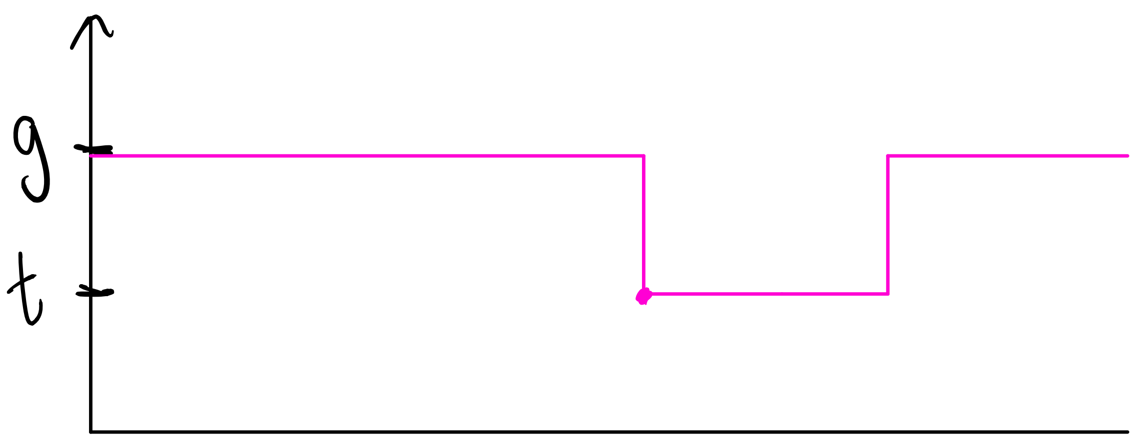
An energy function tells you how you will move but it is not so simple with a free energy. Now $V(\phi)$ tells about the mean force.





By specifying only ϕ, we are already clumping together microstates. Let's take this a step further...





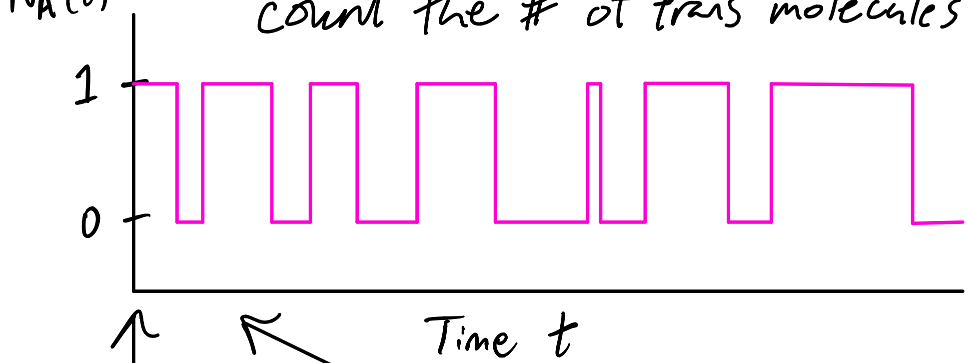
Let's develop a statistical model that can randomly generate trajectories for our

"coarse-grained two-state kinetics"

$A \rightleftharpoons B$

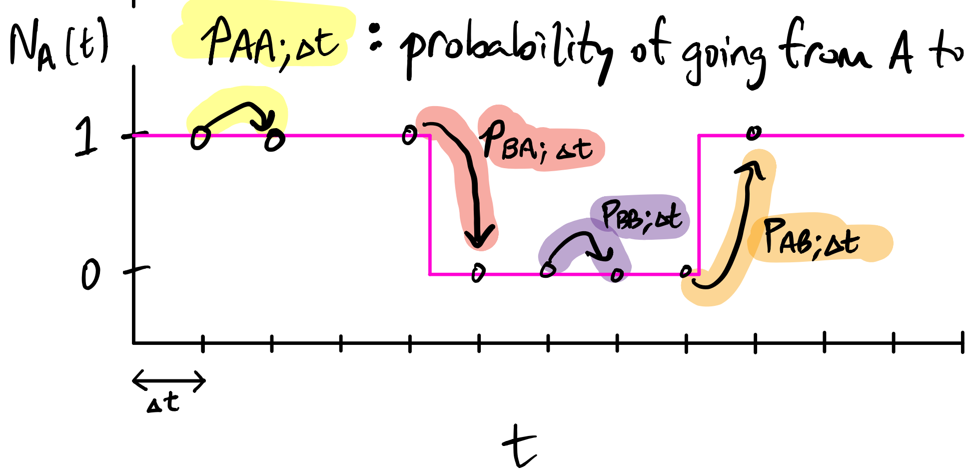
p_A: probability of A (trans)
p_B: probability of B (gauche)

Look at a single butane molecule & count the # of trans molecules (either 0 or 1)



zoom in

$P_{AA;\Delta t}$: probability of going from A to A in time Δt.



"Markov approximation: Only my current state impacts the probability of the next event. The past history has become irrelevant."

Start in A.

Probability of being in A at Δt? $p_{AA;\Delta t}$

Probability of being in B at Δt? $p_{BA;\Delta t}$

Probability of being in some state, A <u>or</u> B, at Δt?

$$1 = p_{AA;\Delta t} + p_{BA;\Delta t}$$

(not all parameters can be tuned independently)

Start in B...

Probability of being in A at Δt? $p_{AB;\Delta t}$

Probability of being in B at Δt? $p_{BB;\Delta t}$

And $1 = p_{AB;\Delta t} + p_{BB;\Delta t}$

Start in a mixed state:

Initial probability p_A of starting in A and p_B of starting in B.

$$p_A(\Delta t) = \text{start in A \& stay there} + \text{start in B \& move to A}$$

$$= p_A(0)\, p_{AA;\Delta t} + p_B(0)\, p_{AB;\Delta t}$$

$$\begin{pmatrix} p_A(\Delta t) \\ p_B(\Delta t) \end{pmatrix} = \underbrace{\begin{pmatrix} p_{AA;\Delta t} & p_{AB;\Delta t} \\ p_{BA;\Delta t} & p_{BB;\Delta t} \end{pmatrix}}_{M} \begin{pmatrix} p_A(0) \\ p_B(0) \end{pmatrix}$$

$$t \xrightarrow{M} t+\Delta t$$

What is the right Δt?

Δt may be more of an artifact & you want to imagine being able to measure the state infinitely quickly, in which case $\Delta t \to 0$.

$$\frac{d}{dt}\begin{pmatrix} p_A(t) \\ p_B(t) \end{pmatrix} = \lim_{\Delta t \to 0} \frac{1}{\Delta t}\left[\begin{pmatrix} p_A(t+\Delta t) \\ p_B(t+\Delta t) \end{pmatrix} - \begin{pmatrix} p_A(t) \\ p_B(t) \end{pmatrix}\right]$$

$$= \lim_{\Delta t \to 0} \frac{1}{\Delta t}\left[\begin{pmatrix} p_{AA;\Delta t} & p_{AB;\Delta t} \\ p_{BA;\Delta t} & p_{BB;\Delta t} \end{pmatrix} - \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}\right]\begin{pmatrix} p_A(t) \\ p_B(t) \end{pmatrix}$$

$$= \lim_{\Delta t \to 0} \begin{pmatrix} \frac{p_{AA;\Delta t} - 1}{\Delta t} & \frac{p_{AB;\Delta t}}{\Delta t} \\ \frac{p_{BA;\Delta t}}{\Delta t} & \frac{p_{BB;\Delta t} - 1}{\Delta t} \end{pmatrix}\begin{pmatrix} p_A(t) \\ p_B(t) \end{pmatrix}$$

$$\lim_{\Delta t \to 0} \frac{p_{AB;\Delta t}}{\Delta t} = k_{AB}$$ Rate constant

$$\lim_{\Delta t \to 0} \frac{p_{BA;\Delta t}}{\Delta t} = k_{BA}$$

Probability per unit time of transitioning from B to A in an infinitesimal moment of time.

Diagonal matrix element?

Remember
$1 = p_{AA;\Delta t} + p_{BA;\Delta t}$

$$\lim_{\Delta t \to 0} \frac{p_{AA;\Delta t} - 1}{\Delta t} = \lim_{\Delta t \to 0} \frac{(1 - p_{BA;\Delta t}) - 1}{\Delta t} = -k_{BA}$$

$$\frac{d}{dt}\begin{pmatrix} p_A(t) \\ p_B(t) \end{pmatrix} = \begin{pmatrix} -k_{BA} & k_{AB} \\ k_{BA} & -k_{AB} \end{pmatrix}\begin{pmatrix} p_A(t) \\ p_B(t) \end{pmatrix}$$

("A continuous-time master equation")

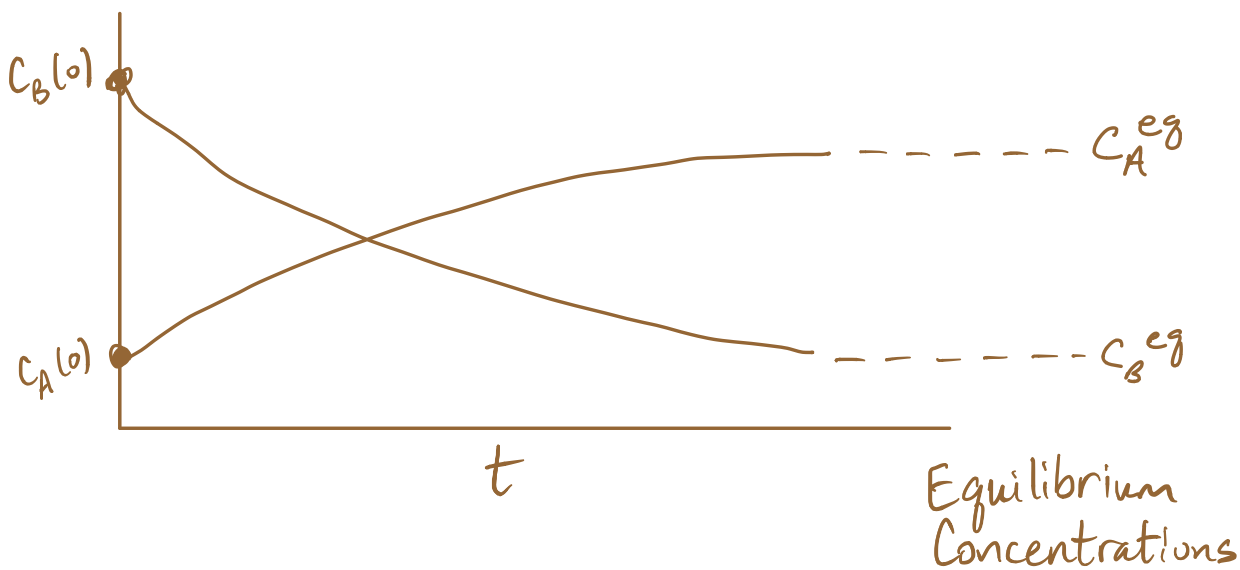
What if I have a lot of butane, not just a single molecule?

Concentration of A $\rightarrow C_A = N * p_A$

total number of butane molecules

$$\Rightarrow \frac{d}{dt}\begin{pmatrix} c_A(t) \\ c_B(t) \end{pmatrix} = \begin{pmatrix} -k_{BA} & k_{AB} \\ k_{BA} & -k_{AB} \end{pmatrix}\begin{pmatrix} c_A(t) \\ c_B(t) \end{pmatrix}$$

Remember, A is trans.



$$\underbrace{\frac{dc_A}{dt}}_{\text{slope is a function of}}(c_A, c_B) = k_{AB}\, c_B(t) - k_{BA}\, c_A(t) \rightarrow 0$$

at equil.

$$\Rightarrow 0 = \underbrace{k_{AB}\, c_B^{eq}}_{\text{Rate of producing A}} - \underbrace{k_{BA}\, c_A^{eq}}_{\text{Rate of losing A (by making B)}}$$

Detailed balance

Note: Detailed balance (rate of producing A = rate of losing A) does not mean $k_{AB} = k_{BA}$. Rate constants are different than rates.

What is the timescale for the relaxation to c_A^{eq} + c_B^{eq}?

There are lots of ways to solve

$$\frac{d}{dt}\begin{pmatrix} c_A(t) \\ c_B(t) \end{pmatrix} = \begin{pmatrix} -k_{BA} & k_{AB} \\ k_{BA} & -k_{AB} \end{pmatrix}\begin{pmatrix} c_A(t) \\ c_B(t) \end{pmatrix}$$

subject to initial conditions $c_A(0)$ and $c_B(0)$.

Here is a quick one...

Define $\Delta C(t)$ as the time-dependent deviation from equilibrium

$$C_A(t) \equiv C_A^{eq} + \Delta C(t)$$

$$C_B(t) \equiv C_B^{eq} - \Delta C(t)$$

Not time-dependent

Time-dependent

$$\frac{d\Delta c(t)}{dt} = \frac{dc_A}{dt} = k_{AB}\, c_B - k_{BA}\, c_A$$

Cancel detailed balance @ equilibrium terms

$$= k_{AB}\left(c_B^{eq} - \Delta c(t)\right) - k_{BA}\left(c_A^{eq} + \Delta c(t)\right)$$

$$= -\left(k_{AB} + k_{BA}\right)\Delta c(t)$$

$$\Rightarrow \quad \Delta c(t) = \Delta c(0)\, e^{-t/\tau}$$

$$\frac{1}{\tau} = k_{AB} + k_{BA}$$

Timescale to relax to equilibrium

$$\frac{d}{dt}\begin{pmatrix} c_A(t) \\ c_B(t) \end{pmatrix} = \underbrace{\begin{pmatrix} -k_{BA} & k_{AB} \\ k_{BA} & -k_{AB} \end{pmatrix}}_{\Uparrow}\begin{pmatrix} c_A(t) \\ c_B(t) \end{pmatrix}$$

$\mathbb{W}$: the "rate matrix"

$$C_A(t) \equiv C_A^{eq} + \Delta C(t)$$
$$C_B(t) \equiv C_B^{eq} - \Delta C(t)$$

$$\begin{pmatrix} C_A(t) \\ C_B(t) \end{pmatrix} = \begin{pmatrix} C_A^{eq} \\ C_B^{eq} \end{pmatrix} + \Delta C(t) \begin{pmatrix} 1 \\ -1 \end{pmatrix}$$

$$\frac{d}{dt}\begin{pmatrix} C_A(t) \\ C_B(t) \end{pmatrix} = \mathbb{W} \begin{pmatrix} C_A(t) \\ C_B(t) \end{pmatrix}$$

$$= \mathbb{W} \begin{pmatrix} C_A^{eq} \\ C_B^{eq} \end{pmatrix} + \Delta C(t)\, \underline{\mathbb{W}} \underline{\begin{pmatrix} 1 \\ -1 \end{pmatrix}}$$

$$= \begin{pmatrix} -k_{BA} C_A^{eq} + k_{AB} C_B^{eq} \\ k_{BA} C_A^{eq} - k_{AB} C_B^{eq} \end{pmatrix} + \Delta C(t) \begin{pmatrix} -k_{BA} - k_{AB} \\ k_{BA} + k_{AB} \end{pmatrix}$$

$$= \underline{0} \underline{\begin{pmatrix} C_A^{eq} \\ C_B^{eq} \end{pmatrix}} - \underbrace{(k_{AB} + k_{BA})}_{\text{eigenvalue}} \Delta C(t) \underbrace{\begin{pmatrix} 1 \\ -1 \end{pmatrix}}_{\text{eigenvector of } \mathbb{W}}$$

(This is handwavy)

$$\frac{d}{dt}\mathbf{c} = \mathbb{W}\mathbf{c} \Rightarrow \frac{d\mathbf{c}}{\mathbf{c}} = \mathbb{W}\,dt$$

Integrate both sides

$$\Rightarrow \ln \mathbf{c} = \mathbb{W}t + \text{const.}$$

Exponentiate both sides

$$\Rightarrow \mathbf{c}(t) = \exp[\mathbb{W}t]\exp[\text{const.}]$$

$$\Rightarrow \mathbf{c}(t) = \exp[\underline{\mathbb{W}}t]\,\mathbf{c}(0)$$

A matrix exponential!

$$\exp[\mathbb{W}t] = \mathbb{1} + \mathbb{W}t + \tfrac{1}{2}t^2\mathbb{W}^2 + \ldots$$

$$\exp\left[\begin{pmatrix} -k_{BA} & k_{AB} \\ k_{BA} & -k_{AB} \end{pmatrix} t\right] = ?$$

$\mathbb{W}$ has eigenvalues ν_0 and ν_1 with associated left and right eigenvectors

$$\langle 0|\mathbb{W} = \langle 0|\nu_0 \qquad \mathbb{W}|0\rangle = \nu_0|0\rangle$$

$$\langle 1|\mathbb{W} = \langle 1|\nu_1 \qquad \mathbb{W}|1\rangle = \nu_1|1\rangle$$

$$\exp\left[\begin{pmatrix} -k_{BA} & k_{AB} \\ k_{BA} & -k_{AB} \end{pmatrix} t\right]$$

$$= |0\rangle\langle 0| e^{\nu_0 t} + |1\rangle\langle 1| e^{\nu_1 t}$$

$$\mathbf{c}(t) = \left(|0\rangle\langle 0| e^{\nu_0 t} + |1\rangle\langle 1| e^{\nu_1 t}\right)\mathbf{c}(0)$$

$$= \left[\begin{pmatrix} p_A^{eq} \\ p_B^{eq} \end{pmatrix}(1 \;\; 1) e^{0t} + \begin{pmatrix} 1 \\ -1 \end{pmatrix}(1 \;\; -1) e^{-(k_{AB}+k_{BA})t}\right]\mathbf{c}(0)$$

$$= \left[\begin{pmatrix} p_A^{eq} \\ p_B^{eq} \end{pmatrix}\left(c_A(0) + c_B(0)\right) + \begin{pmatrix} 1 \\ -1 \end{pmatrix} e^{-(k_{AB}+k_{BA})t}\left(c_A(0) - c_B(0)\right)\right]$$

$$\mathbf{c}(t) = \left[\begin{pmatrix} c_A^{eq} \\ c_B^{eq} \end{pmatrix} + \underbrace{\begin{pmatrix} 1 \\ -1 \end{pmatrix} e^{-(k_{AB}+k_{BA})t}\left(c_A(0) - c_B(0)\right)}_{}\right]$$

$\Delta c(t)$ from last time decays with $\tau = (k_{AB}+k_{BA})^{-1}$

Long time... ? $\lim_{t\to\infty} \mathbf{c}(t) = \begin{pmatrix} c_A^{eq} \\ c_B^{eq} \end{pmatrix}$

Relaxation timescales are reciprocals of eigenvalues of $\mathbb{W}$!

What determines k_{AB} + k_{BA}?
How are they related to $V(\phi)$?