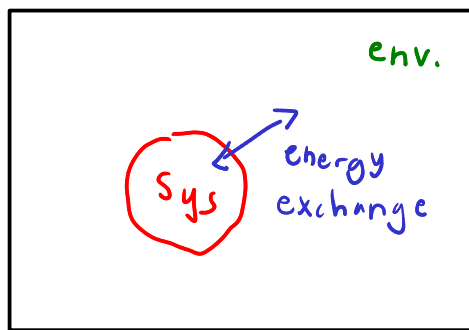
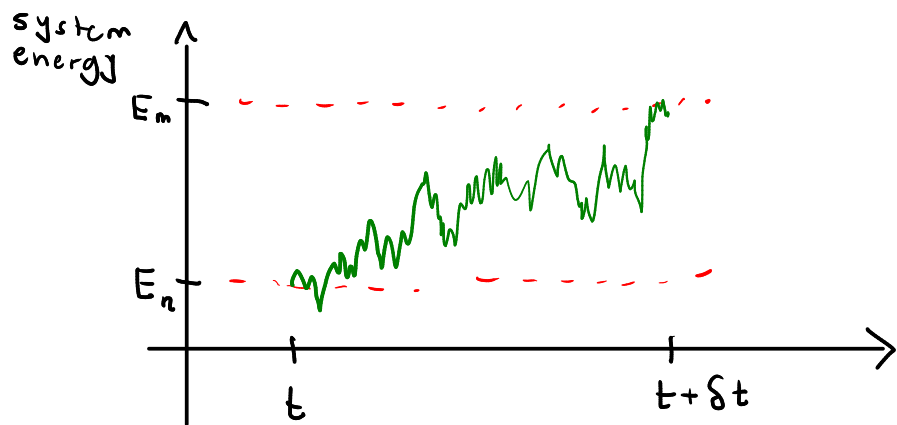




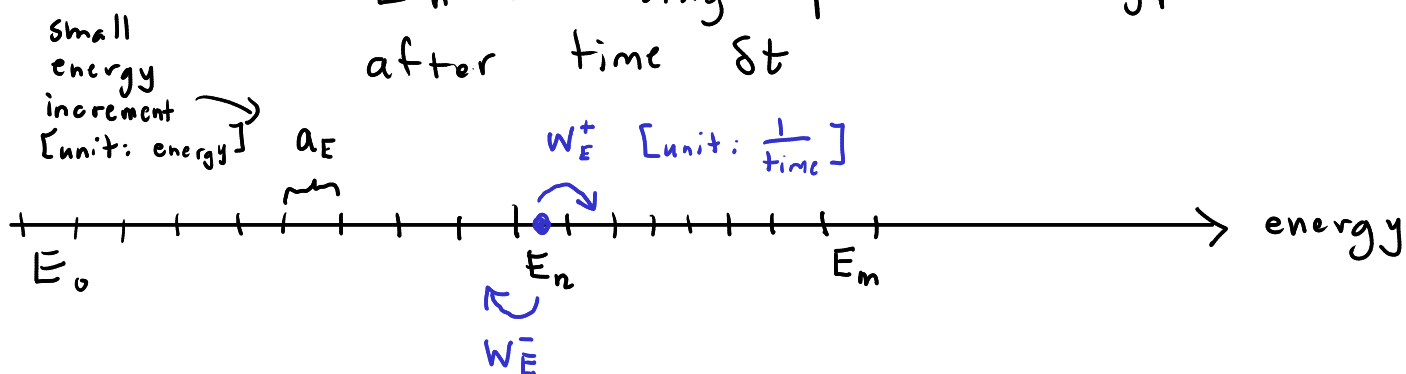
how does energy exchange
affect trans. rates
 Ω_{mn} b/t sys. states?



energy exchange:
biased random walk
in energy space, w/
env. donating or
removing energy in
small increments

$\Omega_{mn} \delta t$ = prob. given start in n that we
trans. to m in time step δt

$\propto$ prob. of system starting w/ energy
 E_n & ending up w/ energy E_m
after time δt



continuum limit: $a_E \rightarrow 0$

"energy diffusion" $D_E = \frac{1}{2} (W_E^+ + W_E^-) a_E^2 = \text{const.}$ unit: $\frac{\text{energy}^2}{\text{time}}$

"mean energy velocity" $V_E = (W_E^+ - W_E^-) a_E$ $\frac{\text{energy}}{\text{time}}$

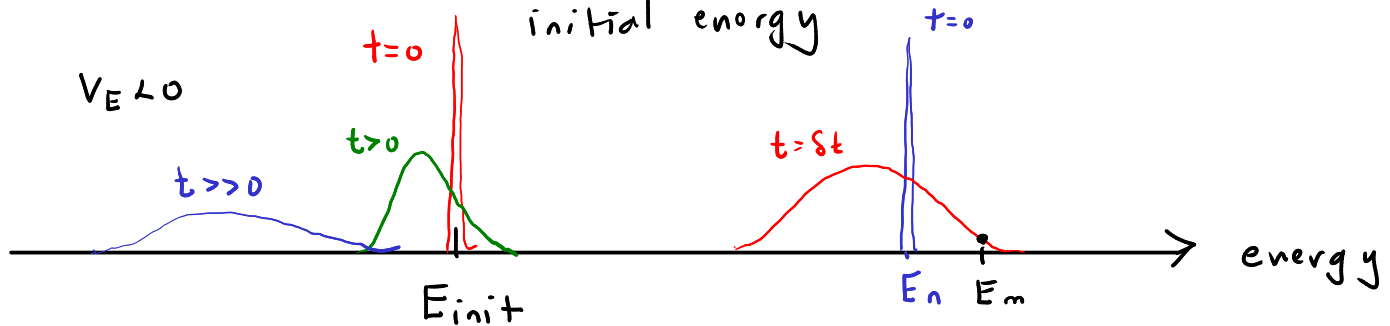
Fokker-Planck
equ.

$$\frac{\partial}{\partial t} P(E, t) = -V_E \frac{\partial}{\partial E} P + D_E \frac{\partial^2}{\partial E^2} P$$

solution: under initial condition that we
start at $E = E_{\text{init}}$

$$P(E, t; E_{\text{init}}) = \frac{1}{\sqrt{4\pi D_E t}} \exp \left[-\frac{(E - E_{\text{init}} - V_E t)^2}{4 D_E t} \right]$$

↑
initial energy



$$P(E_m, \delta t; E_n) = \frac{1}{\sqrt{4\pi D_E \delta t}} \exp \left[-\frac{(E_m - E_n - V_E \delta t)^2}{4 D_E \delta t} \right]$$

prob. to start
at E_n + end
up at E_m after δt

construct a ratio to get rid of
proportionality constants:

$$\frac{P(E_m, \delta t; E_n)}{P(E_n, \delta t; E_m)} = \frac{\Omega_{mn} \delta t}{\Omega_{nm} \delta t} = \exp \left[\frac{V_E}{D_E} (E_m - E_n) \right]$$

forward
backward

$$\equiv \exp \left[-\beta (E_m - E_n) \right]$$

$$\beta \equiv -\frac{V_E}{D_E} \equiv \frac{1}{k_B T}$$

units: 1/energy

T = temp. in Kelvin

$$k_B = 1.38 \times 10^{-23} \text{ J/K}$$

$$D_E > 0 \quad \text{b/c } W_E^+, W_E^- > 0$$

$$V_E \text{ is typically } < 0 \quad \text{b/c } W_E^+ < W_E^-$$

$\Rightarrow$ b/c env. $\gg$ sys so it is easier to lose energy to env. than to gain from it

$\Rightarrow$ typically $T > 0$

As $T \rightarrow \infty$, β becomes smaller

$\Rightarrow V_E$ becoming less negative

$$T = \infty : V_E = 0 \Rightarrow W_E^+ = W_E^-$$

implication: i) for every $\Omega_{nm} \neq 0$ there has to be $\Omega_{mn} \neq 0$
(microscopic reversibility)

ii) puts constraints on how energy moves b/t states

in sys

uphill

$$\frac{\Omega_{mn}}{\Omega_{nm}}$$

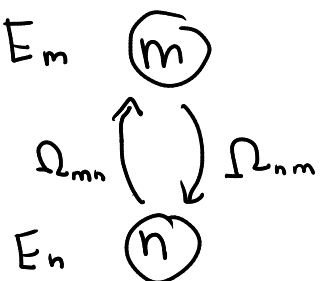
downhill

$$\Omega_{nm}$$

$$= e^{-\beta(E_m - E_n)}$$

local detailed balance (LDB)

$$E_m > E_n$$



uphill $\Omega_{mn} < \text{downhill } \Omega_{nm}$

b/c of $T > 0$; consequence of
 $W_E^+ < W_E^-$