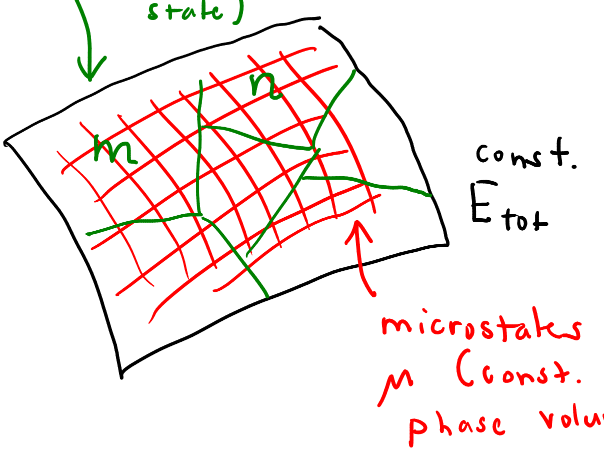
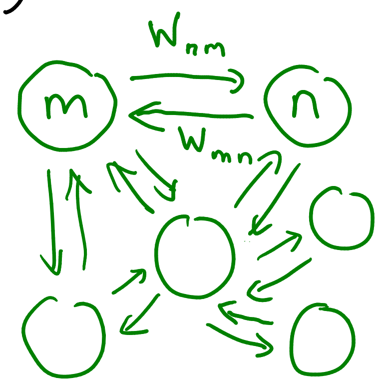
Summary: 1) isolated total system w/ const total energy E_{tot} which is ergodic + mixing

2) divide up total into "system" (focus) + "environment" (rest)



$\Longleftrightarrow$



3) network of transitions w/ matrix W whose entries satisfy local detailed balance (LDB):

$$p_n^s = \frac{\Theta_n}{\Theta_{tot}}$$

$\Theta_n \rightarrow$ # microst. in macrost. n

$$\boxed{W_{nm}\, p_m^s = W_{mn}\, p_n^s}$$

Consequences of LDB:

1) microscopic reversibility (MR):

if $W_{nm} \neq 0 \Rightarrow W_{mn} \neq 0$

if arrow exists in one direc., has to exist in reverse

$\Rightarrow$ get a unique stationary state

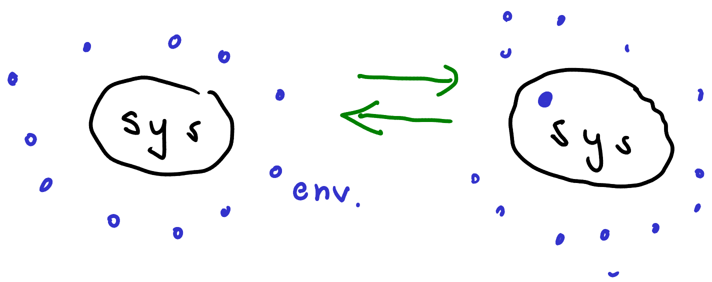
2) Can we describe this stationary state?

To do this, we need a couple more assumptions:

- Θ_n = counts # of microstates available to environ. when sys. is in state n + hence should depend on conserved quantities describing environ.

examples: energy $\quad E_{tot} = \underset{\text{sys}}{E_n} + \underset{\text{env.}}{E_n^{env}} \Rightarrow E_n^{env} = E_{tot} - E_n$

exchange of particles



$$\underset{\#\text{ part. in tot.}}{N_{tot}^{part}} = \underset{\text{sys}}{N_n^{part}} + \underset{\text{env.}}{N_n^{part,env}}$$

Θ_n is a function of conserved quantities:

$$\Theta_n = \Theta\left(E_n^{env}, N_n^{part,env}, \ldots\right)$$

Θ ← universal function (≈ continuous)

focus on case where only energy is exchanged:

LDB: $\quad W_{nm} p_m^s = W_{mn} p_n^s \qquad p_m^s = \frac{\Theta_m}{\Theta_{tot}}, \quad p_n^s = \frac{\Theta_n}{\Theta_{tot}}$

$$\Rightarrow \quad \frac{W_{nm}}{W_{mn}} = \frac{\Theta_n}{\Theta_m} = \frac{\Theta(E_{tot} - E_n)}{\Theta(E_{tot} - E_m)}$$

env >> system: $E_{tot} >> E_n$ Taylor expand!

$$\frac{W_{nm}}{W_{mn}} = \exp\left[\ln \Theta(E_{tot}-E_n) - \ln \Theta(E_{tot}-E_m)\right]$$

$$\ln \Theta(E_{tot}-E_n) \approx \ln \Theta(E_{tot}) - \underbrace{\left.\frac{\partial \ln \Theta}{\partial E}\right|_{E_{tot}}}_{\beta} E_n + \cdots$$

$$= \ln \Theta(E_{tot}) - \beta E_n + \cdots$$

$$\Rightarrow \quad \frac{W_{nm}}{W_{mn}} = \exp\left[-\beta(E_n - E_m) + \cdots\right]$$

traditionally: $\beta \equiv \frac{1}{k_B T} = \left.\frac{\partial \ln \Theta}{\partial E}\right|_{E_{tot}}$

definition of temp. T

k_B = Boltzmann's const. $= 1.38 \times 10^{-23}$ J/K

T = units of Kelvins (K)

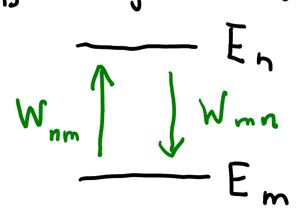
$k_B T$ = units of J

β = units of J^{-1}

$$\frac{\text{uphill}}{\text{downhill}} = \frac{W_{nm}}{W_{mn}} = e^{-\beta \underbrace{(E_n - E_m)}_{\text{energy diff.}}}$$

β: how "easy" it is to get energy from env.

energy diff. = needs to be donated from env. if uphill trans.



case:

$E_n > E_m$

$\beta > 0$

$\beta > 0$ $(T > 0)$: $\frac{\text{uphill}}{\text{downhill}} < 1$ environ. is "stingy": less likely to give than to take away energy

(typical for env >> sys)

$\beta \to +\infty$ $(T \to 0^+)$: $\dfrac{\text{uphill}}{\text{downhill}} \to 0$ all uphill trans. are forbidden (absolute zero temp.)

$\beta \to 0^+$ $(T \to +\infty)$: $\dfrac{\text{uphill}}{\text{downhill}} \to 1$ uphill trans. equally likely to downhill

untypical case:

$\beta < 0$ $(T < 0)$: $\dfrac{\text{uphill}}{\text{downhill}} > 1$ extremely generous environ.

$\Rightarrow$ how do we get this?

next time: example of a "gas" of spins

$\ln \Theta(E_{Tot})$