Concrete example of thermal heat bath

$N+1$ spins : $\uparrow$ or $\downarrow$ $\Rightarrow$ label spin 1 "system"
remaining N spins "environ."

energy : $\underset{>0}{\epsilon}$ or 0

total (sys + env) has energy $E_{tot} = k\epsilon$ (k $\uparrow$ spins)

the system (spin 1) has states $E_1 = 0$ ($\downarrow$)
$E_2 = \epsilon$ ($\uparrow$)

Dynamics: at every time step δt, choose at random one $\downarrow$ spin & one $\uparrow$ spin, flip the pair (preserves E_{tot})

$\Rightarrow$ clearly ergodic & mixing, since any configuration of k $\uparrow$ spins can evolve in time to any other config. of k $\uparrow$ spins

For the system itself:

$W_{12}\,\delta t =$ prob. to go from $\uparrow$ to $\downarrow$ in time step δt given spin 1 is $\uparrow$ $= \dfrac{1}{k}$ (prob. to choose spin 1 as the $\uparrow$ spin to flip)

$W_{21}\,\delta t =$ prob. to go from $\downarrow$ to $\uparrow$ given spin 1 is $\downarrow$ $= \dfrac{1}{N+1-k}$ (prob. to choose spin 1 as the $\downarrow$ spin to flip)

note: $2 \to 1$ ($\uparrow \to \downarrow$) leads to loss of energy ϵ from sys. to environment

$1 \to 2$ ($\downarrow \to \uparrow$) gain of energy ϵ from environment

Let us check detailed balance:

$$\frac{W_{12}}{W_{21}} \overset{?}{=} \frac{\Theta_1}{\Theta_2}$$

Θ_1 = # env. states when sys. is in state 1 $= \binom{N}{k} = \dfrac{N!}{(N-k)!\,k!}$

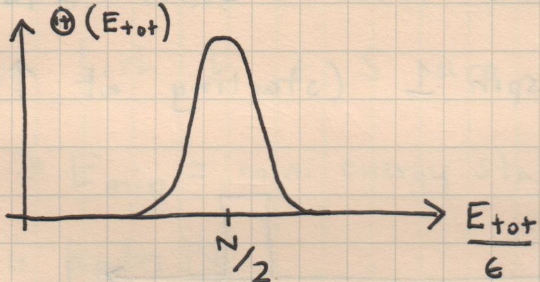
Θ_2 = " " " state 2 $= \binom{N}{k-1} = \dfrac{N!}{(N-k+1)!\,(k-1)!}$

$$\frac{\Theta_1}{\Theta_2} = \frac{N-k+1}{k} = \frac{W_{12}}{W_{21}}$$ det. balance works!

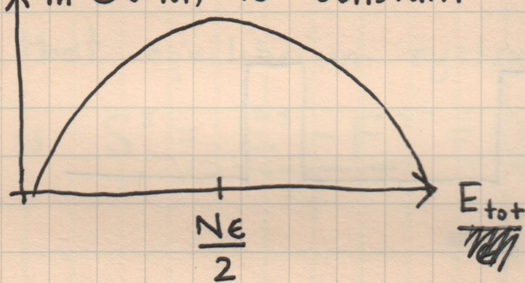
What is the temperature of the system?

$$\Theta_1 = \Theta(E_{tot}) \equiv \binom{N}{E_{tot}/\epsilon} \quad \text{since } k = \frac{E_{tot}}{\epsilon}$$

$$\Theta_2 = \Theta(E_{tot}-\epsilon) < \Theta(E_{tot}) \quad \text{when } E_{tot}/\epsilon \le \frac{N}{2}$$



$$\ln \Theta(E_{tot}) \approx \text{constant} - \frac{\left(N - \frac{2E_{tot}}{\epsilon}\right)^2}{2N}$$



$$\frac{W_{12}}{W_{21}} = \frac{\Theta_1}{\Theta_2} \approx e^{-\beta(E_1-E_2)} = e^{\beta\epsilon}$$

for large E_{tot} not near edges
$(k \gg 1)$
$k \ll N$

where constant $= \ln \dfrac{2^N}{\sqrt{\frac{1}{2}N\pi}}$

$$\frac{1}{k_B T} = \beta = \frac{\partial \ln \Theta}{\partial E_{tot}}(E_{tot})$$

$$\approx \frac{2}{\epsilon}\left(1 - \frac{2E_{tot}}{\epsilon N}\right) = \begin{cases} \text{positive for } \frac{E_{tot}}{\epsilon} < \frac{N}{2} \\ \text{negative for } \frac{E_{tot}}{\epsilon} > \frac{N}{2} \end{cases}$$

when $1 \ll k \ll \frac{N}{2}$ ⇒ increasing k increases the ability of environ. to "lend" energy to sys ⇒ inc. T

When $\beta > 0$, $W_{12} > W_{21}$ (down flip is more likely than up flip)

$\Rightarrow$ it is easier to lose energy to env. than gain

$\beta < 0$, $W_{21} > W_{12}$ (easier to gain energy from environ. than lose it)

[Note: would get same answer for β from:

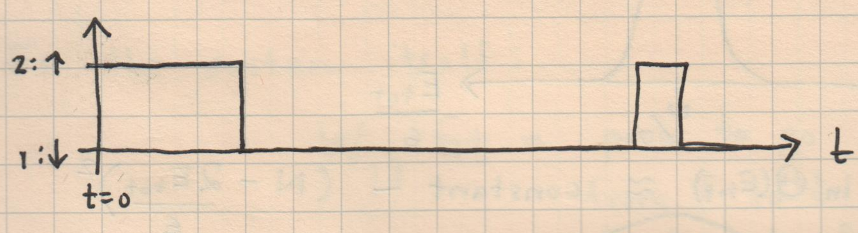
$$e^{\beta\epsilon} = \frac{\Theta_1}{\Theta_2} = \frac{N-k+1}{k} \approx \frac{N-k}{k} \quad \text{for} \quad 1 \ll k \ll N$$

$$\beta = \frac{1}{\epsilon} \ln \frac{N-k}{k} \approx \frac{2}{\epsilon}\left(1 - \frac{2k}{N}\right) \quad \text{~~when~~} \quad \text{(Taylor series around } k \text{ near } \tfrac{N}{2}\text{)}$$

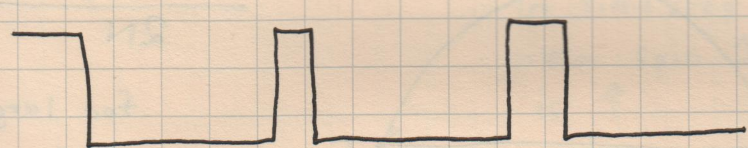
$$= \frac{2}{\epsilon}\left(1 - \frac{2E_{tot}}{\epsilon N}\right)$$]

Imagine traj. of spin 1 (starting at $\uparrow$ at time $t=0$)

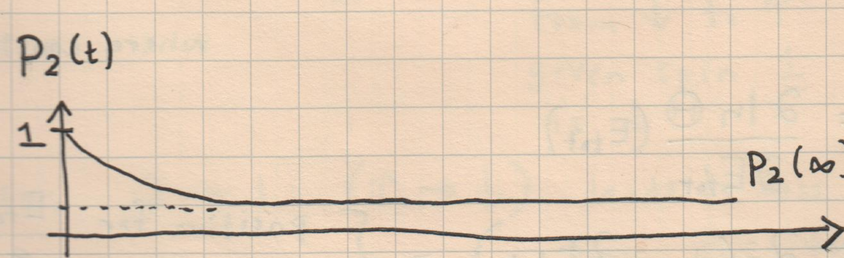
traj. 1:



traj. 2:



⋮



$$P_2(\infty) = p_2^s = \frac{e^{-\beta E_2}}{Z} = \frac{e^{-\beta\epsilon}}{1 + e^{-\beta\epsilon}}$$

$$p_1(\infty) = p_1^s = \frac{e^{-\beta E_1}}{Z} = \frac{1}{1 + e^{-\beta\epsilon}}$$

What happens when energy exchange allowed?

state n

E_n different

env. state q with energy $E_n^{env} = E_{tot} - E_n$

$$P(A|B) = \frac{P(A,B)}{P(B)}$$

$$S^{tot}(t) = -k_B \sum_{n,q} p_{n,q}(t) \ln p_{n,q}(t)$$

cond. prob

$$= -k_B \sum_{n,q} p_n p_{q|n} \ln p_n p_{q|n}$$

$$= -k_B \sum_n \left[\sum_q p_n p_{q|n} \ln p_n + \sum_q p_n p_{q|n} \ln p_{q|n} \right]$$

$$= \underbrace{-k_B \sum_n p_n(t) \ln p_n(t)}_{S(t) = \text{sys. entropy}} + \sum_n p_n \left[-k_B \sum_q p_{q|n} \ln p_{q|n} \right]$$

assume $p_{q|n} = \frac{1}{\Theta_n}$ for q with energy E_n^{env}

(env. relaxes quickly to equilibrium at E_n^{env})

$p_{q|n} = 0$ otherwise

$$= S(t) + \sum_n p_n \left[+k_B \underbrace{\ln \Theta_n}_{} \right]$$

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

$$\approx k_B \ln \Theta (E_{tot}) - \frac{1}{T} E_n$$

using $\frac{1}{k_B T} = \frac{\partial \ln \Theta (E_{tot})}{\partial E_{tot}}$

$$= S(t) + k_B \ln \Theta (E_{tot}) - \frac{1}{T} \bar{E}(t)$$

$$-\frac{\mathring{\bar{E}}(t)}{T} \equiv \text{env. entropy flow}$$

time change in total entropy:

$$\dot{S}^{tot}(t) = \mathring{S}(t) - \frac{1}{T}\mathring{\bar{E}}(t) = \text{sys. entropy change} + \text{env. entropy change due to energy flow}$$

But we also know that

$$D_{KL}(\vec{p}(t) \,||\, \vec{p}^{s}) = \frac{1}{k_B T}(F(t) - F_{min})$$

$$\frac{d}{dt}(\;''\;) = \frac{1}{k_B T}\dot{F}(t) \leq 0 \quad \text{~~for t < ∞~~}$$

$$F(t) = \bar{E}(t) - T\,S(t) \quad \text{sys. free energy}$$

$$\Rightarrow S(t) = \frac{\bar{E}(t) - F(t)}{T} \Rightarrow \mathring{S}(t) = \frac{\mathring{\bar{E}}(t) - \dot{F}(t)}{T}$$

$$\dot{S}^{tot}(t) = \frac{\mathring{\bar{E}}(t) - \mathring{F}(t)}{T} - \frac{1}{T}\mathring{\bar{E}}(t)$$

$$= -\mathring{F}(t) \geq 0$$

and note: $$\mathring{S}(t) = \underbrace{-\frac{\mathring{F}(t)}{T}}_{\text{term always } \geq 0} + \underbrace{\frac{\mathring{\bar{E}}(t)}{T}}_{\text{term can be } <0 \text{ or } \geq 0}$$

Entropy budgeting: (per unit time)

env. ~~gai~~ change in entropy: $-\frac{1}{T}\mathring{\bar{E}}(t)$

sys. change in entropy: $+\frac{1}{T}\mathring{\bar{E}}(t) - \frac{\mathring{F}(t)}{T} = \mathring{S}(t)$

universe change in entropy: $\mathring{S}_{tot}(t)$ $\quad -\frac{\mathring{F}(t)}{T} \geq 0$

call $\frac{1}{T}\mathring{\bar{E}}(t) \equiv \dot{S}^{e}(t)$ = entropy "flow" from env. to system = − entropy flow from sys. to env — can be >0 or <0

~~cor~~

$$-\dot{F}(t) \equiv \dot{S}^i(t) = \text{"irreversible entropy production"}$$

$$\geq 0 \quad \text{always}$$

$$= 0 \quad \text{only when } F(t) = F_{min} \text{ (equilibrium)}$$

entropy "conservation laws":

for system: $\dot{S}(t) = \dot{S}^i(t) + \dot{S}^e(t)$

for universe: $\dot{S}^{tot}(t) = \dot{S}^i(t)$

As realized by Ilya Prigogine (Nobel in chemistry, 1977) this division into $\dot{S}^i(t) + \dot{S}^e(t)$ is quite general, independent of particular form of $\frac{W_{nm}}{W_{mn}}$:

$$S(t) = -k_B \sum_n p_n(t) \ln p_n(t)$$

$$\dot{p}_n(t) = \sum_m J_{nm}(t) \quad \text{where } J_{nm}(t) = W_{nm}(t) p_m(t) - W_{mn}(t)$$

note W can be time dependent

$$\Rightarrow \quad \dot{S}(t) = -k_B \sum_n \dot{p}_n(t) \ln p_n(t)$$

$$- k_B \underbrace{\sum_n \dot{p}_n(t)}_{= \frac{d}{dt} \sum_n p_n(t) = \frac{d}{dt} 1 = 0}$$

$$= -k_B \sum_{nm} J_{nm} \ln p_n$$

$$= -\frac{k_B}{2} \sum_{nm} J_{nm} \ln \frac{p_n}{p_m} \quad \text{using } J_{nm} = -J_{mn}$$

$$= +\frac{k_B}{2} \sum_{nm} J_{nm} \ln \frac{p_m}{p_n}$$

$$= \underbrace{\frac{k_B}{2}\sum_{nm} J_{nm} \ln \frac{W_{nm}p_m}{W_{mn}p_n}}_{\equiv \mathring{S}^i(t)} - \underbrace{\frac{k_B}{2}\sum_{nm} J_{nm} \ln \frac{W_{nm}}{W_{mn}}}_{\equiv \mathring{S}^e(t)}$$

most general form

note since $J_{nm} = W_{nm}p_m - W_{mn}p_n$

& $(x-y)\ln\frac{x}{y} \geq 0$

$=0$ only ~~except~~ when $x=y$

$$\Rightarrow \mathring{S}^i(t) \geq 0$$

$= 0$ iff $W_{nm}p_m = W_{mn}p_n$

or $\frac{W_{nm}}{W_{mn}} = \frac{p_n}{p_m}$ (this is the detailed balance condition)

satisfied only at equilibrium!

Form of $\mathring{S}^e(t)$ depends on $\frac{W_{nm}}{W_{mn}}$.

~~Let us write~~

i) "isolated" system, i.e. universe :

$$\frac{W_{nm}}{W_{mn}} = 1 \Rightarrow \mathring{S}^e(t) = 0 \Rightarrow \mathring{S}(t) = \mathring{S}^i(t) \geq 0$$

ii) system exch. energy w/ env. at temp T

$$\frac{W_{nm}}{W_{mn}} = e^{-\beta\underbrace{(E_n - E_m)}_{\equiv Q_{nm}}} \Rightarrow \mathring{S}^e(t) = \frac{1}{2T}\sum_{nm} J_{nm}(E_n - E_m)$$

"heat" flow from env. to sys. in $n \to m$ trans.

$$= \frac{1}{T}\sum_{nm} J_{nm}E_n$$

$$= \frac{1}{T}\sum_n \dot{p}_n(t)E_n$$

$$= \frac{1}{T}\frac{d}{dt}\sum_n p_n(t)E_n = \frac{\mathring{E}(t)}{T}$$

rate of heat flow

also can write $\dot{S}^e(t) = \frac{1}{2T}\sum_{nm} J_{nm} Q_{nm} \equiv \frac{\dot{Q}(t)}{T}$

compare: $dS = \frac{đQ}{T}$ for reversible process in traditional stat mech.

Note the following: equilibrium is boring

if W_{nm} matrix constant in time

$\Rightarrow \quad p_n(t) \to p_n^s$ time indep.

$$= \begin{cases} \frac{1}{N} & \text{for case i} \\ \frac{e^{-\beta E_n}}{Z} & \text{for case ii} \end{cases}$$

In both cases $\frac{W_{nm}}{W_{mn}} = \frac{p_n^s}{p_m^s}$ (detailed balance)

and hence $W_{nm} p_m^s - W_{mn} p_n^s = J_{nm}^s \equiv J_{nm}(t \to \infty)$
$= 0$

Hence $\dot{S}^i(t) = \frac{k_B}{2}\sum_{nm} J_{nm} \ln \frac{W_{nm} p_m}{W_{mn} p_n} \to 0$ as $t \to \infty$

$\dot{S}^e(t) = \frac{-k_B}{2}\sum' J_{nm} \ln \frac{W_{nm}}{W_{mn}} \to 0$ as $t \to \infty$

and $\dot{S}(t) = \frac{d}{dt}\left(-k_B \sum_n' p_n(t) \ln p_n(t)\right) \to 0$ as $t \to \infty$

Everything approaches zero!

System connected to heat bath at temp T has no net currents in long time limit!