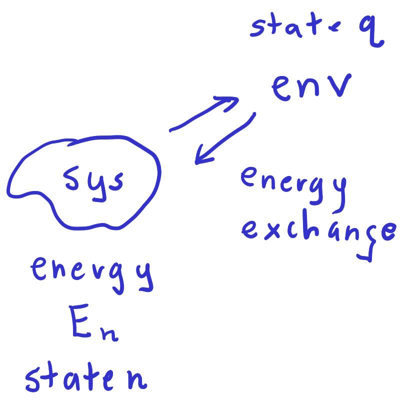
# Welcome to PHYS 414 online

As people get connected, let's initially unmute microphones to diagnose any tech issues.

(Don't connect video to minimize bandwidth.)

## REVIEW:




$$p_n^s = \frac{e^{-\beta E_n}}{Z}$$

$$Z = \sum_n e^{-\beta E_n}$$

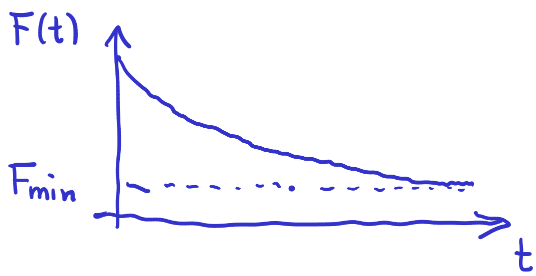
$$\beta = \frac{1}{k_B T}$$

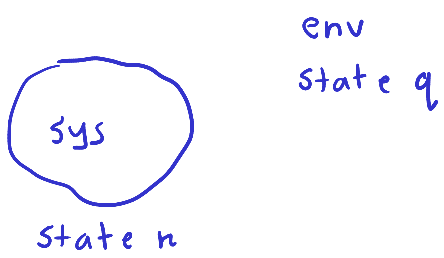
$$D_{KL}(\vec{p}(t) \,||\, \vec{p}^{\,s}) = \frac{1}{k_B T}\left(F(t) - F_{min}\right)$$

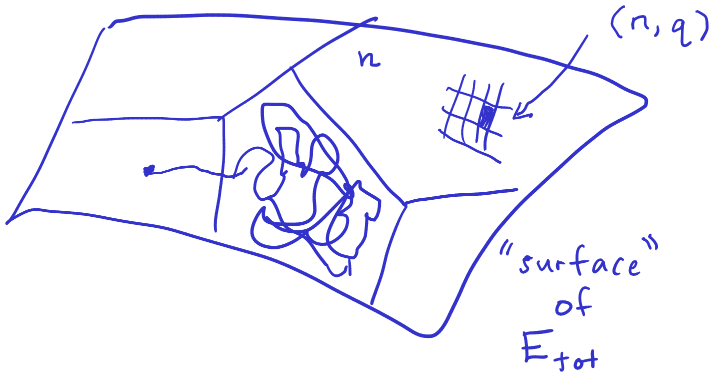
$$F(t) = \bar{E}(t) - T S(t) \qquad \bar{E}(t) = \sum_n p_n(t) E_n$$

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

$$F(t) \to F_{min} = -k_B T \ln Z$$






$E_n^{env}$ = energy of env. when sys is state n

$= E_{tot} - E_n$

$P_{n,q}$ = prob. of being in microstate (n, q)

entropy of total (sys + env) = $\underline{S_{tot}(t)} = -k_B \sum_{n,q} P_{n,q}(t) \ln P_{n,q}(t)$

entropy of system = $S(t) = -k_B \sum_n P_n(t) \ln P_n(t)$

$P_{n,q}$ = joint prob. that sys is in state n + env. is in state q $= P_{q|n} P_n$

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

$\sum_A \mathcal{P}(A|B) = 1$

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

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

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

$$= \underbrace{-k_B \sum_n P_n \ln P_n}_{S(t)} - k_B \sum_n P_n \left[ \sum_q P_{q|n} \ln P_{q|n} \right]$$

assume

$P_{q|n} = \dfrac{1}{\Theta_n}$

$\Theta_n$ = # of env. states when sys is in state n

$\Rightarrow$ fast mixing assumption

env relaxes quickly + explores all possible states q associated w/ n

If q belongs to state n

$P_{q|n} \neq 0$

otherwise

$P_{q|n} = 0$

$$S^{tot}(t) = S(t) + k_B \sum_n p_n \ln \Theta_n \qquad \Theta_n = \Theta(E_{tot} - E_n)$$

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

$$\bar{E}(t) = \sum_n p_n E_n$$

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

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

rate of change: $\frac{d}{dt}$ of both sides

$$\dot{S}^{tot}(t) = \dot{S}(t) - \underbrace{\frac{1}{T} \dot{\bar{E}}(t)}_{\text{env. entropy change rate due to energy exchange w/ sys}} \qquad dS \sim \frac{đQ}{T}$$

$=$ sys entropy change rate

$T > 0$

$$D_{KL}(\vec{p}(t) \,||\, \vec{p}^{\,s}) = \frac{1}{k_B T}(F(t) - F_{min}) \geq 0$$

$$\frac{d}{dt}(\,''\,) = \frac{1}{k_B T} \dot{F}(t) \leq 0 \qquad F(t) = \bar{E}(t) - TS(t)$$

$$\underline{\underline{S(t)}} = \frac{\bar{E}(t) - F(t)}{T}$$

$$\dot{S}^{tot} = \frac{\dot{\bar{E}} - \dot{F}}{T} - \frac{1}{T}\dot{\bar{E}} = -\frac{\dot{F}}{T} \geq 0$$

1) $\dot{S} = \frac{\dot{\bar{E}}}{T} - \frac{\dot{F}}{T}$ rate of change of sys. entropy

2) $-\frac{\dot{\bar{E}}}{T}$ rate of change of env. entropy

3) $\dot{S}^{tot} = -\frac{\dot{F}}{T} \geq 0$ rate of change of tot. entropy

entropy budget

$$\frac{1}{T}\dot{\bar{E}}(t) \equiv \dot{S}^e$$ = entropy "flow" from env. to sys = − entropy flow from sys. to env.

$-\dot{F} \equiv \dot{S}^i \geq 0$ always = "irreversible entropy production"

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

$$\dot{S}^{tot} = \dot{S}^{i}$$