Lecture #6

$\Delta S \overset{?}{\Rightarrow} \beta \delta Q$ entropy originally defined this way!

Summary

Max. Entropy

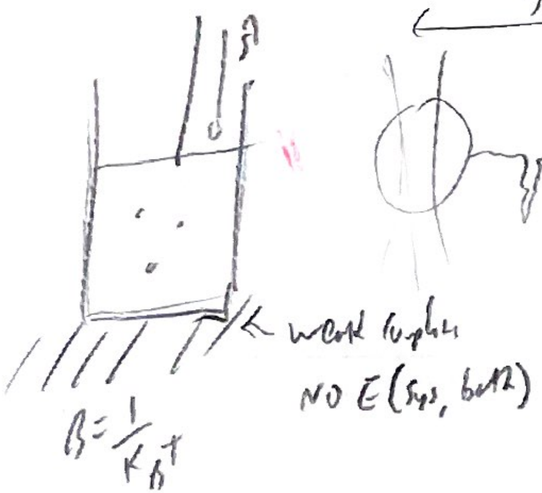
$$P_A(x;\lambda) = \frac{e^{-\beta E(x,\lambda)}}{Z}$$

$\beta = \frac{\partial S}{\partial E}$

$\beta F(A) = \underbrace{-S}_{\text{entropy of system}} + \underbrace{\beta\langle E\rangle}_{\text{potential entropy}}$

$\delta E = \langle E\rangle - E$

$\beta F \overset{eq}{=} -\ln Z \qquad \frac{\partial \beta F}{\partial \beta} = \langle E\rangle \qquad \frac{\partial \langle E\rangle}{\partial \beta} = \langle \delta E\, \delta E\rangle$



History Gilbert Lewis

Gilman Hall

Free energy

$$\beta \Delta F = \underbrace{-\Delta S}_{-\Delta S^{sys}} + \underbrace{\beta \langle \Delta E \rangle}_{-\Delta S^{env}} = -\Delta S^{tot}$$

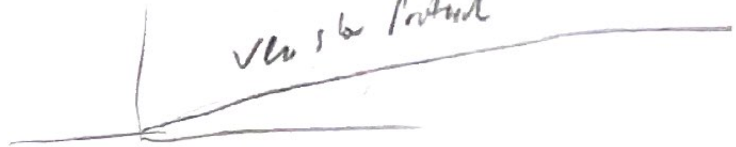
(~~Don't have to~~ Total entropy maximized, ~~E~~ is entropy that matters)

$$\beta F = -S + \underbrace{\beta \langle E \rangle}_{\text{Potential entropy}} = + \sum P_x \ln P_x + \beta \sum P_x E(x)$$

"Free entropy"

$$\beta F \leq \langle w \rangle$$
$$= W^{rev}$$

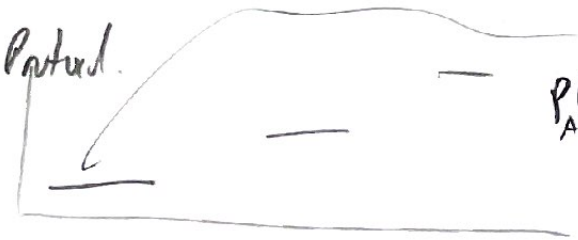
very slow protocol



If put this energy into bath, entropy increases by $\beta \langle E \rangle$

Instantaneous equilibration protocol

E



$P_A(E)$

$P =$

$\propto e^{-\beta E_x}$

$P_A(x)$ = out of equil.

$P_c(x) = \frac{e^{-\beta E_x}}{Z}$

Control all energy levels, change so now in equilibrium $P_B(x) = P_A(x)$

But $E_B(x) = -\frac{1}{\beta} \ln P(x) + c$

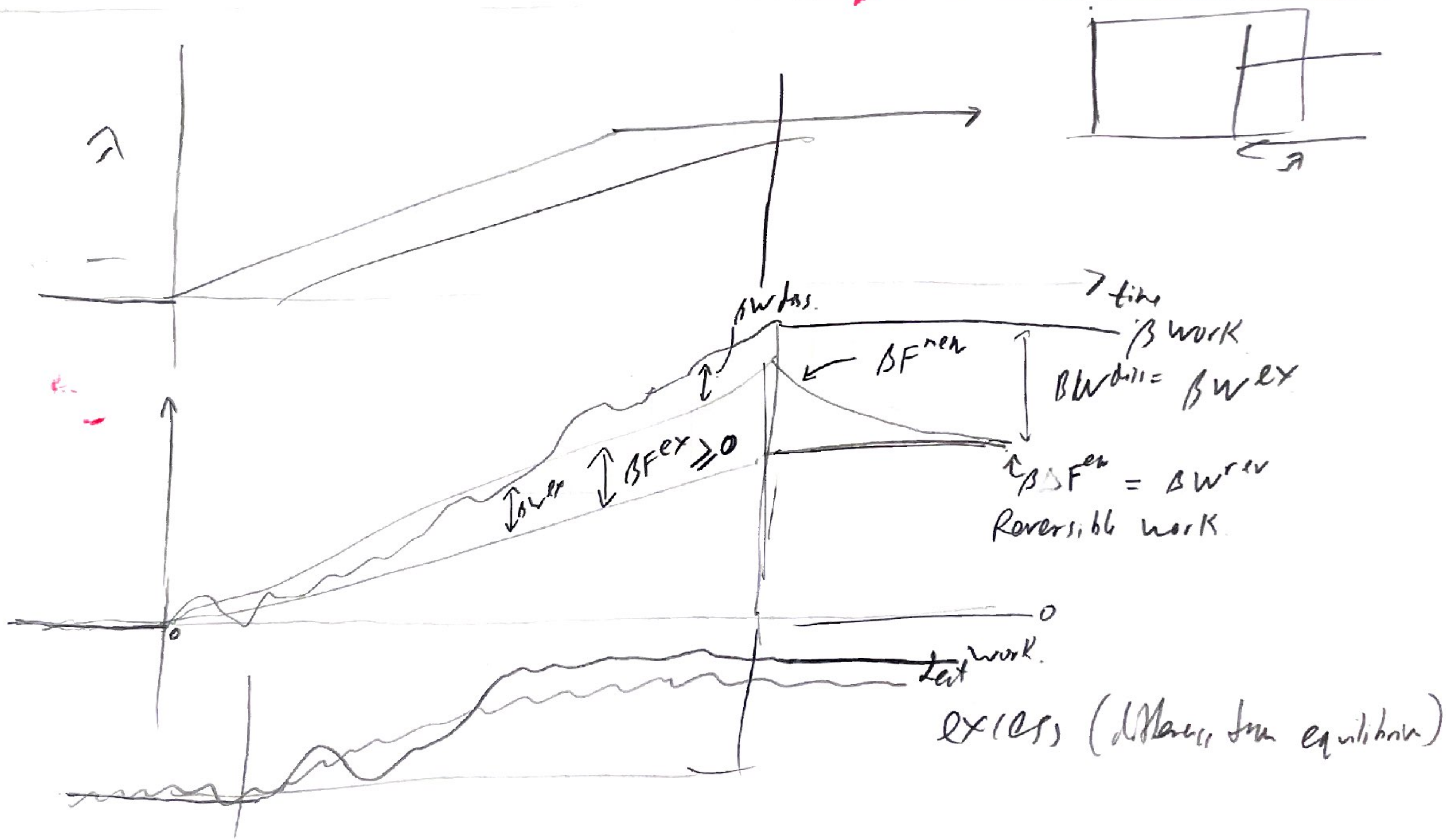
No change in Entropy, No change in $\langle E \rangle$ ←

$\langle E_A \rangle = \langle E_B \rangle$

Reversible work

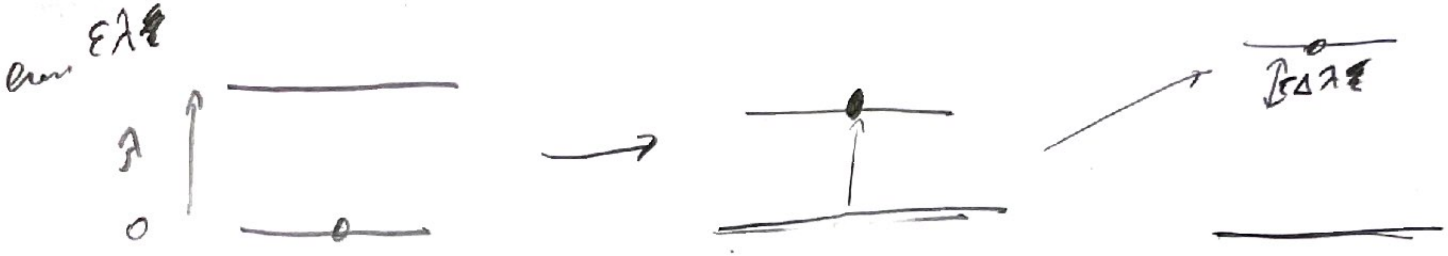
$F_A = F_B$ "Thermodynamically Reversible!) Memorable!

excess work, excess FE dissipation.



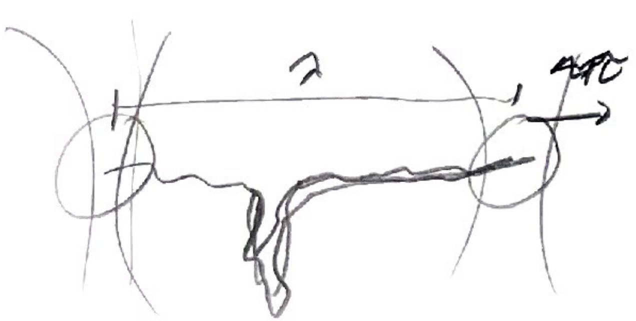
Work 4 Heat

1902
Gibbs, Schrodinger, 1946 Jarzynski 1997



$Q = \lambda\varepsilon$ $W = \varepsilon\Delta\lambda$

$$\frac{dE}{dt}(x,\lambda) = \underbrace{\frac{\partial E}{\partial x}\frac{dx}{dt}dt}_{\text{heat}} + \underbrace{\frac{\partial E}{\partial \lambda}\frac{\partial \lambda}{\partial t}dt}_{\text{work}}$$



work = force × displacement

Control distance $\frac{\partial E}{\partial L}\frac{\partial L}{\partial t}$

Control force $\frac{\partial E}{\partial \cancel{F}}\frac{\partial \tau}{\partial t}$