

$$\delta \stackrel{\text{ent. prod.}}{=} \geq 0$$

case 1:  $\dot{Q}_2 > 0 \Rightarrow \eta = \frac{P}{\dot{Q}_2} = 1 - \frac{T_1}{T_2} - T_1 \delta \leq 1 - \frac{T_1}{T_2} \stackrel{\text{Carnot bound}}{=} \eta_{\max}$

case 2:  $\dot{Q}_1 > 0$  (draw heat out of cold env.)

1st:  $P = \dot{Q}_1 + \dot{Q}_2 \Rightarrow \frac{\dot{Q}_2}{T_2} = -\frac{\dot{Q}_1}{T_1} - \delta$

2nd:  $\delta = -\frac{\dot{Q}_1}{T_1} - \frac{\dot{Q}_2}{T_2} \geq 0 \Rightarrow \dot{Q}_2 < 0$   
 (Stat. state or cycle) dumping heat into hot envir.

example: refrigerators  
heat pumps

$$\begin{aligned} \dot{Q}_2 &= -\frac{T_2}{T_1} \dot{Q}_1 - T_2 \delta \quad \frac{T_2}{T_1} > 1 \\ \Rightarrow |\dot{Q}_2| &> |\dot{Q}_1| \\ \Rightarrow P &= \dot{Q}_1 + \dot{Q}_2 = \dot{Q}_1 - |\dot{Q}_2| < 0 \\ \Rightarrow &\text{needs net power} \end{aligned}$$

input into system  
 $\Rightarrow$  plug in your fridge

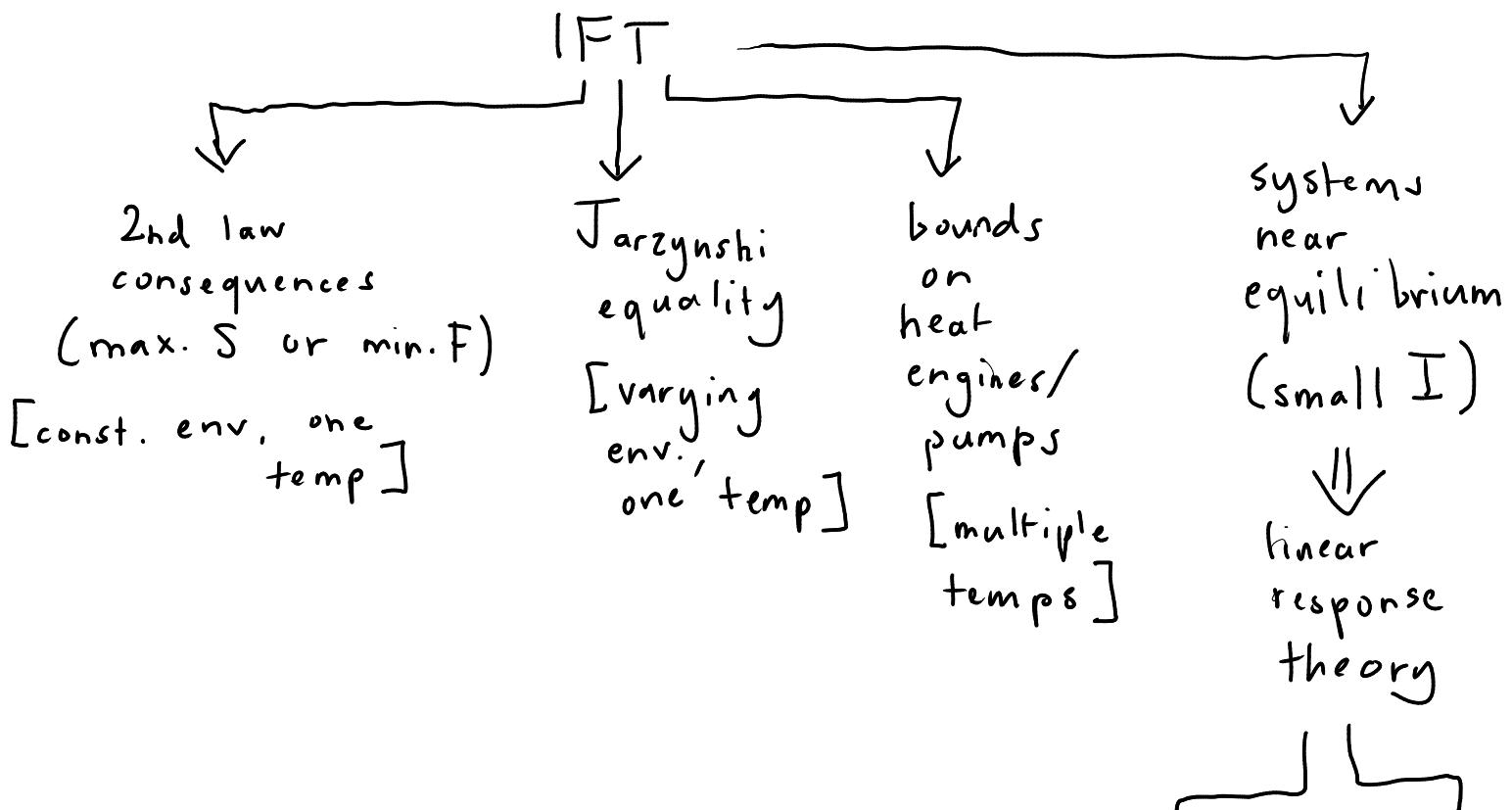
Coeff. of performance  $\eta_R = \frac{\dot{Q}_1}{-P} = \frac{\text{heat rate out of cold bath}}{\text{input power}}$

$$\eta_R = \frac{\dot{Q}_1}{-\dot{Q}_1 - \dot{Q}_2} = \text{algebra} = \frac{T_1}{T_2 - T_1} - \frac{T_1 T_2 \alpha}{\underbrace{T_2 - T_1}_{\leq 0}}$$

$$\eta_R \leq \frac{T_1}{T_2 - T_1} \stackrel{\sim 300K}{\underset{\sim 30K}{=}} \eta_R^{\max}$$

$\eta_R^{\max}$  can be quite large (on order  $\approx 10$ )

Big picture perspective: "messy children of IFT"



# Linear thermodynamics

single temp.  $T$  + stat. state

(not necessarily equil.)

Onsager reciprocity

fluctuation-dissipation theorem

$$2\text{nd: } I = -\frac{1}{T} \Delta F^{\circ} - \frac{1}{T} W \geq 0 \quad \Delta F^{\circ} = \Delta E^{\circ} - T \Delta S^{\circ}$$

$$1\text{st: } Q = \Delta E^{\circ} + \bar{W}$$

$$I = -\frac{1}{T} \bar{W} = -\frac{1}{T} Q \Rightarrow \begin{array}{l} Q = \bar{W} = -TI \leq 0 \\ \leq 0 \end{array}$$

heat into env.      work on sys.

$$I = 0 \Rightarrow ESS \quad (Q = \bar{W} = 0)$$

$$I > 0 \Rightarrow NESS \quad (Q = \bar{W} < 0)$$

"near" equil:  $I$  small ( $Q = \bar{W}$  is small)

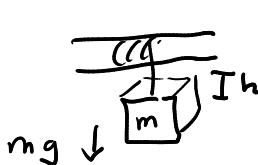
focus on one time step  $\delta t$ :  $M_0 = (n_0, n_1)$

$$I = \langle I(M_0) \rangle = -\frac{1}{T} \bar{W} = -\frac{1}{T} \langle W(\mu_0) \rangle P_{n_0}^s P_{n_1}^s$$

assume form for work:  $\bar{W}(M_0) = \omega_{n_1, n_0}$

$= -f \delta x_{n_1, n_0}$   
 $\uparrow$   
 "force"      "distance":

(some phys. change in obsr.  
 quantity we control)



$$f = mg$$

$$\delta x_{n_1, n_0} = \begin{cases} +h & \text{if } n_1 = n_0 + 1 \\ -h & \text{if } n_1 = n_0 - 1 \\ 0 & \text{otherwise} \end{cases}$$

$$f = 0 \Rightarrow \bar{W}(\mu_0) = 0 \Rightarrow \bar{W} = 0 \Rightarrow J = 0$$

ESS

assume:  $\delta_{X_{nm}} = -\delta_{X_{mn}}$      $\delta_{X_{nn}} = 0$

when  $f \neq 0$ :  $\bar{W} = -f \langle \delta_X \rangle = -f \sum_{n,n_0} P(\mu_0) \delta_{X_{n,n_0}}$   
 $= -f \sum_{n,n_0} W_{n,n_0} p_n^s \delta_{X_{n,n_0}}$

LDB:  $\frac{W_{n,n_0}}{W_{n_0,n_1}} = e^{-\beta(E_{n_1} - E_{n_0} - f \delta_{X_{n,n_0}})}$   
 $\vec{W_p}^s = \vec{p}^s$

$\Rightarrow$  both  $W$  &  $\vec{p}^s$  (it's right e-vec)  
depend on  $f$

in limit  $f \rightarrow 0$ :  $p_n^s \rightarrow p_n^{eq} = \frac{e^{-\beta E_n}}{\bar{Z}}$   
(ESS)

$$W_{nm} \rightarrow W_{nm}^{eq}$$
 (equil. trans.  
matrix)

$$\underbrace{W_{nm} p_m^s}_{g(f)} = W_{nm}^{eq} p_m^{eq} \left( 1 + c_{nm} f + \dots \right)$$

$\uparrow$  coeff. related  
to Taylor exp:  $\frac{g'(0)}{g(0)}$

$$\begin{aligned} g(f) &= g(0) + g'(0)f + \frac{1}{2} g''(0)f^2 + \dots \\ &= g(0) \left( 1 + \frac{g''(0)}{g(0)}f + \frac{1}{2} \frac{g'''(0)}{g(0)}f^2 + \dots \right) \end{aligned}$$

Plug into avg.  $\bar{W}$  expression

$$W = -f \sum_{n,n_0} \underbrace{W_{n,n_0}^{eq}}_{\text{Symm. under } n_0 \leftrightarrow n_1} \underbrace{P_{n_0}^{el}}_{\text{anti-symm.}} \delta x_{n,n_0}$$

$$-f \sum_{n,n_0} W_{n,n_0}^{el} P_{n_0}^{eq} C_{n,n_0} f \delta x_{n,n_0} + \dots$$

LDB in equil:  $W_{n,n_0}^{el} P_{n_0}^{eq} = W_{n_0,n_1}^{el} P_{n_1}^{eq}$