Recap from L2

$\vec{X} = \{X_1, X_2 \ldots\}$ TD coords

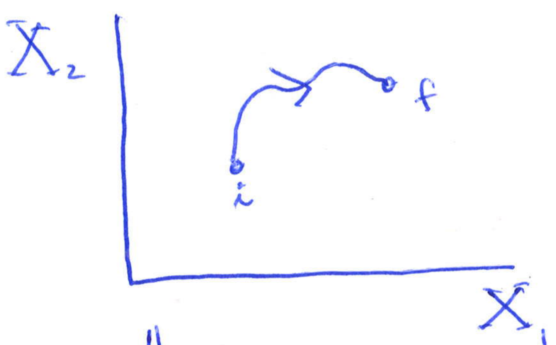
$$* \; \underline{1^{st}\text{ Law}}: \quad \underbrace{dE(\vec{X})}_{\text{depends on } \underline{\text{State}}} = \underbrace{đW + đQ}_{\text{depends on } \underline{\text{Path}}}$$

* Group TD coords $\{X_i\}$ into
- generalized forces $\{J_i\}$ intensive $(F, \sigma, -P, \vec{B}, \vec{E})$
- generalized displacements $\{x_i\}$ extensive $(L, A, V, \vec{M}, \vec{P})$

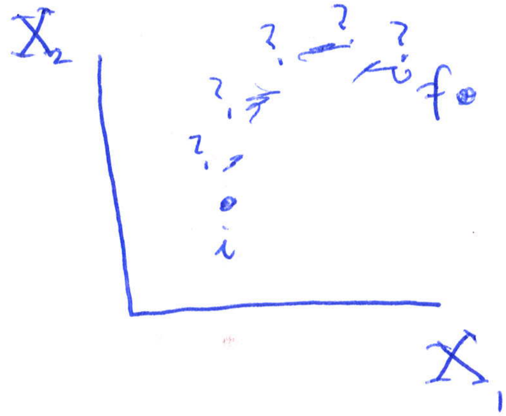
$\Downarrow$

* quasi-static changes (inf. close to equilibrium)

"Know where we are in $\vec{X}$-space at all intermediate steps"



vs



$\Downarrow$

$$dE(\vec{X}) = \sum_{i=1}^{n} J_i \, dx_i + đQ$$

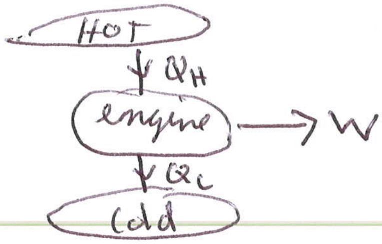
n: # of ways to do work on system

* Analogy w/ Mechanical equilibrium between 2 systems $J_i^{(1)} = J_i^{(2)}$

$\Rightarrow$ Thermal eq. implies $T^{(1)} = T^{(2)}$

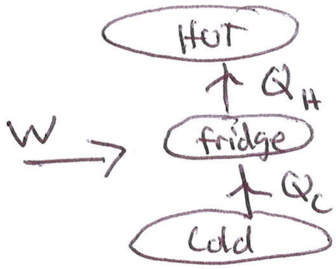
$\therefore$ "guess" that $đQ = T \, \underbrace{d(?)}_{\text{will turn out to be entropy } dS}$

Heat engines



$$\eta = \frac{W}{Q_H} = 1 - \frac{Q_C}{Q_H}$$

Refrigerators



$$\omega = \frac{Q_C}{W} = \frac{Q_C}{Q_H - Q_C}$$

Carnot Engine: (reversible, cyclic, operates between $T_H > T_C$)

Carnot theorem: ① $\eta_{CE}(T_H, T_C) \geq \eta_E(T_H, T_C)$ (i.e., CE = max. theoretical efficiency)

② all CE have same $\eta_{CE}(T_H, T_C)$.

$\Downarrow$

③ $$1 - \eta(T_1, T_2) = \frac{Q_2}{Q_1} = \frac{f(T_2)}{f(T_1)} \overset{\text{conv}}{=} \frac{T_2}{T_1}$$

$\Rightarrow$ absolute TD temperature scale °K

$\Rightarrow$ Universal (unlike ideal gas)

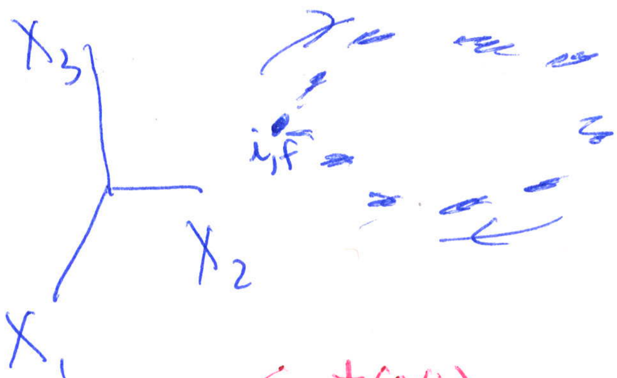
$\Rightarrow$ no $T < 0$

* To complete our discussion of the 2nd Law, we need to come back to our handwaving guess that

$$đQ = T\, d(?)$$

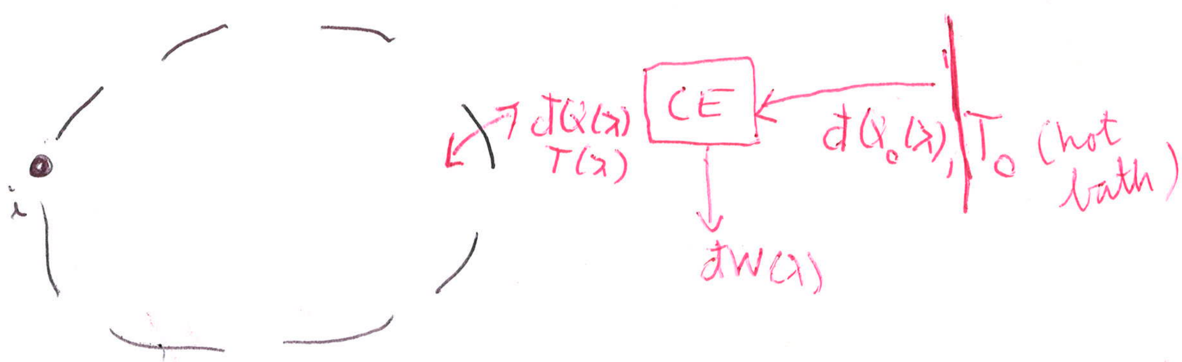
* Now we complete the argument following Clausius: "Clausius's theorem"

Theorem: Consider an arbitrary (i.e, don't restrict to quasi static) complex cyclic process carried out on some system.



then $\displaystyle\oint \frac{đQ(\lambda)}{T(\lambda)} \leq 0$ (λ = some parametric rep. of where we are in the cyclic process)

* proof: break the cycle into infinitesimal steps labelled by λ, and for each step assume $đQ(\lambda)$ (which can be >0 or <0) delivered by a Carnot engine that always takes heat from T_0

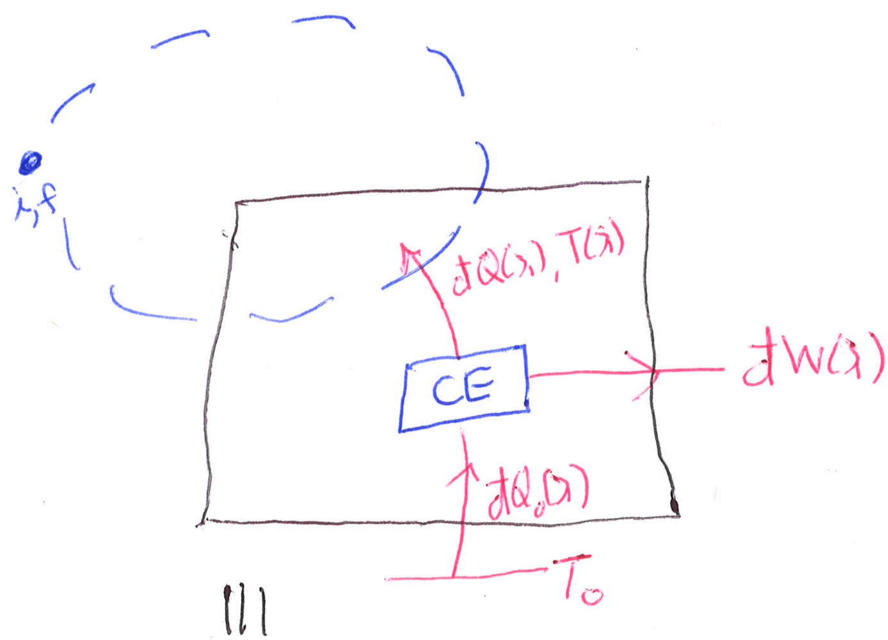


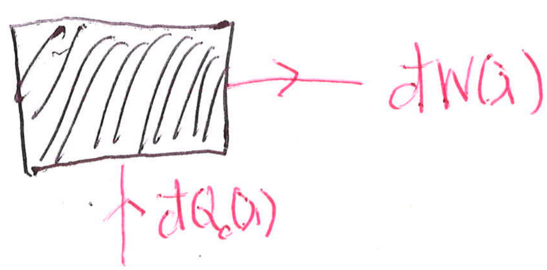
* Remarks:

1.) $T(\lambda)$ requires some finesse. For arbitrary (i.e, non quasi-static) changes, the system is not in equilibrium. Therefore, need to view $T(\lambda)$ as a "local" temperature (e.g., at the port where the CE is injecting/removing heat from system)

2.) At this point, Clausius' theorem seems kind of pointless, but it will eventually lead us to discover entropy & the famous result that it must increase or stay the same.

* Now we do our usual "black box" trick





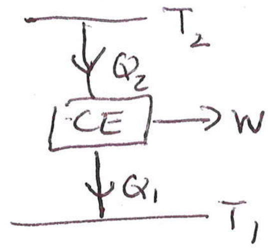
Net extracted heat converted to work

$$= \oint đQ_0(\lambda)$$

Net heat extracted from CE $= \oint đQ_0(\lambda)$

---

* Now recall our earlier result $1-\eta(T_1,T_2) = \dfrac{Q_1}{Q_2} = \dfrac{T_1}{T_2}$



$$\therefore \frac{đQ_0(\lambda)}{đQ(\lambda)} = \frac{T_0}{T(\lambda)}$$

$$\therefore \oint đQ_0(\lambda) = T_0 \oint \frac{đQ(\lambda)}{T(\lambda)}$$ = total heat extracted/ work performed.

* But recall Kelvin's statement of the 2nd law: impossible for a process where the sole effect is to convert heat entirely to work. (Reverse is ok though - can convert work entirely to heat)

$\Downarrow$

Therefore, must have $\oint đQ_0(\lambda) \leq 0$

(since $T_0 > 0$)

$$\Rightarrow \cancel{T_0} \oint \frac{đQ(\lambda)}{T(\lambda)} \leq 0$$

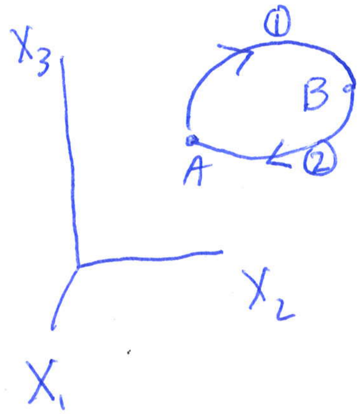
$\therefore$ Have shown $\displaystyle\oint \frac{đQ(\lambda)}{T(\lambda)} \leq 0$

QED.

Consequences of Clausius Theorem

① Reversible Processes

(note: Reversible ⇒ quasistatic)



$$\oint \frac{đQ(\lambda)}{T(\lambda)} \leq 0$$

$\Downarrow$ reverse path

$$đQ(\lambda) \to -đQ(\lambda)$$

$$\therefore \pm \oint \frac{đQ(\lambda)}{T(\lambda)} \leq 0$$

$$\boxed{\Rightarrow \oint \frac{đQ(\lambda)}{T(\lambda)} \underset{\text{process}}{\overset{\text{rev.}}{=}} 0}$$

② Path independence:

$$\oint \frac{đQ}{T} = 0 = \underset{\text{Path ①}}{\int_A^B} \frac{đQ}{T} + \underset{\text{Path ②}}{\int_B^A} \frac{đQ}{T} = 0$$

$$\therefore \underset{\text{Path ①}}{\int_A^B} \frac{đQ}{T} = \underset{\text{Path ②}' = -②}{\int_A^B} \frac{đQ}{T}$$

Suggests introducing a new state function $S(\vec{X})$ "entropy"

$$\boxed{\therefore \int_A^B \frac{đQ}{T} = S(B) - S(A)} \xrightarrow{\text{taking } A \to B} \boxed{đQ = T\,dS \text{ for reversible processes}}$$

③ Completed form of 1st Law

$$\boxed{\begin{aligned} dE &= đW + đQ \\ &= \sum_i J_i dx_i + T dS \end{aligned}}$$

Comment: Even though we used the notion of reversible processes to derive this, it holds regardless.
(i.e., it is a relation between 2 functions of state, $E(\vec{X})$ + $S(\vec{X})$)

④ Number of independent variables

* Say n conjugate pairs (x_i, J_i) → n ways of doing work on the system

$$dE = \sum_{i=1}^{n} J_i dx_i + T dS$$

$$\boxed{\Rightarrow (n+1) \text{ independent variables needed (free to choose which)}}$$

e.g. taking $(E, \{x_i\})$ as indep. variables

$$dS(E, \{x_i\}) = \frac{1}{T} dE - \frac{1}{T} \sum_{i=1}^{n} J_i dx_i$$

$$\Rightarrow \boxed{\left.\frac{\partial S}{\partial E}\right|_{\vec{x}} = \frac{1}{T} \quad \text{and} \quad \left.\frac{\partial S}{\partial x_i}\right|_{x_{j \neq i}, E} = -\frac{J_i}{T}}$$

(5) Increase of Entropy

* Here we use Clausius' theorem to derive the famous result that any spontaneous process on an isolated system must increase (or not change) its entropy

* Consider an arbitrary <u>irreversible process</u> A→B, followed by a <u>reversible</u> process B→A:

$$\oint \frac{đQ}{T} \leq 0$$

$$\Rightarrow \int_A^B \frac{đQ_{irr}}{T} + \int_B^A \frac{đQ_{rev}}{T} \leq 0$$

$$\therefore \int_A^B \frac{đQ_{irr}}{T} \leq S(B) - S(A)$$

* taking B→A inf. close

$$\Rightarrow \boxed{dS \geq \frac{đQ}{T}}$$

(equality for reversible, $dS > \frac{đQ}{T}$ for irrev.)

* Now let the system be <u>isolated w/adiabatic walls</u> ($đQ = 0$)

$$\Rightarrow \boxed{dS \geq 0 \quad \text{for isolated Closed System}}$$

alternative statement of the 2nd Law based on $dS \geq 0$

2nd Law: When equilibrium is disturbed in an isolated system, the entropy increases.

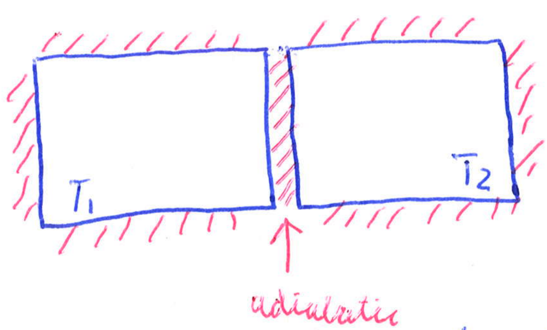
... or more succinctly ...

S is maximized at equilibrium

Subtle point: $S(E,\{x_i\})$ is a state function, only defined in equilibrium. How can you maximize a function that is only defined in equilibrium at its maximum ?!?

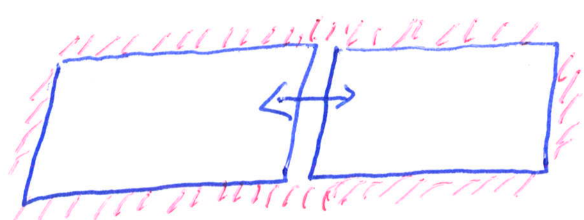
What it really means is this. Say you have a system in equilibrium with some internal constraint

e.g.) 2 isolated boxes of gas at T_1 + T_2



/// (e.g, insulation)

Now remove the insulation so the boxes can exchange heat w/ each other



$$dS = dS_1 + dS_2$$

$$= \frac{dQ_1}{T_1} + \frac{dQ_2}{T_2}$$

but $dQ_1 + dQ_2 = 0$
(isolated sys + cons. of energy)

$$= dQ_1 \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

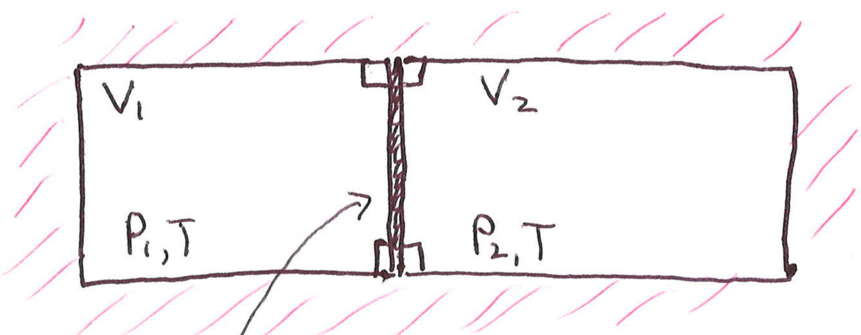
$\underline{T_1 > T_2} \Rightarrow dQ_1 < 0$ by Clausius's version of 2^{nd} Law

$\underline{T_2 > T_1} \Rightarrow dQ_1 > 0$ " "

* So entropy of the closed system increases when you remove the insulation so the 2 boxes exchange heat

* The "new equilibrium" achieved when
$dS = 0 \Rightarrow T_1 = T_2$

<u>ex 2</u>:



heat conducting (i.e, diathermal) piston that is clamped down so it can't slide

* Now remove the clamps so the piston is free to slide.

let $V_1 = \alpha V$ $\qquad V_1 + V_2 = V$

$V_2 = (1-\alpha) V$

$$S = S_1(V_1) + S_2(V_2) = S_1(\alpha V) + S_2((1-\alpha)V)$$

$\therefore$ new equilibrium is when

$$dS = 0 = \frac{\partial S_1}{\partial V_1} dV_1 + \frac{\partial S_2}{\partial V_2} dV_2$$

$$= \frac{P_1}{T} dV_1 + \frac{P_2}{T} dV_2$$

$dV_1 = \alpha dV$

$dV_2 = -\alpha dV$

$$0 = \frac{\alpha dV}{T}(P_1 - P_2)$$

or $P_1 = P_2$ (as expected)