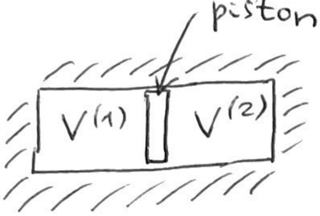
Lecture 2

Variational statement of 2nd law

Consider an <u>internal</u> constraint applied quasi-statically at const $E, \vec{X}$.

<u>Ex.</u>

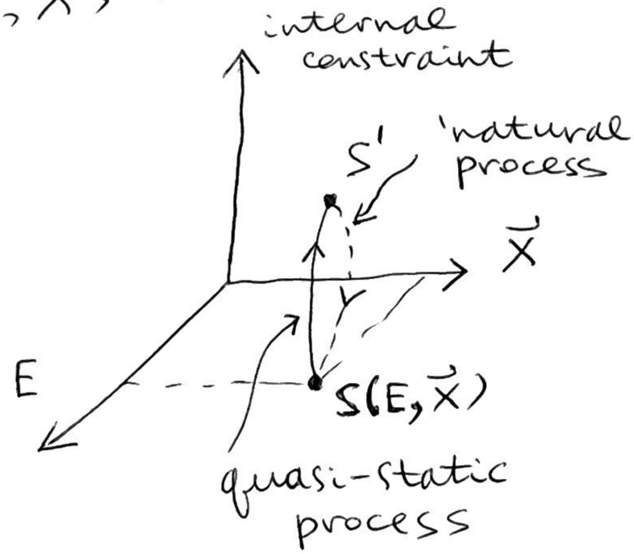


Move the piston: $V = V^{(1)} + V^{(2)} = \text{const}$

but in general $W \neq 0 \Rightarrow \Delta E \neq 0$.

Now, consider a system initially at equil. with $E, \vec{X} \Rightarrow S(E, \vec{X})$. Then imagine an internal constraint applied reversibly to s.t. the system goes to

$S' = S(E, \vec{X}; \text{internal constraint})$



E–$\vec{X}$ plane = = manifold of equilibrium states w/out the constraint

Since work is done in imposing the constraint, we need heat flows to enforce $E_f = E_i = E$ $\Rightarrow$ non-adiabatic process.

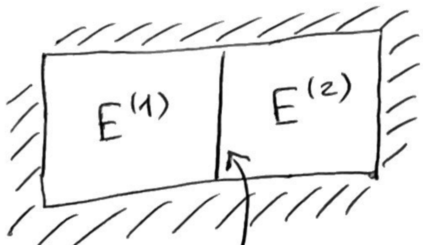
Now, insulate the system adiabatically (no more heat flows) & release the constraint. The system will go back 'naturally' to $S(E,X)$.

2$^{\text{nd}}$ law: $S - S' > 0$ [S is adiabatically accessible from S', the process is non-reversible]

$$\Downarrow$$

$$S(E,\vec{X}) > S(E,\vec{X}; \text{internal constraint})$$

Ex.



heat-conducting wall

$$t=0: \quad E = E_i^{(1)} + E_i^{(2)} \Rightarrow S(E,\vec{X}; E_i^{(1)}, E_i^{(2)})$$

$$\wedge$$

$$t=\infty: \quad E = E_f^{(1)} + E_f^{(2)} \Rightarrow S(E,\vec{X}; E_f^{(1)}, E_f^{(2)})$$

In other words, $E_f^{(1)}$ will maximize

$$S(E,\vec{X}; E^{(1)}, E - E^{(1)}) \Rightarrow \text{max entropy principle}$$

Now, consider

$$S(E_f^{(1)} + E_f^{(1)}, \vec{X}^{(1)} + \vec{X}^{(2)}) >$$

$$> S(E_f^{(1)} - \Delta E, \vec{X}^{(1)}) + S(E_f^{(2)} + \Delta E, \vec{X}^{(2)}),$$

where ΔE = energy transferred $1 \to 2$

Recall that $S \uparrow$ as $E \uparrow$. Then

$\exists \quad E < E_f^{(1)} + E_f^{(2)}$ s.t.

$$S(E_f^{(1)} - \Delta E, \vec{X}^{(1)}) + S(E_f^{(2)} + \Delta E, \vec{X}^{(2)}) =$$

$$= S(E, \vec{X}^{(1)} + \vec{X}^{(2)}).$$

In other words, if $\underset{S_1 + S_2}{\underset{\parallel}{S}}$ & $\overset{\vec{X}^{(1)} + \vec{X}^{(2)}}{\overset{\parallel}{\vec{X}}}$ stay

fixed, $(E_f^{(1)} - \Delta E) + (E_f^{(2)} + \Delta E) = \underbrace{E_f^{(1)} + E_f^{(2)}}_{\text{with constraints}} >$

$> \underbrace{E}_{\text{without constraints}} \quad \Leftarrow$ min E principle

$\downarrow$

$E(S, \vec{X})$ is a global min of $E(S, \vec{X};$ internal constraints$)$

Now, consider

constraint (internal) extensive variable

$$\Delta E = E(S, \vec{X}; \delta Y) - E(S, \vec{X}; 0) =$$

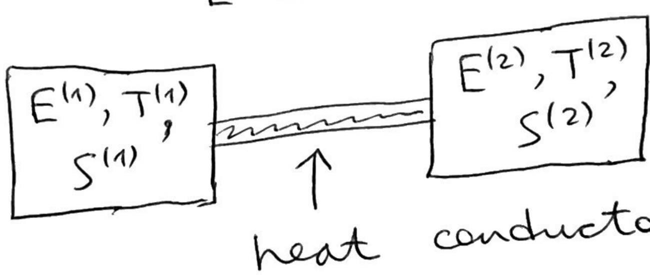
$$= \underbrace{\left(\frac{\partial E}{\partial Y}\right)_{S,\vec{X}}\Bigg|_{Y=0} \delta Y}_{\equiv\, (\delta E)_{S,\vec{X}}} + \underbrace{\frac{1}{2}\left(\frac{\partial^2 E}{\partial Y^2}\right)_{S,\vec{X}}\Bigg|_{Y=0} (\delta Y)^2}_{\equiv\, (\delta^2 E)_{S,\vec{X}}} + \ldots$$

$(\Delta E)_{S,\vec{X}} > 0$ for a small variation away from the stable equil. state, ($(\delta^2 E)_{S,\vec{X}} > 0$) yielding $(\delta E)_{S,\vec{X}} \geq 0$ to 1^{st} order.

Similarly, $(\Delta S)_{E,\vec{X}} < 0 \Rightarrow (\delta S)_{E,\vec{X}} \leq 0$.

$$E = E^{(1)} + E^{(2)} = \text{const}$$

Ex.



How are $T^{(1)}$ & $T^{(2)}$ related @ equil.?

Imagine a small displacement from equil. due to an internal constraint:

$$(\delta S)_{E,\vec{X}} \leq 0.$$

Moreover, $E = \text{const} \Rightarrow \delta E^{(1)} = -\delta E^{(2)}$.

Since $S = S^{(1)} + S^{(2)}$,

$$\delta S = \delta S^{(1)} + \delta S^{(2)} =$$

$$= \left(\frac{\partial S^{(1)}}{\partial E^{(1)}}\right)_{\vec{x}} \delta E^{(1)} + \left(\frac{\partial S^{(2)}}{\partial E^{(2)}}\right)_{\vec{x}} \delta E^{(2)} =$$

$$= \left(\frac{1}{T^{(1)}} - \frac{1}{T^{(2)}}\right) \delta E^{(1)} \leq 0 .$$

It's true for $\delta E^{(1)} \gtrless 0 \Rightarrow$

$\Rightarrow \boxed{T^{(1)} = T^{(2)}}$ @ equil.

$\hookrightarrow \delta S = 0$ @ equil.

· So, $T^{(1)} = T^{(2)}$ @ equil. follows from the 2nd law (max S principle).

What if $T^{(1)} \neq T^{(2)}$ @ $t = 0$?

as the system relaxes to equil., as $t \to \infty$

$\Delta S > 0$

$\parallel$ $\Delta S^{(1)} + \Delta S^{(2)}$, or to 1st order

$$\left(\frac{\partial S^{(1)}}{\partial E^{(1)}}\right)_{\vec{x}} \Delta E^{(1)} + \left(\frac{\partial S^{(2)}}{\partial E^{(2)}}\right)_{\vec{x}} \underbrace{\Delta E^{(2)}}_{-\Delta E^{(1)}\ (E = \text{const})} > 0,$$

$$\left(\frac{1}{T^{(1)}} - \frac{1}{T^{(2)}}\right)\Delta E^{(1)} > 0 .$$

If $T^{(1)} > T^{(2)} \Rightarrow \frac{1}{T^{(1)}} - \frac{1}{T^{(2)}} < 0 \Rightarrow$

$\Rightarrow \Delta E^{(1)} < 0 \Leftarrow$ heat flows hot $\to$ cold

If $T^{(1)} < T^{(2)} \Rightarrow \Delta E^{(1)} > 0 .$

[So, heat is energy flow due to gradient of T.]

Thus, it makes sense to introduce <u>heat capacities</u>:

$$C = \frac{đQ}{dT} = T\frac{dS}{dT} .$$

More precisely, one can define

$$C_{\vec{f}} = T\left(\frac{\partial S}{\partial T}\right)_{\vec{f}} , \quad C_{\vec{X}} = T\left(\frac{\partial S}{\partial T}\right)_{\vec{X}} .$$

Both $C_{\vec{f}}$ & $C_{\vec{X}}$ are extensive.

Legendre transforms

Consider
$$\vec{f}\cdot d\vec{x} = -\underset{\substack{\uparrow\\ \text{pressure}}}{p}\, d\overset{\text{volume}}{V} + \sum_{i=1}^{r} \overset{\text{chemical potential}}{\mu_i}\, dn_i$$

n_i = # particles of species i

Chemical potentials are intensive; control particle equil. just as T controls thermal equil.

Then $dE = TdS - pdV + \sum_{i=1}^{r} \mu_i dn_i$

$\searrow E = E(S, V, n_1, \dots, n_r)$

Variational principle:

$$(\Delta E)_{S,V,n} > 0 \Rightarrow (\delta E)_{S,V,n} \geq 0$$

$n = (n_1, \dots, n_r)$

But what if we want to work with T, V, n instead of S, V, n?

Suppose $f = f(x_1, \dots, x_n)$, then

$$df = \sum_{i=1}^{n} \underbrace{\left(\frac{\partial f}{\partial x_i}\right)_{x_{j\neq i}}}_{= u_i} dx_i .$$

Consider $g = f - \sum_{i=r+1}^{n} u_i x_i$, then

$$dg = df - \sum_{i=r+1}^{n} (u_i dx_i + x_i du_i) =$$

$$= \sum_{i=1}^{r} u_i dx_i - \sum_{i=r+1}^{n} x_i du_i$$

$$\searrow$$

$$g = g(x_1, \ldots, x_r, u_{r+1}, \ldots, u_n)$$

is a Legendre transform of f.

Now, construct

$$\underbrace{A}_{\text{Helmholtz free en.}} = E - TS \Rightarrow dA = -S dT - p dV + \sum_{i=1}^{r} \mu_i dn_i$$

$A = A(T, V, n)$ as desired

$$\left\{ \begin{array}{l} (S, V, n) \\ (T, V, n) \end{array} \right. \quad \begin{array}{l} (S, p, n) \\ (T, p, n) \end{array}$$

can all be used to describe the equil. state

Indeed, $\underbrace{G}_{\text{Gibbs free en.}} = E - TS + pV = G(T, p, n)$

$$\underbrace{H}_{\text{enthalpy}} = E + pV = H(S, p, n)$$

$$\begin{cases} dG = -SdT + Vdp + \sum_{i=1}^{r} \mu_i dn_i \\ dH = TdS + Vdp + \sum_{i=1}^{r} \mu_i dn_i \end{cases}$$

[Variational principles:]

non-equil. (constrained) $\to$ equil. $\quad T\Delta S \geq \Delta Q$ (T = const here)

(see p. 15 below Ex. 1.3)

Then for equil. $\to$ constrained

$$T\Delta S \leq \Delta Q$$

Now, $T\Delta S \leq \Delta Q = \Delta E - \Delta W$

If $V = \text{const}$, $\Delta W = 0$ (no mechanical work)

and $(\Delta E - T\Delta S)_{T,V,n} = (\Delta A)_{T,V,n} > 0$.

A is minimum @ equil. with T & V const

By the previous argument, $(\delta A)_{T,V,n} \geq 0$

If mechanical work is done @ $p = \text{const}$, $\Delta W = -p\Delta V$ and

$$T\Delta S \leq \Delta Q = \Delta E + p\Delta V, \text{ or}$$

$$(\Delta E + p\Delta V - T\Delta S)_{T,p,n} > 0,$$

$$(\Delta G)_{T,p,n} > 0 \Rightarrow (\delta G)_{T,p,n} \geq 0$$

G is minimum @ equil. with T & p const

Finally, one can show that

$$(\Delta H)_{S,p,n} > 0 \implies (\delta H)_{S,p,n} \geq 0$$

Indeed, $\Delta S = 0$ in this case and therefore $\Delta Q \gtrsim 0$ (need to pump heat into the constrained system to keep $\Delta S = 0$, otherwise $\Delta S < 0$ as discussed above)

$p = \text{const} \Rightarrow \Delta W = -p\Delta V$

Then $\Delta E - \Delta W = \Delta E + p\Delta V = (\Delta H)_{S,p,n} > 0$,

yielding $(\delta H)_{S,p,n} \geq 0$ as before.