Reversibility

def. applies when a change is made to a system in such a way that
thermal equilibrium is always maintained

In practice, this means the changes happen on a timescale slower than the equilibration timescale.

PRESSURE

For typical thermodynamic systems, like molecules of gas in a box, the energy U depends on the volume (often in direct proportion, but not always).

Suppose we do a volume change

$$V \to V - \Delta V$$

and we do it by reducing the size of a cube uniformly:

$$\Delta V = A\,\Delta x + A\,\Delta y + A\,\Delta z$$

Work done? (by energy conservation, this is energy added)

$$\Delta U = \underbrace{\overset{\substack{\boxed{\text{pressure}}\\ \downarrow}}{p}\,A}_{\substack{\text{force}\\ \text{in } x \text{ direction}}}\,\Delta x + pA\,\Delta y + pA\,\Delta z = p\,\Delta V$$

We want to keep each state in the story the same during the $\Delta V \Rightarrow$ degeneracy unchanged

$$\Rightarrow \boxed{p = -\left(\frac{\partial U}{\partial V}\right)_\sigma}$$

Now let's suppose

$$\sigma = \sigma(U,V)$$

$$\left.\begin{array}{l}\text{Let's • allow } U \text{ \& } V \text{ to vary} \\ \text{but • demand entropy is constant.}\end{array}\right\} \circledast$$

$$d\sigma = \left(\frac{\partial \sigma}{\partial U}\right)_V dU + \left(\frac{\partial \sigma}{\partial V}\right)_U dV \qquad U,V \text{ vary}$$

$$d\sigma = 0 \qquad \sigma \text{ constant}$$

$$\Rightarrow \underbrace{\left(\frac{\partial \sigma}{\partial U}\right)_V}_{\frac{1}{\tau}} \underbrace{\left(\frac{\partial U}{\partial V}\right)_\sigma}_{-p} + \left(\frac{\partial \sigma}{\partial V}\right)_U = 0$$

$$\Rightarrow \boxed{p = \tau\left(\frac{\partial \sigma}{\partial V}\right)_U}$$

This sort of game $\circledast$ is VERY common in thermo.
I need you all to be comfortable with it.

Now let's allow σ to vary freely

$$d\sigma = \left(\frac{\partial\sigma}{\partial U}\right)_V dU + \left(\frac{\partial\sigma}{\partial V}\right)_U dV$$

$$= \frac{1}{\tau} dU + \frac{p}{\tau} dV$$

$$\Rightarrow \boxed{dU = \tau\, d\sigma - p\,dV}$$

For reversible changes this says

(added energy) = (heat) − (work)

Helmholtz Free Energy

Let us define

$$\boxed{F \equiv -\tau \log Z}$$

i.e. we compute F directly from Z.

Let's find some of F's properties.

First, $-\frac{F}{\tau} = \log Z$ so $Z = e^{-F/\tau}$

Then the probability of being in state s, energy ε_s, is $P(\varepsilon_s) = \frac{e^{-\varepsilon_s/\tau}}{Z} = e^{-(\varepsilon_s - F)/\tau}$

We can use F to find U:

Since $U = \tau^2 \left(\frac{\partial \log Z}{\partial \tau}\right)$,

$$U = \tau^2 \frac{\partial}{\partial \tau}\left(-\frac{F}{\tau}\right)$$

$$= -\tau \frac{\partial F}{\partial \tau} + \tau^2 F\left(\frac{+1}{\tau^2}\right)$$

$$= F - \tau \frac{\partial F}{\partial \tau}$$

So $\boxed{U = \left(1 - \tau \frac{\partial}{\partial \tau}\right) F}$

Consider now this ↑ : $F = U + \tau\left(\frac{\partial F}{\partial \tau}\right)$ (*)

combined with $dU = \tau d\sigma - p dV$

$dU - \tau d\sigma = -p dV$

$\therefore dU - \tau d\sigma - \sigma d\tau = -p dV - \sigma d\tau$

$= d(U - \tau\sigma)$

Let us suppose that $U - \tau\sigma = f$ for some $f(\tau, V)$.

Then we have

$$df = \left(\frac{\partial f}{\partial V}\right)_\tau dV + \left(\frac{\partial f}{\partial \tau}\right)_V d\tau \Rightarrow p = -\left(\frac{\partial f}{\partial V}\right)_\tau \text{ and}$$

$$\sigma = -\left(\frac{\partial f}{\partial \tau}\right)_V \Rightarrow f = U + \tau\left(\frac{\partial f}{\partial \tau}\right)_V \quad \text{c.f. (*)}$$

$\Rightarrow f$ <u>is</u> F. $\Rightarrow \boxed{F = U - \tau\sigma}$

So. $\boxed{F = U - \tau\sigma}$

So $dF = dU - \tau\, d\sigma - \sigma\, d\tau$

$\quad = -p\,dV - \sigma\, d\tau$

So $\boxed{p = -\left(\frac{\partial F}{\partial V}\right)_\tau}$, $\boxed{\sigma = -\left(\frac{\partial F}{\partial \tau}\right)_V}$

Look more closely at the pressure.

$$p = -\left(\frac{\partial F}{\partial V}\right)_\tau$$

But $F = U - \tau\sigma$, so

$$p = -\underset{\substack{\uparrow \\ \text{familiar} \\ \text{piece from} \\ \text{gas-in-box}}}{\left(\frac{\partial U}{\partial V}\right)_\tau} + \tau \underset{\substack{\uparrow \\ \text{this part is} \\ \text{also important!}}}{\left(\frac{\partial \sigma}{\partial V}\right)_\tau}$$

- Consider varying U at constant τ.

$F = U - \tau\sigma$

$\Rightarrow dF = dU - \tau\, d\sigma$ at constant τ

Recall definition of temperature: $\frac{1}{\tau} = \left(\frac{\partial \sigma}{\partial U}\right)_V$.

So at constant V and τ,

$dF = 0$ $\quad$ F is extremised.

Two-state System (KK problem 3.1)

Energy levels 0 and ε.

$$Z = \sum_s e^{-\varepsilon_s/\tau}$$
$$= 1 + e^{-\varepsilon/\tau}$$

- Free energy?

$$F = -\tau \log Z$$
$$= -\tau \log(1 + e^{-\varepsilon/\tau})$$

← {fundamental definition/formula (that I did <u>not</u> prove)}

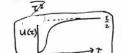
- Average energy?

$$U = \tau^2 \left(\frac{\partial \log Z}{\partial \tau}\right)$$

← (we derived this from scratch)

$$= \tau^2 \frac{\partial}{\partial \tau} \log Z$$
$$= \tau^2 \frac{1}{Z} \frac{\partial Z}{\partial \tau} = \frac{\cancel{\tau^2}}{(1+e^{-\varepsilon/\tau})} \, e^{-\varepsilon/\tau} \cdot \frac{+\varepsilon}{\cancel{\tau^2}}$$
$$= \frac{\varepsilon \, e^{-\varepsilon/\tau}}{(1 + e^{-\varepsilon/\tau})}$$

$(\rightarrow \varepsilon/2$ @ large-$\tau)$



✓

- Entropy?

$$\sigma = -\left(\frac{\partial F}{\partial \tau}\right)_V = -\frac{\partial}{\partial \tau}\left\{-\tau \log(1 + e^{-\varepsilon/\tau})\right\}$$

∵ const V ⇒ const ε

$$= \log(1 + e^{-\varepsilon/\tau}) + \frac{\tau \, 1 \, e^{-\varepsilon/\tau}}{(1+e^{-\varepsilon/\tau})}\left(\frac{+\varepsilon}{\tau^2}\right)$$
$$= \log(1 + e^{-\varepsilon/\tau}) + \frac{\varepsilon/\tau \, e^{-\varepsilon/\tau}}{(1+e^{-\varepsilon/\tau})}$$