Now, let's define temperature as

$$\frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)_{V,N}$$

$$\Rightarrow T_1 = T_2$$

- Finally, in this model of two subsystems, we can define "Equilibrium". Equilibrium is the condition that $T_1 = T_2$, which is the same as maximizing entropy $S_1 + S_2$, which is the same as ensuring that $\rho(E_1)$ has a sharp peak at some value E_1^*.

- For a system weakly coupled to the outside world, for each parcel of energy added to the system δE_1, we must accept entropy

$$\frac{\delta E}{T} = \delta E\left(\frac{\partial S}{\partial E}\right) = \delta S$$

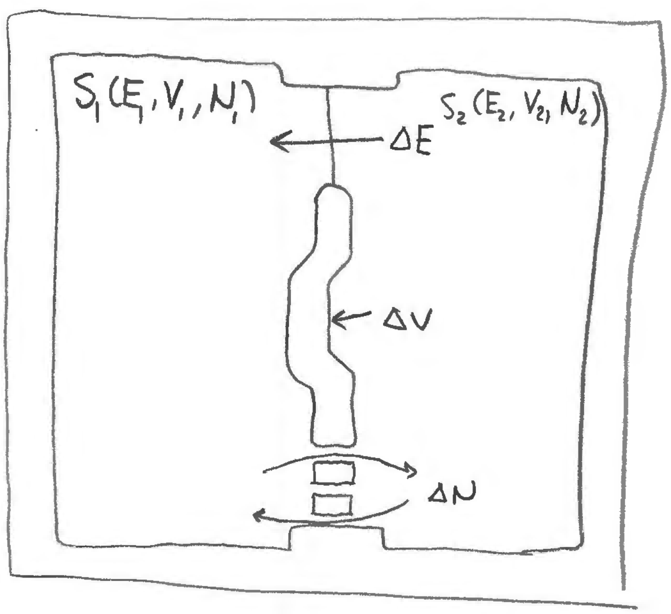
Pressure and Chemical Potential

In classical thermo, we defined pressure and chemical potential in terms of the energy of the system:

$$p = -\left(\frac{\partial E}{\partial V}\right)_{N,S} \qquad \mu = \left(\frac{\partial E}{\partial N}\right)_{S,V}$$

In this case, Energy $E(S,V,N)$ was our thermodynamic potential. $E(S,V,N)$ forms a surface, and the partial derivatives $\frac{\partial}{\partial S}$, $\frac{\partial}{\partial V}$, and $\frac{\partial}{\partial N}$ gave us a way to find pressure, chemical potential and other intensive quantities.

Using stat mech, we can do the same using entropy $S(E,V,N)$ for two subsystems:



How does $S(E,V,N)$ change as a result of changing E, V, and/or N?

Note:

$$E = E_1 + E_2 \Rightarrow E_2 = E - E_1 \qquad dE_2 = -dE_1$$
$$N = N_1 + N_2 \Rightarrow N_2 = N - N_1 \qquad dN_2 = -dN_1$$
$$V = V_1 + V_2 \Rightarrow V_2 = V - V_1 \qquad dV_1 = -dV_1$$

So

$$\Delta S = \left[\left(\frac{\partial S}{\partial E_1} \right)_{V,N} - \left(\frac{\partial S}{\partial E_2} \right)_{V,N} \right] \Delta E$$

$$+ \left[\left(\frac{\partial S}{\partial V_1} \right)_{E,N} - \left(\frac{\partial S}{\partial V_2} \right)_{E,N} \right] \Delta V$$

$$+ \left[\left(\frac{\partial S}{\partial N_1} \right)_{E,V} - \left(\frac{\partial S}{\partial N_2} \right)_{E,V} \right] \Delta N$$

At equilibrium $T_1 = T_2$ and

$$\left(\frac{\partial S}{\partial E_1} \right)_{V,N} = \left(\frac{\partial S}{\partial E_2} \right)_{V,N}$$

So the first term vanishes. What about the other two?

We assume that at equilibrium, entropy is maximized i.e. $\Delta S = 0$

$$\therefore \left(\frac{\partial S_1}{\partial V_1} \right)_{E,N} - \left(\frac{\partial S_2}{\partial V_2} \right)_{E,N} = 0$$

Now, recall if $f = f(x,y)$,

$$\left(\frac{\partial f}{\partial x} \right)_y \left(\frac{\partial x}{\partial y} \right)_f \left(\frac{\partial y}{\partial f} \right)_x = -1$$

and

$$\left(\frac{\partial f}{\partial x} \right)_y = \frac{1}{\left(\frac{\partial x}{\partial f} \right)_y}$$

Then

$$\left(\frac{\partial S}{\partial V}\right)_{E,N}\left(\frac{\partial V}{\partial E}\right)_{S,N}\left(\frac{\partial E}{\partial S}\right)_{V,N} = -1$$

$$\left(\frac{\partial S}{\partial V}\right)_{E,N} \cdot \left[\frac{1}{\left(\frac{\partial E}{\partial V}\right)_{S,N}}\right] \cdot T = -1$$

$$\left(\frac{\partial S}{\partial V}\right)_{E,N} T = \underbrace{-\left(\frac{\partial E}{\partial V}\right)_{S,N}}_{P!}$$

So

$$\boxed{\frac{P}{T} = \left(\frac{\partial S}{\partial V}\right)_{E,N}}$$

We can do the same trick for μ:

$$\mu = \left(\frac{\partial E}{\partial N}\right)_{S,V}$$

$$\boxed{-\frac{\mu}{T} = \left(\frac{\partial S}{\partial N}\right)_{E,V}}$$