

## Recap:

$$S = k_B \ln \Omega(N, V, E)$$

$\uparrow$  "natural variables"

$$dS = \left(\frac{\partial S}{\partial E}\right)_{N,V} dE + \left(\frac{\partial S}{\partial V}\right)_{N,E} dV + \left(\frac{\partial S}{\partial N}\right)_{V,E} dN$$

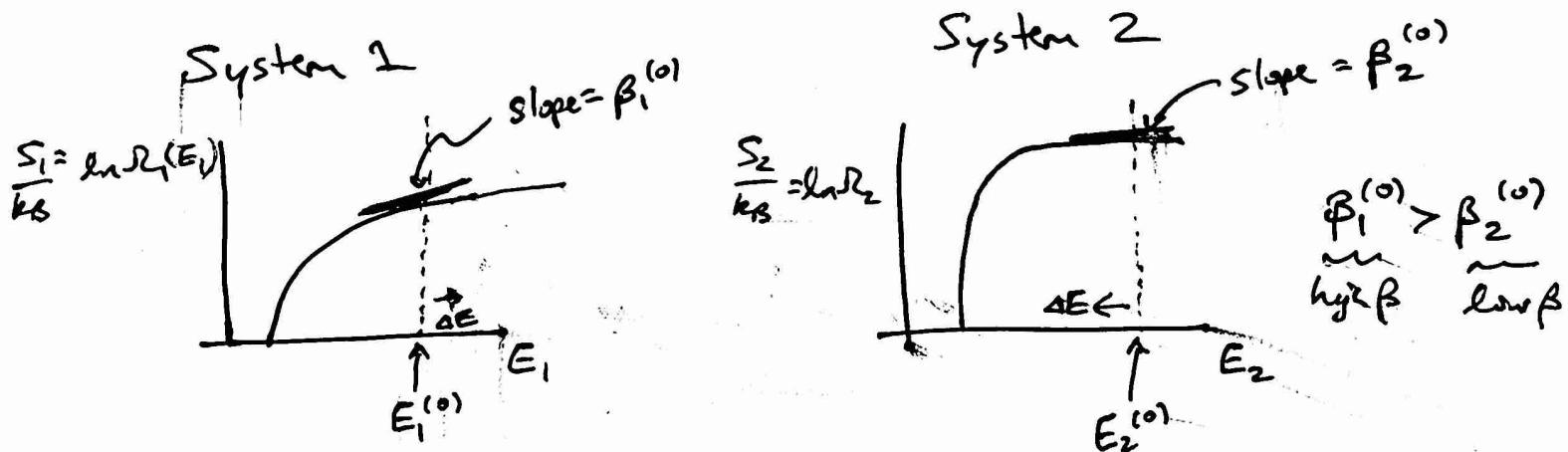
$$\left(\frac{\partial S}{\partial E}\right)_{N,V} = k_B \left(\frac{\partial \ln \Omega}{\partial E}\right)_{N,V} = k_B \beta = \frac{1}{T}$$

Put on the board after the bit below:

$$\left(\frac{\partial S}{\partial V}\right)_{N,E} \leftarrow \text{something to do w/ pressure}$$

$$\left(\frac{\partial S}{\partial N}\right)_{V,E} \leftarrow \text{something to do with chemical potential.}$$

We said  $\left(\frac{\partial S}{\partial E}\right)_{N,V} = k_B \beta$  means energy flows from low  $\beta$  to high  $\beta$ . Why?



$(S_1 + S_2)$  increases if  $\Delta E$  is transferred from system 2 (low  $\beta$ ) to system 1 (high  $\beta$ )

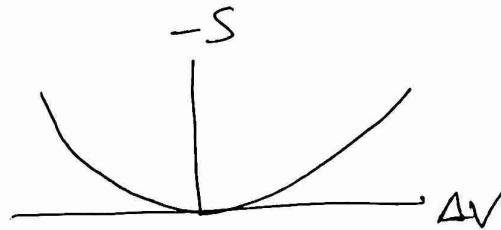
System 1 gains  $\beta_1^{(0)} \Delta E$ . System 2 loses  $\beta_2^{(0)} \Delta E$ . Collective gain of  $(\beta_1^{(0)} - \beta_2^{(0)}) \Delta E > 0$ . This energy flow continues until finally  $\beta_1 = \beta_2$ .



deformable,  
impermeable  
membrane

$$V_1 = V_1^{(eq)} + \Delta V$$

$$V_2 = V_2^{(eq)} - \Delta V$$



$\frac{\partial S}{\partial \Delta V} = 0$  at  
equilibrium

$$\Rightarrow \left( \frac{\partial S_1}{\partial V} \right)_{N_1, E_1} = \left( \frac{\partial S_2}{\partial V} \right)_{N_2, E_2}$$

After the volumes have equilibrated, what do you expect to equal?  
Pressure!

So  $\left( \frac{\partial S}{\partial V} \right)_{N, E} = p$  ? Not quite

$S = k_B \ln \Omega$  has units of...? Energy / Temperature

So  $\frac{\partial S}{\partial V}$  has units of  $\frac{\text{Energy}}{\text{Volume} \times \text{Temperature}}$

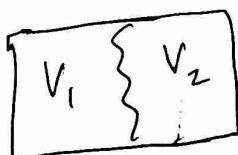
$$\Rightarrow \left( \frac{\partial S}{\partial V} \right)_{N, E} = \frac{p}{T}$$

Similarly when particles are exchanged,

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

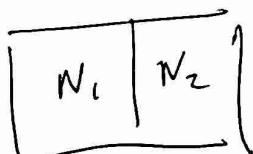
chemical potential

Why the minus sign? Particles flow from high  $\mu$  to low  $\mu$ .



Suppose  $p_1 > p_2 \Rightarrow V_1$  gets bigger

(They're  
opposite -  
just a  
convention)



Suppose  $\mu_1 > \mu_2 \Rightarrow N_1$  gets smaller

$$\text{Hence } dS = \left(\frac{\partial S}{\partial E}\right)_{N,V} dE + \left(\frac{\partial S}{\partial V}\right)_{N,E} dV + \left(\frac{\partial S}{\partial N}\right)_{E,V} dN$$

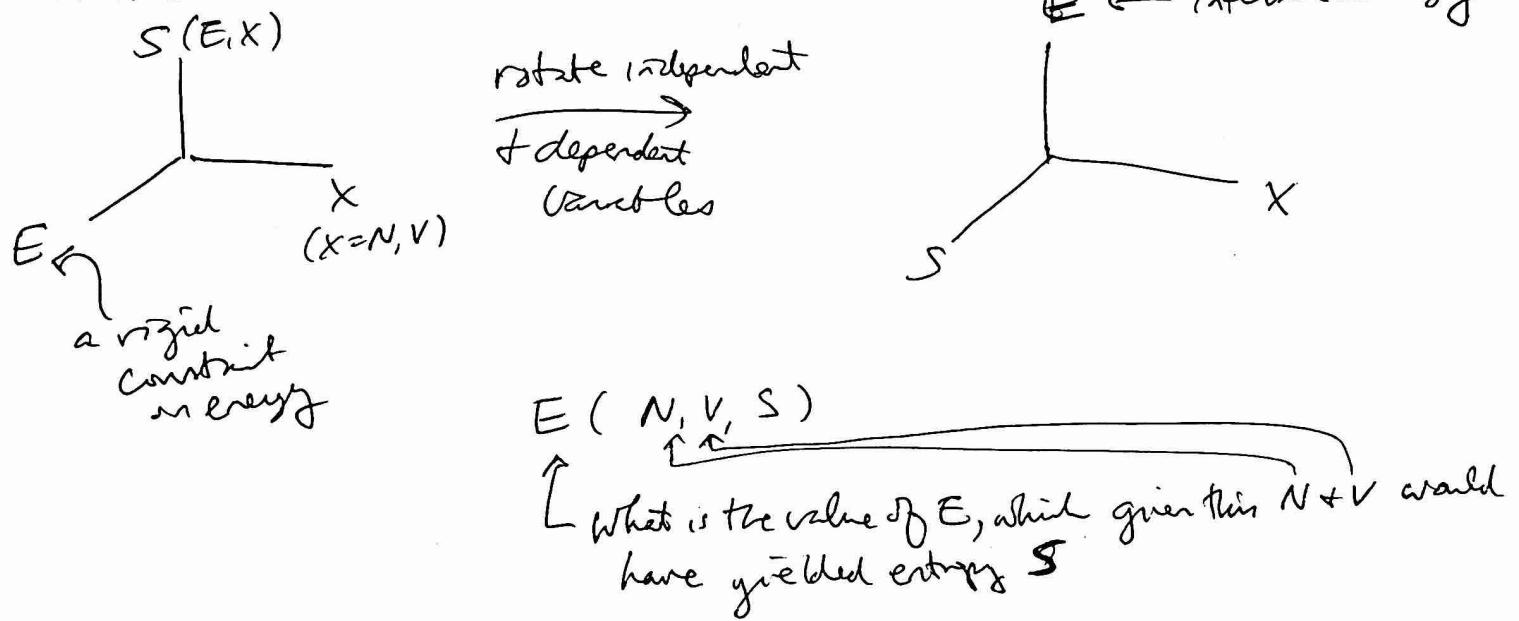
$$= \frac{1}{T} dE + \frac{P}{T} dV - \frac{\mu}{T} dN$$

$$\Rightarrow TdS = dE + pdV - \mu dN$$

$$\Rightarrow \boxed{dE = TdS - pdV + \mu dN}$$

Now we are thinking of  $E$  as a function of  $S, V, N$   
 $E(S, V, N)$

How can we do this?



This is all a little weird. With entropy we had

$S(N, V, E)$

3 macroscopic constraints that you could tune like knobs

$$dS = \left(\frac{\partial S}{\partial N}\right)_{V,E} dN + \left(\frac{\partial S}{\partial V}\right)_{N,E} dV + \left(\frac{\partial S}{\partial E}\right)_{N,V} dE$$

Now we are acting like we have control over an entropy knob and measuring energy as a result

$$E(N, V, S)$$

Well this is awkward.  
2 Macroscopic constraints  
that you can really think of tuning

Still...

$$dE = \left(\frac{\partial E}{\partial N}\right)_{V,S} dN + \left(\frac{\partial E}{\partial V}\right)_{N,S} dV + \left(\frac{\partial E}{\partial S}\right)_{N,V} dS \quad \leftarrow \text{This is just the chain rule}$$

Comparing with earlier, we see

$$\begin{aligned} \left(\frac{\partial E}{\partial S}\right)_{N,V} &= T \\ \left(\frac{\partial E}{\partial V}\right)_{N,S} &= -p \\ \left(\frac{\partial E}{\partial N}\right)_{V,S} &= \mu \end{aligned} \quad \left. \begin{array}{l} \text{We had previously} \\ \text{defined these in terms} \\ \text{of slopes of entropy.} \end{array} \right\}$$

But the "entropy knobs" is awkward! What would it mean in an experiment? Much more likely is that we can adjust the temperature  $T$  (along w/ $V+N$ ). Let us define a new function

$$A \equiv E - TS : \text{Helmholtz Free Energy}$$

$\uparrow$   
extensive variable  
 $\downarrow$   
conjugate intensive variable

What is the purpose of doing this?

$$dA = dE - d(TS) = dE - SdT - TdS = \underbrace{TdS}_{\text{in}} - pdV + \mu dN - SdT - \underbrace{TdS}_{\text{in}}$$

$$= - SdT - pdV + \mu dN \Rightarrow A(T, V, N)$$

↑ now we're thinking of a temperature knob.

$S(E, V, N)$

$\Sigma(E, V, N)$

Microcanonical

(all  $v$  have  
equal probability)

$A(T, V, N)$

[?]

Canonical

(probability of  $v$   
determined by  $T$  - or equivalently  $\beta$ )

"Thermodynamic Potential"

"Partition Function"

$Q(\beta, V, N)$

$$S = k_B \ln \Sigma \quad \text{and similarly} \quad A = -k_B T \ln Q$$

$S$  &  $A$  have to do with macroscopic systems - thermodynamics.  
 $\Sigma$  &  $Q$  have to do with sums over microstates - statistical mechanics

$$\Sigma = \sum_v (1)$$

$\omega(v, V, E)$

$$Q(T, V, N) = \sum_{\substack{v \\ v, V \\ V, N}} e^{-E(v)/k_B T}$$

If you know how to list out possible  $v$ 's and compute their energies, then you can (at least in principle) compute  $Q$  & therefore  $A = -k_B T \ln Q$  to determine the thermodynamic behavior from microscopic origins ( $v + E(v)$ ).

$$\begin{aligned}
 Q(T, V, N) &= \sum_E \Sigma(E, V, N) e^{-\beta E} \\
 &= \sum_E e^{S(E, V, N) / k_B} e^{-\beta E} \\
 &= \sum_E e^{\beta(T S(E, V, N) - E)}
 \end{aligned}$$