8.044 Statistical Physics I
Spring 2008

Microcanonical: E fixed + equal a priori probabilities

$\Rightarrow$ microscopic probability densities [S.M.]

Together with the definition of entropy

$\Rightarrow$ temperature scale and 2^{ND} law inequalities [Thermodynamics]

$$\left.\begin{array}{lll} \Delta S & \geq 0 & (3 \cdot 4 \cdot 7) \\ dS_1 & \geq \frac{đQ_1}{T} & (3 \cdot 6 \cdot 5) \end{array}\right\} 2^{ND} \text{ Law}$$

Quasi-static means arbitrarily close to equilibrium.

- Necessary for work differentials to apply
- Required for = in above 2^{ND} law relations

7. Entropy as a Thermodynamic Variable

$$\left(\frac{\partial S}{\partial E}\right)_{đW=0} \equiv \frac{1}{T} \qquad \text{gives us } T$$

Other derivatives give other thermodynamic variables.

$$đW = \left\{ \begin{array}{r} -PdV \\ \mathcal{S}dA \\ \mathcal{F}dL \end{array} \right\} + HdM + \mathcal{E}d\mathcal{P} + \cdots \equiv \sum_i X_i\, dx_i$$

We chose to use the extensive external variables (a complete set) as the constraints on Ω. Thus

$$S \equiv k \ln \Omega = S(\ E, V, M, \cdots\ )$$

Now solve for E.

$$S(E, V, M, \cdots) \leftrightarrow E(S, V, M, \cdots)$$

We know

$$dE|_{\not{d}W=0} = \not{d}Q \quad \text{from the } 1^{ST} \text{ law}$$

$$dE|_{\not{d}W=0} \leq TdS \quad \text{utilizing the } 2^{ND} \text{ law}$$

Now include the work.

$$dE = đQ + đW$$

$$dE \le TdS + đW$$

$$dE \le TdS + \left\{ \begin{array}{r} -PdV \\ \mathcal{S}dA \\ \mathcal{F}dL \end{array} \right\} + HdM + \mathcal{E}d\mathcal{P} + \cdots$$

<u>The last line expresses the combined</u>
<u>1^{ST} and 2^{ND} laws of thermodynamics.</u>

Solve for dS.

$$dS = \frac{1}{T}dE + \frac{P}{T}dV - \frac{H}{T}dM - \frac{\mathcal{E}}{T}d\mathcal{P} + \cdots$$

Examine the partial derivatives of S.

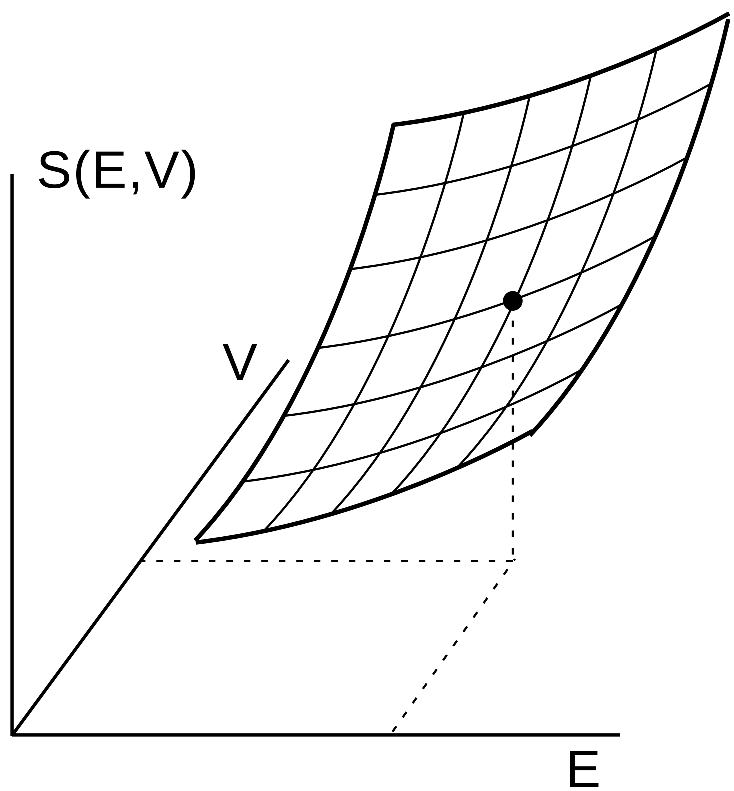
$$\left(\frac{\partial S}{\partial E}\right)_{V,M,\mathcal{P}} = \frac{1}{T}$$

$$\left(\frac{\partial S}{\partial M}\right)_{E,V,\mathcal{P}} = -\frac{H}{T}$$

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

$$\left(\frac{\partial S}{\partial x_j}\right)_{E,x_i \neq x_j} = -\frac{X_j}{T}$$

INTERPRETATION



$$dS = \left(\frac{\partial S}{\partial E}\right)_V dE + \left(\frac{\partial S}{\partial V}\right)_E dV$$

$$= \frac{1}{T}\, dE + \frac{P}{T}\, dV$$

UTILITY

Internal Energy

$$\left(\frac{\partial S(E,V,N)}{\partial E}\right)_V = \frac{1}{T} \;\rightarrow\; T(E,V,N) \leftrightarrow E(T,V,N)$$

Equation of State

$$\left(\frac{\partial S(E,V,N)}{\partial V}\right)_E = \frac{P}{T} \;\rightarrow\; P(E,T,V,N) \rightarrow P(T,V,N)$$

Example Ideal Gas

$$S(E,N,V) = k \ln \Phi = kN \ln \left\{ V \left(\frac{4}{3} \pi e m \left(\frac{E}{N} \right) \right)^{3/2} \right\}$$

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

$$\underline{PV = NkT}$$

COMBINATORIAL FACTS

different orderings (permutations) of K distinguishable objects $= K!$

of ways of choosing L from a set of K:

$$\frac{K!}{(K-L)!} \quad \text{if order matters}$$

$$\frac{K!}{L!(K-L)!} \quad \text{if order does not matter}$$

EXAMPLE Dinner Table, 5 Chairs (places)

Seating, 5 people $$5 \cdot 4 \cdot 3 \cdot 2 \cdot 1 = 5! = 120$$

Seating, 3 people $$5 \cdot 4 \cdot 3 = \frac{5!}{2!} = 60$$

Place settings, 3 people $$5 \cdot 4 \cdot 3/6 = \frac{5!}{2!}\,\frac{1}{3!} = 10$$