

Microcanonical: E fixed + equal a priori probabilities

⇒ microscopic probability densities [S.M.]

Together with the definition of entropy

⇒ temperature scale and 2^{ND} law inequalities [Thermodynamics]

$$\begin{array}{l}
 \Delta S \geq 0 \quad (3 \cdot 4 \cdot 7) \\
 dS_1 \geq \frac{dQ_1}{T} \quad (3 \cdot 6 \cdot 5)
 \end{array}
 \left. \vphantom{\begin{array}{l} \Delta S \geq 0 \\ dS_1 \geq \frac{dQ_1}{T} \end{array}} \right\} 2^{ND} \text{ Law}$$

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

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

Other derivatives give other thermodynamic variables.

$$dW = \left\{ \begin{array}{l} -PdV \\ SdA \\ \mathcal{F}dL \end{array} \right\} + HdM + \mathcal{E}d\mathcal{P} + \dots \equiv \sum_i X_i dx_i$$

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

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

Now solve for E .

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

We know

$$dE|_{\delta W=0} = \delta Q \quad \text{from the 1}^{ST} \text{ law}$$

$$dE|_{\delta W=0} \leq TdS \quad \text{utilizing the 2}^{ND} \text{ law}$$

Now include the work.

$$dE = \delta Q + \delta W$$

$$dE \leq TdS + \delta W$$

$$dE \leq TdS + \left\{ \begin{array}{l} -PdV \\ SdA \\ \mathcal{F}dL \end{array} \right\} + HdM + \mathcal{E}d\mathcal{P} + \dots$$

The last line expresses the combined
1ST and 2ND laws of thermodynamics.

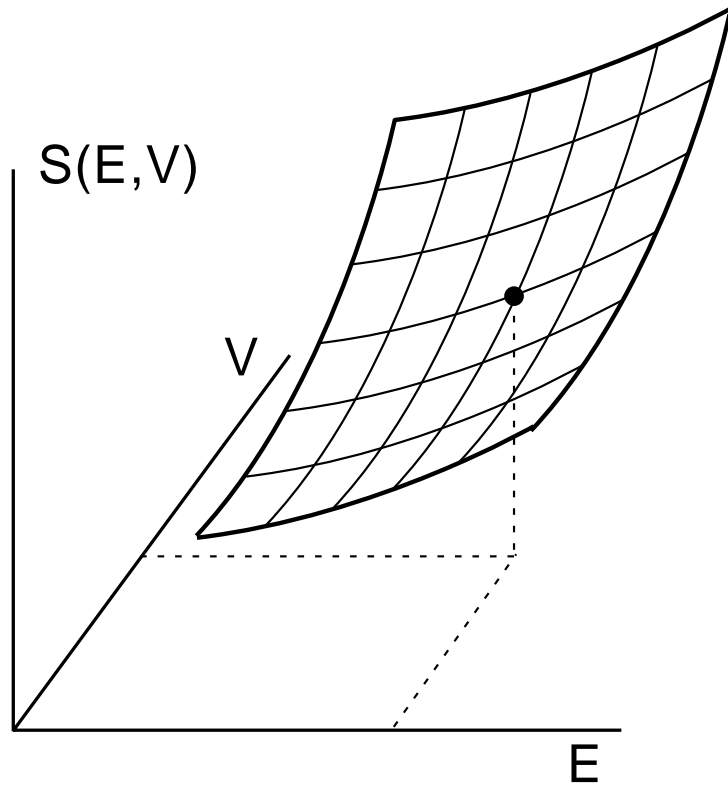
Solve for dS .

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

Examine the partial derivatives of S .

$$\left(\frac{\partial S}{\partial E}\right)_{V,M,\mathcal{P}} = \frac{1}{T} \qquad \left(\frac{\partial S}{\partial M}\right)_{E,V,\mathcal{P}} = -\frac{H}{T}$$
$$\left(\frac{\partial S}{\partial V}\right)_{E,M,\mathcal{P}} = \frac{P}{T} \qquad \left(\frac{\partial S}{\partial x_j}\right)_{E,x_i \neq x_j} = -\frac{X_j}{T}$$

INTERPRETATION



$$\begin{aligned} dS &= \left(\frac{\partial S}{\partial E} \right)_V dE + \left(\frac{\partial S}{\partial V} \right)_E dV \\ &= \frac{1}{T} dE + \frac{P}{T} dV \end{aligned}$$

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

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