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.

$$dE = đQ + đW$$

$$dE \leq TdS + đW$$

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

<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.

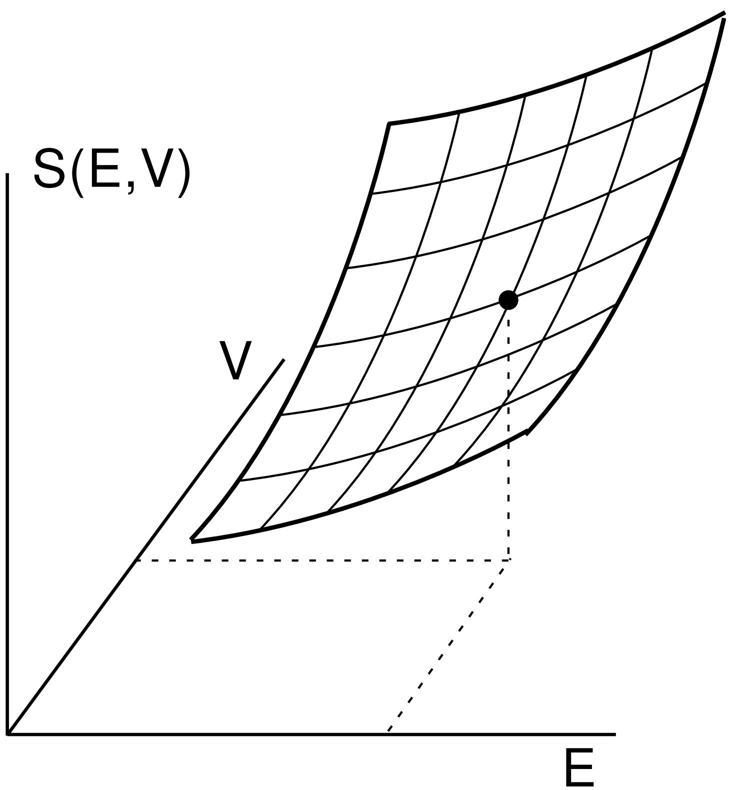
$$\left(\frac{\partial S}{\partial E}\right)_{V,M,\mathcal{P}} = \frac{1}{T}$$

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

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

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

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

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

Equation of State

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

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:

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

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

EXAMPLE Dinner Table, 5 Chairs (places)

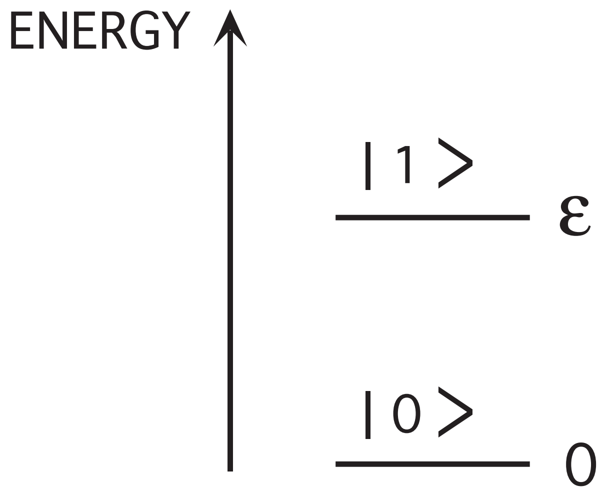
Seating, 5 people $5 \cdot 4 \cdot 3 \cdot 2 \cdot 1 = 5! = 120$

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

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

<u>EXAMPLE</u> 2 Level System

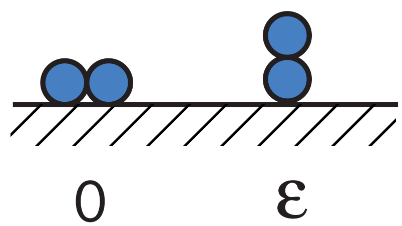
Ensemble of N "independent" systems



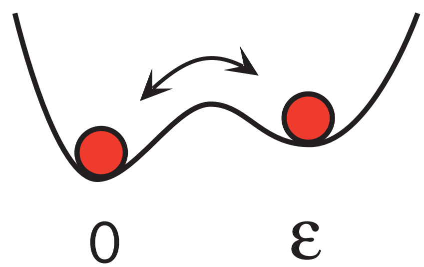
$$N = N_0 + N_1$$

$$E = \varepsilon N_1$$

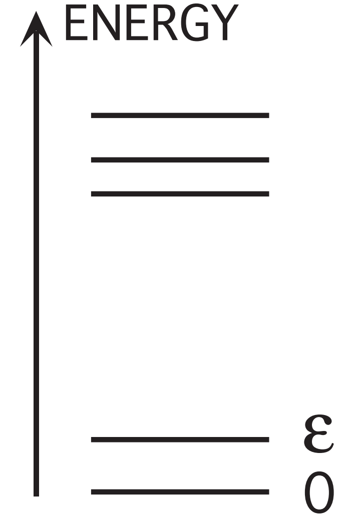
SURFACE MOLECULES



IONS IN A CRYSTAL



LOWEST LYING STATES



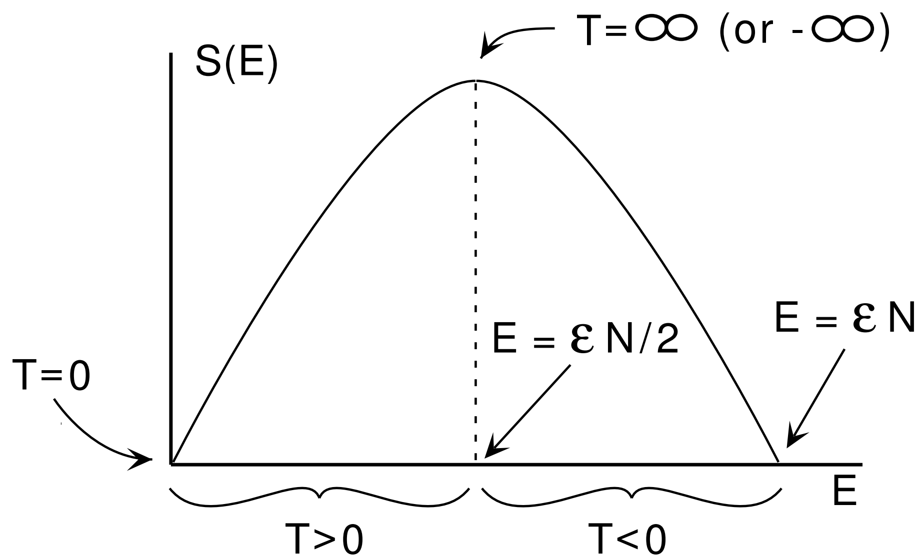
- $E \leftrightarrow N_1$
- NO WORK POSSIBLE (JUST HEAT FLOW)

$$\Omega(E) = \frac{N!}{N_1!(N-N_1)!}$$

1 when $N_1 = 0$ or N

Maximum when $N_1 = N/2$

$$S(E) = k \ln \Omega(E)$$



$$\ln N! \approx N \ln N - N$$

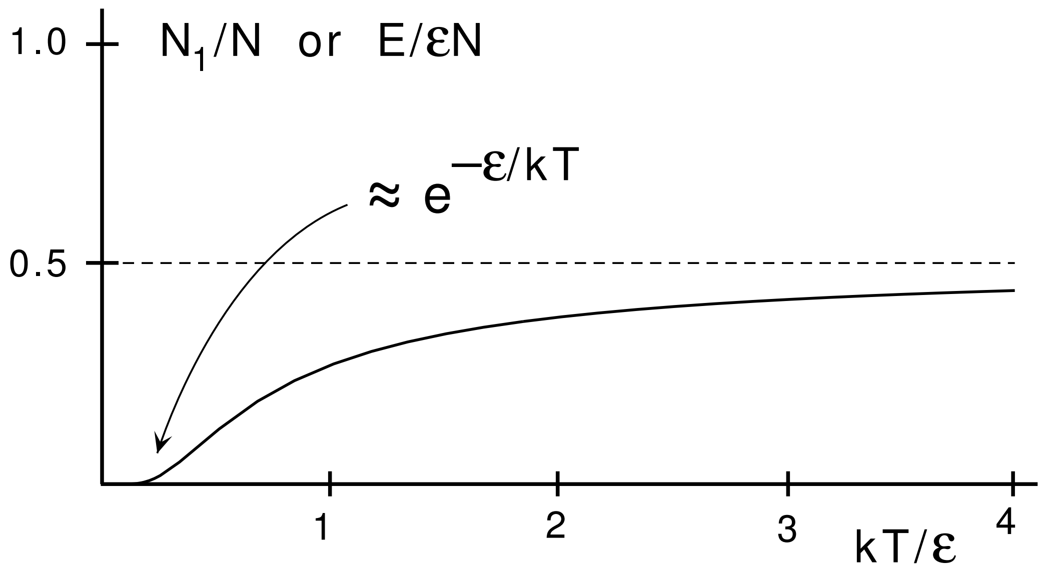
$$S(E) = k[N \ln N - N_1 \ln N_1 - (N - N_1) \ln(N - N_1)$$
$$- N + N_1 + N - N_1]$$

$$\frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)_N = \frac{\partial S}{\partial N_1} \underbrace{\frac{\partial N_1}{\partial E}}_{1/\epsilon} = \frac{k}{\epsilon}[-1 - \ln N_1 + 1 + \ln(N - N_1)]$$

$$= \frac{k}{\epsilon} \ln\left(\frac{N - N_1}{N_1}\right) = \frac{k}{\epsilon} \ln\left(\frac{N}{N_1} - 1\right)$$

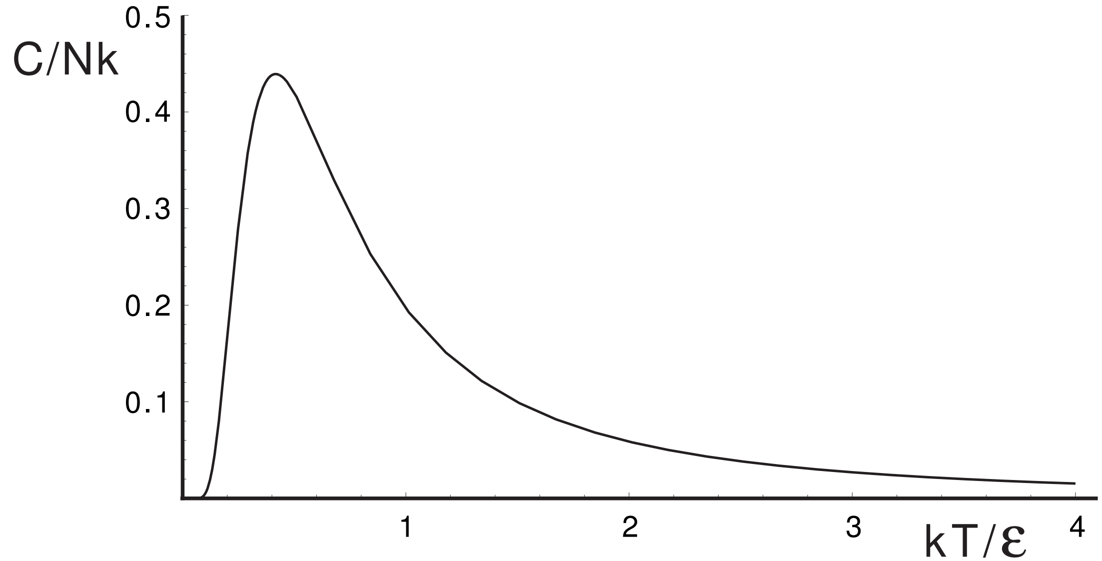
$$\frac{N}{N_1} - 1 = e^{\epsilon/kT} \quad \rightarrow \quad N_1 = \frac{N}{e^{\epsilon/kT} + 1}$$

$$E = \epsilon N_1 = \frac{\epsilon N}{e^{\epsilon/kT} + 1}$$



$$C \equiv \frac{\partial E}{\partial T} = Nk\left(\frac{\epsilon}{kT}\right)^2 \frac{e^{\epsilon/kT}}{(e^{\epsilon/kT}+1)^2}$$

$$\rightarrow Nk\left(\frac{\epsilon}{kT}\right)^2 e^{-\epsilon/kT} \;\; \text{low } T, \quad \rightarrow \frac{Nk}{4}\left(\frac{\epsilon}{kT}\right)^2 \;\; \text{high } T$$



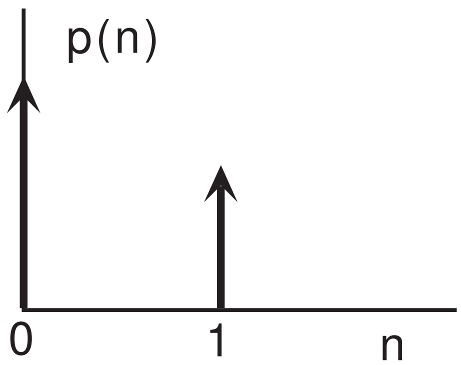
$p(n) = ?\quad n = 0, 1$ $\qquad\qquad$ $p(n) = \dfrac{\Omega'}{\Omega}$

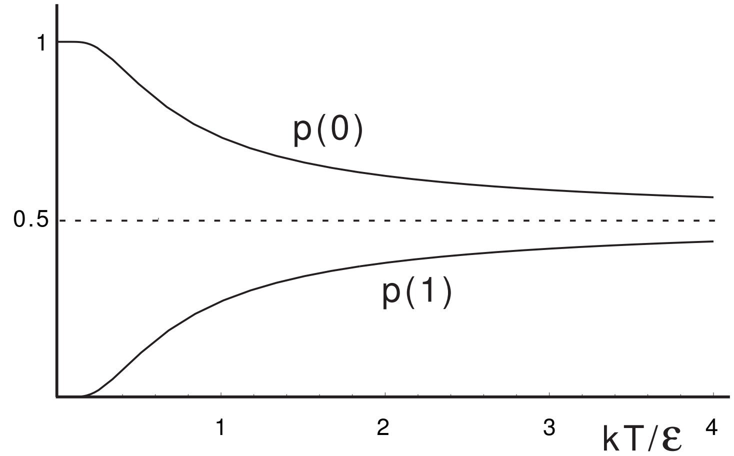
In Ω' $\quad N \to N - 1$ and $N_1 \to N_1 - n$

$$p(n) = \frac{\frac{(N-1)!}{(N_1-n)!(N-1-N_1+n)!}}{\frac{N!}{N_1!(N-N_1)!}}$$

$$p(n) = \underbrace{\frac{(N-1)!}{N!}}_{1/N} \; \underbrace{\frac{N_1!}{(N_1-n)!}}_{\substack{1 \;\; n=0 \\ N_1 \;\; n=1}} \; \underbrace{\frac{(N-N_1)!}{(N-N_1-1+n)!}}_{\substack{N-N_1 \;\; n=0 \\ 1 \;\; n=1}}$$

$$\left.\begin{aligned} p(0) &= \tfrac{N-N_1}{N} = 1 - \tfrac{N_1}{N} \\ p(1) &= \tfrac{N_1}{N} = [e^{\epsilon/kT}+1]^{-1} \end{aligned}\right\} \; p(0)+p(1) = 1$$





$$E = (0) N\, p(0) + (\epsilon) N\, p(1) = \frac{\epsilon N}{e^{\epsilon/kT} + 1}$$

But we knew E, so we could have worked backwards to find $p(1)$.

MICROCANONICAL ENSEMBLE

MODEL THE SYSTEM

↓

FIND $\Omega(E,N,V \ldots.)$

THERMODYNAMIC RESULTS

FIND $S(E,N,V \ldots.)$

↓

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

$$\left.\frac{\partial S}{\partial V}\right|_{E,N} = \frac{P}{T}$$

etc.

MICROSCOPIC INFORMATION

$P(\sim\sim\sim) = \Omega'/\Omega$

The microcanonical ensemble is the starting point for Statistical Mechanics.

- We will no longer use it to solve problems.

- We will develop our understanding of the 2^{ND} law.

- We will derive the canonical ensemble, the real workhorse of S.M.

8.044 Statistical Physics I
Spring 2013