Lecture #8

Canonical Ensemble.

Return first to our problem:

$$S = \frac{3}{2} k N + k N \ln \left[\frac{V}{h^3} \left(\frac{4}{3} \pi m \frac{E}{N} \right)^{3/2} \right]$$

is Not an extensive function.?! Why?

In calculating the number of Micro states,

$$\Omega = \int_{E-\Delta/2}^{E+\Delta/2} g(E')\, dE' \quad ; \quad g = \int \frac{d^D p\, d^D q}{h^D}\, \delta(E-H)$$

we treated the particles in the gas as distinguishable.

Q.M. $\Rightarrow$ if they are the same type of atom, these are indistinguishable $\Rightarrow$ divide by $N!$

particle at site i w/ coordinates (q_i, p_i)
and " at site j " " (q_j, p_j)
are indistinguishable.

$$\therefore \Omega = \frac{1}{N!} \int \frac{dq_i\, dp_i}{h^{3N}}\, \delta(E-H)$$

(1)∘ (3)∘
(2)∘ (4)∘

N ways to put a particle at point 1, $N-1$ ways to put a particle at site 2, etc.

$$\therefore S^{new} = S^{old} - k_B \ln N! \simeq S^{old} - k_B N \ln N + k_B N$$

fixes the entropy to be extensive.

More on indistinguishability later.

Canonical Formulation of Stat Mech.

It is usually difficult to thermally isolate system. It is usually also difficult to calculate the # of microstates corresponding to a fixed energy.

Energy of the system is NOT fixed

We can allow the energy to vary by putting the system in contact with a thermal reservoir. We use our previous method in which each microstate of the combined system (system + reservoir) is equally probable. [Neglect interaction energy]

Simple Analogy: 3 dice: 1 red, 2 white
(system) (bath)

Consider only throws that give the sum of all three dice to be 12 (like total energy). For these throws, we record the value of the red die:

Red	White	#
1	(6,5) (5,6)	2
2	(6,4) (5,5) (4,6)	3
3	(6,3) (5,4) (4,5) (3,6)	4
4	(6,2) (5,3) (4,4) (3,5) (2,6)	5
5	(6,1) (5,2) (4,3) (3,4) (2,5) (1,6)	6
6	(5,1) (4,2) (3,3) (2,4) (1,5)	5

What is the probability of finding n on the red die?

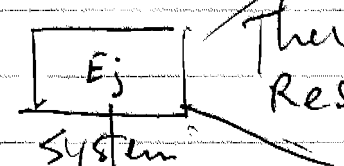
There are 25 possible states. Given fair dice,

$$n: \quad 1 \quad 2 \quad 3 \quad 4 \quad 5 \quad 6$$

$$P_n: \quad \tfrac{2}{25} \quad \tfrac{3}{25} \quad \tfrac{4}{25} \quad \tfrac{5}{25} \quad \tfrac{6}{25} \quad \tfrac{5}{25}$$

$\therefore$ The most probable is $\boxed{n=5}$

Apply the same ideas to energy.



$$E_{tot} = E_{RES} + E_j$$

What is the probability the system has energy E_j?

$$P_j = \frac{\Omega_{RES}(E_{tot} - E_j)}{\Omega_{tot}(E_{tot})}$$

; Ω_{tot} is the total number of microstates having energy E_{tot}.

Again, we assume each state has equal apriori probability.

Since $\Omega = e^{S/k}$

$$P_j = \exp\left\{\left[S_{RES}(E_{tot}-E_j) - S_{tot}(E_{tot})\right]/k\right\}$$

Express this in terms of the average system energy U: $S_{tot}(E_{tot}-E_j) = S_{RES}(E_{tot}-S) + S(U)$

[Additivity of S]

$$S_{RES}(E_{tot}-E_j) = S_{RES}(E_{tot}-U+U-E_j)$$

$$= S_{RES}(E_{tot}-U) + \frac{\partial S_{RES}}{\partial U_{RES}}(U-E_j) + \cdots + \underbrace{\frac{\partial^n S}{\partial U^n}(U-E_j)^n \frac{1}{n!}}_{\text{neglect}}$$

because

$\frac{\partial^n S_{RES}}{\partial E^n_{RES}}$ scales as $\left(\frac{1}{N_{RES}}\right)^{n-1}$

$$S_{RES}(E_{tot}-E_j) = S_{RES}(E_{tot}-U) + \frac{1}{T}(U-E_j)$$

$$\therefore \quad P_j = \exp\left[-\frac{1}{k}\left(S(U) - \frac{U}{T}\right) - \frac{E_j}{kT}\right]$$

but $S - \frac{U}{T} \equiv F/T$ is the Legendre transform of S.

Probability is normalized $\Rightarrow$

$$\sum_j P_j = 1 \Rightarrow e^{F/kT} \sum_j e^{-E_j/kT} = 1$$

$$\boxed{\therefore\ e^{-F/kT} = \sum_j e^{-E_j/kT} \equiv Z}$$

Z is the canonical partition function

define $\beta \equiv 1/kT$

$$P_j = \frac{e^{-E_j/kT}}{Z} \ ; \quad Z(T,V,N) \equiv e^{-\beta F} = \mathrm{Tr}\, e^{-\beta \hat{H}}$$

$\therefore$ In Microcanonical formalism $S = k \ln \Omega^{(U,V,N)}$

Gives over fn. $-\frac{F}{T}(T,V,N) = k \ln Z$

Central result of stat. Mech.

$$\text{Recall } U = \left.\frac{\partial (F/T)}{\partial (\frac{1}{T})}\right|_{V,N} = -k \frac{\partial}{\partial(\frac{1}{T})} \ln Z \Big|_{V,N}$$

$$U = -\frac{\partial}{\partial \beta} \ln Z \Big|_{V,N} = \frac{\sum_j E_j e^{-\beta E_j}}{\sum_j e^{-\beta E_j}} \equiv \langle E \rangle$$

$$U = \frac{\mathrm{Tr}\, \hat{H} e^{-\beta \hat{H}}}{\mathrm{Tr}\, e^{-\beta \hat{H}}}$$

expectation value of energy.

Sim) $\frac{P}{T} = k \frac{\partial \ln Z}{\partial V}\Big|_{T,N}$

$-\frac{\mu}{T} = k \frac{\partial \ln Z}{\partial N}\Big|_{T,N}$

Note, we ~~can~~ also obtain Z from the Density of states $g(E)$

QN pathria

$$Z = \int dE\, g(E)\, e^{-E/kT} = \int dE \int \frac{d^D p\, d^D q}{h^D} \frac{\delta(E-H)}{N!} e^{-\beta E}$$

$$= \int \frac{d^D p\, d^D q}{h^D} \frac{1}{N!} e^{-\beta H(p,q)}$$

Energy fluctuations: what is ΔE?

$$\langle E^2 \rangle = \sum_j E_j^2 e^{-\beta E_j} \Big/ \sum_j e^{-\beta E_j} \; ; \; \langle E \rangle = \sum_j E_j e^{-\beta E_j} / Z$$

$$\Delta E^2 = -\frac{\partial}{\partial \beta}\langle E \rangle = \frac{\partial^2}{\partial \beta^2} \ln Z = -\frac{\partial^2}{\partial \beta^2}(\beta F)$$

$$= -\frac{\partial}{\partial \beta}\langle E \rangle = kT^2 \frac{\partial \langle E \rangle}{\partial T}\Big|_V = kT^2 C_V$$

specific heat @ const. volume

Note: $\langle E \rangle \sim N$

$C_V \sim N$

$$\therefore \frac{\Delta E}{\langle E \rangle} = \frac{\sqrt{kT^2 C_V}}{\langle E \rangle} \sim \frac{\sqrt{N}}{N} = \frac{1}{\sqrt{N}} \to 0 \text{ as } N \to \infty$$