L23
April 7, 2021

Quantum / Statistical Thermodynamics

⇒ Classical Statistical Thermodynamics

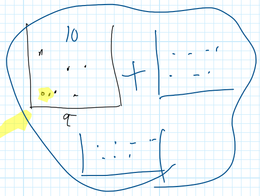
Boltzman
Maxwell.

Concept of: Thermodynamic State, Macrostate
Assembly of microscopic states: Microstate

① Atomistic Picture: Solids, Liquids, Gases } consist of almost infinite number of microscopic particles

② Each particle occupies a given energy state

③ microstate is specified by the number of particle in each energy state, and the way of their distributions
- degeneracy counts how many particles can occupy a given energy state
- there can be many microstates



④ Macrostate is characterized by total energy and total number of particles furnishing a given macrostate

⑤ The number of microstates leading to a given macrostate is called Thermodynamic Probability: w_k

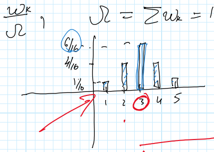
⑥ True / Normalized Probability $P = \frac{w_k}{N_{microstates}}$

⇒ Example of coin tossing: $N = 4$ coins, N_1 – Heads (Local), $N_2 = N - N_1$ – Tails

Macrostate Label K	Macrostate Specification N_1 N_2	Microstate Coin1 Coin2 Coin3 Coin4	Thermod. Prob. w_k	True Probability P
1	4 0	H H H H	1	1/16
2	3 1	H H H T H H T H H T H H T H H H	4	4/16
3	2 2	H H T T T T H H H T H T T H T H H T T H T H H T	6	6/16
4	1 3	H T T T T H T T T T H T T T T H	4	4/16
5	0 4	T T T T	1	1/16

Total Number of Microstates 16

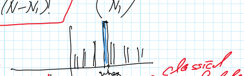
$P = \frac{w_k}{\Omega}$, $\Omega = \sum w_k = 16$, $P_{max} = \frac{6}{16}$



$\boxed{w_{max} = 6}$

Formula for $\boxed{w = \frac{N!}{N_1! N_2!} = \frac{N!}{N_1!(N-N_1)!}} = \binom{N}{N_1}$

if $N = 8$ $w_{max} = \frac{8!}{4!4!} = \boxed{70}$



if $N = 1000$ $w_{max} \approx 10^{3000}$

w_{max} — reality

⇒ Above example corresponds to a two level problem H, T

⇒ for n-level problem

$$\left\{\begin{array}{l} w = \frac{N!}{\prod_{j=1}^{n} N_j!} \\ \sum N_j = N \\ \sum N_j \varepsilon = U \end{array}\right\}$$

$\boxed{S = k \ln w}$

$k = 1.38 \times 10^{-23}\ J K^{-1}$

Boltzman

$w = \frac{N!}{N_1! N_2! N_3! N_4!}$

$\prod_{j=1}^{n} N_j$

⇒ Boltzman Statistic

- N distinguishable Particles, g_i – degeneracy

$w = N! \prod_{j=1}^{n} \frac{g_i^{N_j}}{N_j!}$

maximize

$\sum N_i = N$
$\sum N_j \varepsilon_j = U$!

- Need to maximize w

- Maximizing J variable function with some constraint
  - $f(x_1, \dots x_J)$ $\sum_{i=1}^{J} \frac{\partial f}{\partial x_i} = 0$
  - if there is a constraints $\phi_1(x_1, \dots x_J) = const$

$\phi_2(x_1 \ldots x_J) = const$

– introduce Lagrange Multipliers

$$\boxed{\frac{\partial f}{\partial x_i} - \alpha \frac{\partial \phi}{\partial x_i} - \beta \frac{\partial \phi}{\partial x_i} = 0 \quad i = 1, \ldots J}$$

⟹ Back to Boltzman Statistics

f: $\quad W = N! \prod_{i=1}^{n} \frac{g^{N_i}}{N_i}$ $\qquad \ln W = \ln N! + \sum_{i=1}^{n} N_i \ln g - \sum_{i=1}^{n} \ln N_i!$

ϕ_1: $\quad \sum_{i=1}^{n} N_i = N$ $\qquad$ Using Stirling Approximation $\ln n! = n\ln n - n \; /_{n \gg 1}$

ϕ_2: $\quad \sum_{i=1}^{n} N_i \varepsilon_i = U$ — const

– to find the maximum of W

$$\frac{\partial \ln W}{\partial N_i} - \alpha \frac{\partial \sum_{i=1}^{n} N_i}{\partial N_i} - \beta \frac{\partial \sum_{i=1}^{n} N_i \varepsilon_i}{\partial N_i} = 0$$

$$\frac{\partial}{\partial N_i}\left(\sum_j N_j \ln g_j - \sum_j N_j \ln N_j + \sum_j N_j\right) - \alpha \frac{\partial \sum N_i}{\partial N_i} - \beta \frac{\partial}{\partial N_i}\left(\sum N_i \varepsilon_i\right) = 0$$

(1) $\quad \ln g_i - \ln N_i - \frac{N_i}{N_i} + 1 - \alpha - \beta \varepsilon_i = 0$

$$\ln\left(\frac{N_i}{g_i}\right) = -\alpha - \beta \varepsilon_i$$

number of particles per one state $\quad \frac{N_i}{g_i} = e^{-\alpha - \beta \varepsilon_i} = f(\varepsilon_i) \quad$ (2)

– multiply Eq(1) by N_i and $\sum_i$ $\quad W$

$$\sum_i N_i \ln g_i - \sum_i N_i \ln N_i - \alpha \sum N_i - \beta \sum_i N_i \varepsilon_i = 0$$

– introduce $C = \ln N! + N + \alpha N$

$$\sum_i N_i \ln g_i - \sum_i N_i \ln N_i = \alpha N + \beta U$$

$$-\ln N! + \ln N! + \sum_i N_i \ln g_i - \sum_i (N_i \ln N_i - N_i) - \sum_i N_i = +\alpha N + \beta U$$

$\sum_i \ln N_i!$

$$\ln W - \ln N! - \sum_i N_i = +\alpha N + \beta U$$

N

$(k) \times \quad \ln W = c + \beta U \quad$ (3)

$$S = k \ln W = ck + k\beta U$$

$$\frac{1}{T} = \left(\frac{\partial S}{\partial U}\right)_V = k\beta \quad \Big| \quad k\beta = \frac{1}{T} \quad \Big| \quad \boxed{\beta = \frac{1}{kT}}$$

– going to Eq(2)

$$\frac{N_i}{g_i} = e^{-\alpha - \beta\varepsilon} \implies N_i = g_i e^{-\alpha} e^{-\frac{\varepsilon_i}{kT}}$$

$$N = \sum N_i = e^{-\alpha} \sum g_i e^{-\frac{\varepsilon_i}{kT}}$$

$$e^{-\alpha} = \frac{N}{\sum g_i e^{-\frac{\varepsilon_i}{kT}}} = \frac{N}{Z}$$

(4)

$$\boxed{\frac{N_i}{g_i} = \frac{N e^{-\varepsilon_i/kT}}{Z}} \qquad \boxed{Z = \sum_{i=1}^{n} g_i e^{-\frac{\varepsilon_i}{kT}} \text{ – partition Function}}$$

Boltzman Distribution

Generalization to Indistinguishable particle

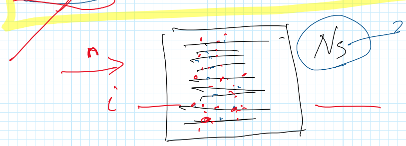
– for one state i

$$f(\varepsilon_i) = C e^{-\alpha N_i - \beta \varepsilon_i N_i} \quad (2)$$

– for assemble of partides (n) $\quad (2')$

$$\boxed{S_{cl}(n) = C e^{-\alpha \sum_i^{N_S} N_i - \beta \sum_{i=1}^{N_S} \varepsilon_i N_i}} \quad ! \; N_i$$

$N_S = 3$



Quantum Statistical Thermodynamics

⟹ Back to Eq(2) and used Relation

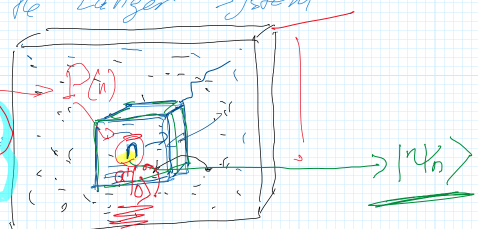
$$!! \quad S_{CL}(n) = C e^{-\alpha \sum_i^{N_S} N_i - \beta \sum_i^{N_S} N_i \varepsilon_i} \quad Eq(2')$$

Introduce True Probability

$$\implies \boxed{P(n) = \frac{1}{Z} e^{-\alpha \sum_i^{N_S} N_i - \beta \sum_i^{N_S} N_i \varepsilon_i}}$$

Then $\quad \sum_n P(n) = 1 \qquad Z = \sum_n e^{-\alpha \sum_i^{N_S} N_i - \beta \sum_{i=1}^{N_S} N_i \varepsilon_i} \quad S(n)$

Consider our system part of the Langer System



Quantum Mechanical Generalization !

– Introduce $|\Psi(n)\rangle$ – for n-particle Quantum state

– Introduce $\rho(n)$ – particle number Density function

Start

– Introduce operator $\hat{\rho}(n) = \frac{1}{Z} e^{-\alpha\hat{N}-\beta\hat{H}}$ Observable

$\rho(n) = \langle \psi_n | \hat{\rho}(n) | \psi_n \rangle$

$\hat{N} = \sum_i^{N_s} a_i^+ a_i$ $\quad \hat{H} = \sum_i^{N_s} \varepsilon_i a_i^+ a_i$

$\{ [a_i, a_j^+] = \delta_{ij}, \quad [a_i, a_j] = [a_i^+, a_j^+] = 0 \}$ For Bosons

$a_i^+ a_i = \hat{n}_i = \hat{N}$

$\left\{ \begin{array}{ll} \hat{N} = \sum_{i=1}^{n} b_i^+ b_i & \hat{H} = \sum_i^n \varepsilon_i b_i^+ b_i \\ \{b_i, b_j^+\} = \delta_{ij}, & \{b_i, b_j\} = \{b_i^+, b_j^+\} = 0 \end{array} \right\}$ For Fermions

$\sum_{n=1}^{N} C_{nn} = \mathrm{Tr}\, C$

– For any observable in this system $\hat{A}$ $\quad |\psi_n\rangle\langle\psi_n| = I$

$\langle A \rangle = \sum_{(n)} \langle \psi_n | \hat{A} | \psi_n \rangle \rho_n = \sum_{(n)} \langle \psi_n | \hat{A} | \psi_n \rangle \langle \psi_n | \hat{\rho} | \psi_n \rangle = \sum_n M_{nn} = \mathrm{Tr}\, M$

$= \sum_n \langle \psi_n | \hat{A}\hat{\rho} | \psi_n \rangle = \sum_n (\hat{A}\hat{\rho})_{nn} =$

$= \mathrm{Tr}\, \hat{A}\hat{\rho} = \mathrm{Tr}\, \hat{\rho}\hat{A}$ $\quad \mathrm{Tr}(AB) = \mathrm{Tr}(BA)$

⇒ Consider now $\hat{A} = a_i^+ a_i$ – number of particle operator in the level i Bosons

⇒ Observed number of particles in the level i

$\langle n_i \rangle = \mathrm{Tr}(\hat{\rho}\, a_i^+ a_i) = \frac{1}{Z} \mathrm{Tr}(e^{-\alpha\hat{N}-\beta\hat{H}} a_i^+ a_i)$

$\hat{N} = \sum_{i=1}^{N_s} a_i^+ a_i$

$\hat{H} = \sum_{i=1}^{N_s} \varepsilon_i a_i^+ a_i$

⇒ Calculation of $\langle n_i \rangle$

– Consider $\mathrm{Tr}(e^{-\alpha\hat{N}-\beta\hat{H}} a_i^+ a_i)$

$[\hat{B}\hat{A}] = [-\alpha\hat{N} - \beta\hat{H}, \hat{a}_i^+]$

$[\hat{N}, a_i^+] = \sum_j [\hat{n}_j a_i^+]$

– Using Baker – Hausdorf Lemma

$\frac{\theta^2}{2!}[\hat{B}, [\hat{B}\hat{A}]]$

$e^{\theta\hat{B}} = 1 + \theta\hat{B} + \frac{\theta^2}{2}\hat{B}^2 + \cdots$

$e^{\theta\hat{B}} \hat{A} e^{-\theta\hat{B}} = \hat{A} + \theta[\hat{B}\hat{A}] + \frac{\theta^2}{2}[\hat{B}, [\hat{B}\hat{A}]] + \cdots$

– Take $\hat{A} = a_i^+$ and $B = -\alpha\hat{N} - \beta\hat{H}$

$a_i a_j^+ = \delta_{ij} + a_j^+ a_i$ $\quad N = \sum_{j=1}^{n} n_j \quad \hat{H} = \sum_{i=1}^{n} \varepsilon_i n_i \quad n_j = a_j^+ a_j$

– Calculate $[n_j, a_i^+] = [a_j^+ a_j, a_i^+] = a_j^+ a_j a_i^+ - a_i^+ a_j^+ a_j =$

$= a_j^+ a_j a_i^+ - a_j^+ a_i^+ a_j = a_j^+ a_j a_i^+ - a_j^+ a_j a_i^+ + \delta_{ij} a_j^+ =$ $\quad [a_i^+, a_j^+] = 0$

$= \delta_{ij} a_j^+ = \delta_{ij} a_i^+$ $\quad [a_j, a_i^+] = \delta_{ij}$

– $[\hat{B}, \hat{A}] = [-\alpha N - \beta H, a_i^+] = \sum_j^n [-\alpha n_j - \beta \varepsilon_j n_j, a_i^+] = -\sum_j (\alpha [n_j a_i^+] + \beta\varepsilon_j [n_j a_i^+])$

$\delta_{ij} a_j^+ \quad \delta_{ij} a_j^+$

?HW $[B, [BA]]$ $\quad = -\sum_j (\alpha + \varepsilon_j \beta)\delta_{ij} a_j^+ = -(\alpha + \varepsilon_i \beta) a_i^+$

– $e^{-\alpha N - \beta H} a_i^+ e^{\alpha N + \beta H} = a_i^+ - (\alpha + \beta\varepsilon_i) a_i^+ + \frac{(\alpha+\beta\varepsilon_i)^2}{2} a_i^+ + \cdots$

$= \left(1 - (\alpha + \beta\varepsilon_i) + \frac{(\alpha+\beta\varepsilon_i)^2}{2}\right) a_i^+ = e^{-\alpha-\beta\varepsilon_i} a_i^+$

– $\langle n_i \rangle = \frac{1}{Z} \mathrm{Tr}(e^{-\alpha N - \beta H} a_i^+ a_i) = \frac{1}{Z}\mathrm{Tr}(e^{-\alpha N - \beta H} a_i^+ e^{\alpha N + \beta H} e^{-\alpha N - \beta H} a_i) =$

$= \frac{1}{Z} e^{-\alpha - \beta\varepsilon_i} \mathrm{Tr}(a_i^+ e^{-\alpha N - \beta H} a_i) = \frac{1}{Z} e^{-\alpha-\beta\varepsilon} \mathrm{Tr}(e^{-\alpha N - \beta H} a_i a_i^+) = //$

$a_i a_i^+$

$[a_i a_i^+] = \delta_{ii} = 1 \quad a_i a_i^+ = a_i^+ a_i + 1 \quad \mathrm{Tr}(ABC) = \mathrm{Tr}(BCA) = \mathrm{Tr}(CAB)$

$// = \frac{1}{Z} e^{-\alpha-\beta\varepsilon_i} \mathrm{Tr}(e^{-\alpha N - \beta H} a_i^+ a_i) + \frac{1}{Z} e^{-\alpha-\beta\varepsilon_i} \mathrm{Tr}(e^{-\alpha N - \beta H})$

$= e^{-\alpha-\beta\varepsilon_i} \langle n_i \rangle + \frac{1}{Z} e^{-\alpha-\beta\varepsilon_i} \mathrm{Tr}(e^{-\alpha N - \beta H}) = \langle n_i \rangle$

1

prove: $\frac{1}{Z}\mathrm{Tr}(e^{-\alpha N - \beta H}) = 1$ $\quad \sum_n \langle \psi_n | \hat{\rho} | \psi_n \rangle$

$Z = \sum e^{-\alpha \sum_i^n n_i - \beta \sum_i^n n_i \varepsilon_i} = \sum_n \langle \psi_n | e^{-\alpha N - \beta H} | \psi_n \rangle$

$Z = \sum \rho_n \quad \mathrm{Tr}\, e^{-\alpha N - \beta H}$

- Thus $\langle n_i \rangle = e^{-\alpha-\beta\varepsilon_i}\left[\langle n_i\rangle + 1\right]$

$\langle n_i\rangle - e^{-\alpha-\beta\varepsilon_i}\langle n_i\rangle = e^{-\alpha-\beta\varepsilon_i}$

$\langle n_i\rangle = \dfrac{e^{-\alpha-\beta\varepsilon_i}}{1-e^{-\alpha-\beta\varepsilon_i}}$

$$\boxed{\langle n_i\rangle = \frac{1}{e^{\alpha+\beta\varepsilon_i}-1}}$$ Bose-Einstein Distribution

$\langle n_i\rangle = \dfrac{e^{-\alpha-\beta\varepsilon_i}}{e^{-\alpha-\beta\varepsilon_i}\left(e^{\alpha+\beta\varepsilon_i}-1\right)}$

- $\beta = \frac{1}{kT}$, For givent temperature average total number of particles

$$\langle N\rangle = \sum_i \langle n_i\rangle = \sum_i \frac{1}{e^{\alpha+\beta\varepsilon_i}-1}$$

⟹ For Fermions

$$\langle n_i\rangle = \frac{1}{Z}\operatorname{Tr}\left(e^{-\alpha\hat N-\beta\hat H}\hat b_i^{+}\hat b_i\right)$$

$\hat N = \sum_i b_i^+ b_i$, $\hat H = \sum_i \varepsilon_i b_i^+ b_i$, $\{b_i b_j^+\} = \delta_{ij}$, $\{b_i b_j\} = \{b_i^+ b_j^+\} = 0$

- Derivation is identical to the Bosonic case until

$$e^{\theta B}\hat A e^{-\theta B} = A + \theta[BA] + \frac{\theta^2}{2}[B,[BA]]$$

$A = b_i^+$ $\qquad B = -\alpha\hat N - \beta\hat H$

$b_i^+ b_j^+ = -b_j^+ b_i^+$

- Need to calculate

$[n_j a_i^+]$

$$[n_j b_i^+] = [b_j^+ b_j b_i^+] = (b_j^+ b_j b_i^+ - b_i^+ b_j^+ b_j) =$$

$$= (b_j^+ b_j b_i^+ + b_j^+ b_i^+ b_j) = (b_j^+ b_j b_i^+ - b_j^+ b_j b_i^+ + \delta_{ij} b_j^+)$$

$$= \delta_{ij} b_j^+ = \delta_{ij} b_i^+$$

$b_i^+ b_j = -b_j b_i^+ + \delta_{ij}$

- $[BA] = [-\alpha N - \beta H, b_i^+] = -\sum_j\left([\alpha n_j b_i^+] + [\beta\varepsilon_j n_j b_i^+]\right) =$

$= -\alpha b_i^+ - \beta\varepsilon_i b_i^+ = -(\alpha+\varepsilon_i\beta)\, b_i^+$

$e^{-\alpha N-\beta H}\, b_i^+\, e^{\alpha N+\beta H} = \mathrm{HW}$

$= e^{-(\alpha+\beta\varepsilon_i)} b_i^+$

- $\operatorname{Tr}\left(e^{-\alpha N-\beta H} b_i^+ b_i\right) = \operatorname{Tr}\left(e^{-\alpha N-\beta H} b_i^+ e^{\alpha N+\beta H} e^{-\alpha N-\beta H} b_i\right) = //$

- $e^{-\alpha N-\beta H} b_i^+ e^{-\alpha N-\beta H} = e^{-(\alpha+\varepsilon_i\beta)} b_i^+$

- $// = e^{-\alpha-\beta\varepsilon_i}\operatorname{Tr}\left(b_i^+ e^{-\alpha N-\beta H} b_i\right) = e^{-\alpha-\beta\varepsilon_i}\operatorname{Tr}\left(e^{-\alpha N-\beta H} b_i b_i^+\right) = //$

$\{b_i b_i^+\} = 1$ $\qquad b_i b_i^+ = 1 - b_i^+ b_i$

$a_i a_i^+ = 1 + a_i^+ a_i$

$// = e^{-\alpha-\beta\varepsilon_i}\operatorname{Tr}\left(e^{-\alpha N-\beta H}\right) - e^{-\alpha-\beta\varepsilon_i}\operatorname{Tr}\left(e^{-\alpha N-\beta H} b_j^+ b_j\right)$

- $\langle n_i\rangle = \frac{1}{Z}\operatorname{Tr}\left(e^{-\alpha N-\beta H} b_j^+ b_j\right) = \frac{1}{Z} e^{-\alpha-\beta\varepsilon_i}\operatorname{Tr}\left(e^{-\alpha N-\beta H}\right) - \frac{1}{Z} e^{-\alpha-\beta\varepsilon_i}\operatorname{Tr}\left(e^{-\alpha N-\beta H} b_j^+ b_j\right)$

HW $\quad 1 \quad \langle n_i\rangle \quad \langle n_i\rangle$

- $\langle n_i\rangle = e^{-\alpha-\beta\varepsilon_i}\left(1 - \langle n_i\rangle\right)$

$\langle n_i\rangle\left(1+e^{-\alpha-\beta\varepsilon_i}\right) = e^{-\alpha-\beta\varepsilon_i}$

$$\boxed{\langle n_i\rangle = \frac{1}{1+e^{\alpha+\beta\varepsilon_i}}}$$ Dirac-Fermi Distributions

$\langle n_i\rangle = \dfrac{e^{-\alpha-\beta\varepsilon_i}}{1+e^{-\alpha-\beta\varepsilon_i}}$

⟹ For Applications

$$\rightarrow \langle n_i\rangle = \frac{1}{e^{\alpha+\beta\varepsilon}-1}$$ Bosons

$\beta = \frac{1}{kT}$

Fermions

— introduce $\alpha = -\mu\beta$ — $\boxed{\mu \text{ — Chemical Potention}}$

$$\boxed{\langle n_i \rangle = \frac{1}{e^{\beta(\varepsilon_i - \mu)} \mp 1}}$$

Bosons

Fermions

any T $\beta = \frac{1}{KT}$

μ — Chemical Potential $\sim T$

$\beta = \frac{1}{KT}$