



COLLEGE OF ARTS AND SCIENCES

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DEPARTMENT OF PHYSICS AND ASTRONOMY

*The* UNIVERSITY *of* OKLAHOMA

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## Statistical Mechanics

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CH. 8 QUANTUM STATISTICAL MECHANICS LECTURE NOTES

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2-28-22

## Quantum Statistical Mechanics

In C.S.M., the partition function  $Q_N(T, V)$  is our bridge between Statistical Mechanics and Thermodynamics. We wish to do the same but Quantum mechanically.

Our Classical partition function is calculated by

$$Q_N(T, V) = \frac{1}{N! h^{3N}} \int e^{-\beta \tilde{H}(\vec{p}, \vec{q})} d^{3N} \vec{p} d^{3N} \vec{q} = \text{Tr}(e^{-\beta \tilde{H}(\vec{p}, \vec{q})})$$

Take for instance the ensemble average

$$\langle f \rangle = \frac{\int e^{-\beta \tilde{H}} f d^{3N} \vec{p} d^{3N} \vec{q}}{\int e^{-\beta \tilde{H}} d^{3N} \vec{p} d^{3N} \vec{q}} = \frac{\frac{1}{N! h^{3N}} \int e^{-\beta \tilde{H}} f d^{3N} \vec{p} d^{3N} \vec{q}}{Q_N}$$

Where we define

$$\rho_{\text{can}} = \frac{e^{-\beta \tilde{H}}}{Q_N(T, V)}$$

We can write  $\langle f \rangle$  as

$$\langle f \rangle = \text{Tr}(f \rho_{\text{can}})$$

3-2-22

In Quantum Mechanics,  $T = 0$

$$\tilde{H} |\Psi_m\rangle = E_m |\Psi_m\rangle$$

which is just the time-independent Schrödinger Equation. The time-dependent Schrödinger Equation of course is

$$i\hbar \frac{\partial}{\partial t} \Psi(\vec{r}, t) = \hat{H} \Psi(\vec{r}, t)$$

We're now interested in making an analogy between the Quantum Statistical Mechanics and Classical Statistical Mechanics.

Let's first examine what the calculation

$$\text{Tr}(e^{-\beta \tilde{H}})$$

means. But we cannot evaluate this without Taylor expanding. The Taylor expansion of course is

$$e^{-x} = \sum_{n=0}^{\infty} \frac{(-1)^n}{n!} x^n$$

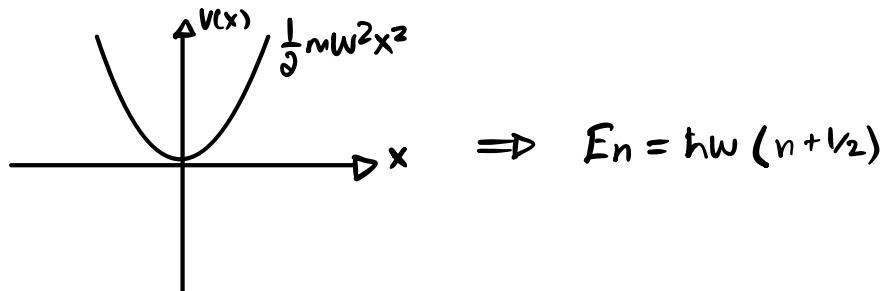
Applying the above we see

$$e^{-\beta \hat{H}P} = \sum_{n=0}^{\infty} \frac{(-1)^n}{n!} (\beta \hat{H}P)^n$$

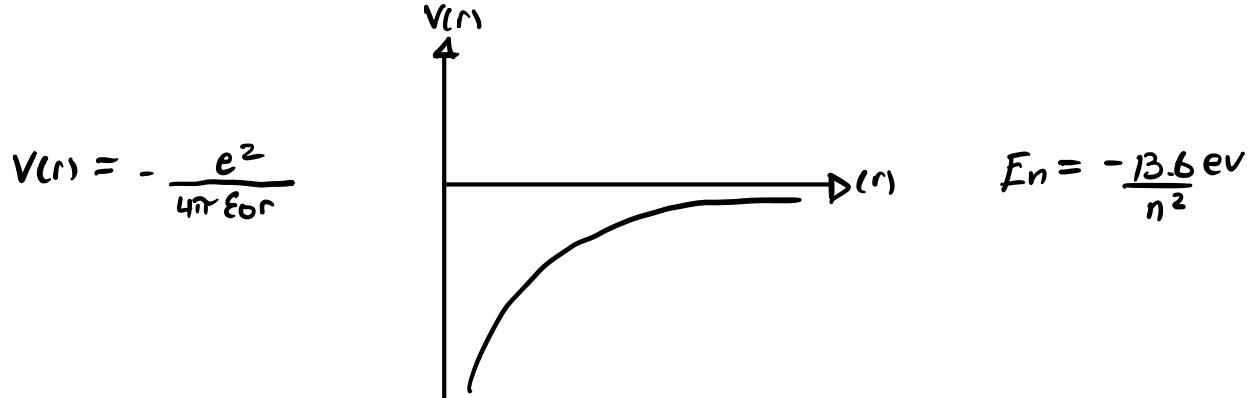
Because we do not know how  $\hat{P}$  will act on our states, we have to expand in a complete set

$$\sum_m |\Psi_m\rangle \langle \Psi_m| \Rightarrow \text{"Completeness Relation"}$$

Where  $\{|\Psi_m\rangle\}$  are the eigenbasis of our Hamiltonian. Take for instance the 1D Harmonic oscillator



Where it is important to know that there is an infinite amount of energy levels. we now look at the potential of an electron



Where the degeneracy is  $n^2$ . we then apply the completeness relation to our system

$$\sum_n \sum_m \frac{(-1)^n}{n!} \beta^n \hat{P}^n |\Psi_m\rangle \langle \Psi_m| = \sum_n \sum_m \frac{(-1)^n}{n!} \beta^n (E_m)^n |\Psi_m\rangle \langle \Psi_m| = \sum_m e^{-\beta E_m} |\Psi_m\rangle \langle \Psi_m|$$

We now shift our focus to how we calculate the Trace

$$\text{Tr}(\hat{A}) = \sum_l \langle \Psi_l | \hat{A} | \Psi_l \rangle$$

Looking at our example we have

$$\text{Tr}(e^{-\beta \hat{H}}) = \sum_{\ell} \langle \psi_{\ell} | \sum_m e^{-\beta E_m} | \psi_m \rangle \langle \psi_m | \psi_{\ell} \rangle$$

We now make the change  $|\psi_{\ell}\rangle \rightarrow |\psi_{\ell}\rangle$

$$\text{Tr}(e^{-\beta \hat{H}}) = \sum_{\ell} \langle \psi_{\ell} | \sum_m e^{-\beta E_m} | \psi_m \rangle \langle \psi_m | \psi_{\ell} \rangle = \sum_{\ell} \langle \psi_{\ell} | e^{-\beta E_{\ell}} | \psi_{\ell} \rangle = \sum_{\ell} e^{-\beta E_{\ell}}$$

We now move on to calculating the density matrix

$$\hat{\rho}_{mm} = \frac{e^{-\beta \hat{H}}}{\text{Tr}(e^{-\beta \hat{H}})} = \sum_m \frac{e^{-\beta E_m} |\psi_m\rangle \langle \psi_m|}{\sum_{\ell} e^{-\beta E_{\ell}}} = \sum_m \frac{e^{-\beta E_m}}{\sum_{\ell} e^{-\beta E_{\ell}}} |\psi_m\rangle \langle \psi_m|$$

We then see

$$\sum_m \frac{e^{-\beta E_m}}{\sum_{\ell} e^{-\beta E_{\ell}}} = 1 \Rightarrow \text{This has to be a probability!}$$

This tells us that  $\hat{\rho}_{mm}$  is consisted upon some probability being multiplied by  $|\psi_m\rangle \langle \psi_m|$ . We can now calculate expectation values for thermal quantities quantum mechanically

$$\langle \hat{A} \rangle = \text{Tr}(\hat{\rho}_{\text{em}} \hat{A}) = \text{Tr}\left(\frac{e^{-\beta \hat{H}}}{\text{Tr}(e^{-\beta \hat{H}})} \hat{A}\right) = \frac{1}{\sum_m e^{-\beta E_m}} \text{Tr}(e^{-\beta \hat{H}} \hat{A})$$

The above turns into

$$\begin{aligned} \langle \hat{A} \rangle &= \frac{1}{\sum_m e^{-\beta E_m}} \sum_{\ell} \langle \psi_{\ell} | e^{-\beta \hat{H}} \sum_{\ell'} |\psi_{\ell'}\rangle \langle \psi_{\ell'} | \hat{A} | \psi_{\ell} \rangle = \frac{1}{\sum_m e^{-\beta E_m}} \sum_{\ell} e^{-\beta E_{\ell}} \langle \psi_{\ell} | \hat{A} | \psi_{\ell} \rangle \\ &= \sum_{\ell} \frac{e^{-\beta E_{\ell}}}{\sum_m e^{-\beta E_m}} \langle \psi_{\ell} | \hat{A} | \psi_{\ell} \rangle = \sum_{\ell} p_{\ell} \langle \psi_{\ell} | \hat{A} | \psi_{\ell} \rangle \end{aligned}$$

### 3-7-2a

Take for instance the 1D Harmonic Oscillator

$$\tilde{\mathcal{H}} = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + m\omega^2 x^2$$

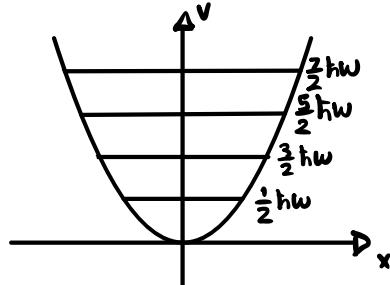
where we wish to make the above equation dimensionless. We make the definitions

$$\tilde{x} = \frac{x}{a}, \quad a^2 = \frac{\hbar}{m\omega}$$

If we make these substitutions we have

$$\tilde{H} = -\frac{1}{2} \frac{\partial^2}{\partial(x/a)^2} + \frac{1}{2} \left(\frac{x}{a}\right)^2$$

When we graph our harmonic oscillator it will look like



Where we now think about our system in terms of temperature

$$K_B T \gg \hbar \omega \rightarrow \text{Classical}$$

$$K_B T \ll \hbar \omega \rightarrow \text{Quantum}$$

We now wish to calculate the trace of our Hamiltonian with the density operator  
we have a wave function

$$\Psi_n(x) = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} \frac{H_n(x/a)}{(2^n n!)^{1/2}} e^{-\frac{1}{2}\left(\frac{x}{a}\right)^2}$$

We then go to solving the eigenvalue equation

$$\tilde{H} \Psi_n(x) = E_n \Psi_n(x)$$

We then will calculate the density operator with

$$\tilde{\rho} = \frac{e^{-\beta \tilde{H}}}{\text{Tr}(e^{-\beta \tilde{H}})}$$

We can then calculate the expectation value of the Hamiltonian

$$\langle \tilde{H} \rangle = \text{Tr}(\tilde{\rho} \tilde{H})$$

The position representation of  $\langle x | e^{-\beta \tilde{H}} | x' \rangle$  is

$$e^{-\beta \tilde{H}} = \sum_m e^{-\beta E_m} |\Psi_m\rangle \langle \Psi_m|$$

This changes to

$$\langle x | e^{-\beta \tilde{H}} | x' \rangle = \sum_m e^{-\beta E_m} \langle x | \Psi_m \rangle \langle \Psi_m | x' \rangle = \sum_m e^{-\beta E_m} \Psi_m(x) \Psi_m^*(x')$$

We now have our position basis

We then find our trace to be,

$$\text{Tr}(e^{-\beta \tilde{H}}) = \sum_{m=0}^{\infty} e^{-\beta(m+\frac{1}{2})\hbar\omega} = \frac{e^{\frac{i}{2}\beta\hbar\omega}}{1-e^{-\beta\hbar\omega}}$$

Where another way to calculate this

$$\text{Tr}(e^{-\beta \tilde{H}}) = \int_{-\infty}^{+\infty} \langle x | e^{-\beta \hat{H}} | x \rangle dx$$

The last step is to write the position representation of  $\tilde{p}$

$$\langle x | \tilde{p} | x \rangle$$

Where the above is our probability distribution

### 3-9-22

If we calculate the probability function for the 1D Harmonic oscillator is

$$\langle x | \hat{p} | x \rangle = \frac{\tanh(\frac{1}{2}\beta\hbar\omega)}{(\pi a_0^2)^{1/2}} \exp\left(-\frac{x^2}{a_0^2} \tanh\left(\frac{\beta\hbar\omega}{2}\right)\right)$$

We can then Taylor expand this quantity to find

$$\langle x | \hat{p} | x \rangle \approx \frac{1}{(\pi a_0^2)^{1/2}} e^{-x^2/a_0^2}$$

We then find that we have arrived back to our expected simple harmonic oscillator result

If we look at  $\langle \tilde{f} \tilde{p} \rangle = \text{Tr}(\hat{p} \tilde{f} \tilde{p})$

$$k_B T \rightarrow 0 : \langle \tilde{f} \tilde{p} \rangle \rightarrow \frac{\hbar\omega}{2}$$

$$k_B T \rightarrow \infty : \langle \tilde{f} \tilde{p} \rangle \rightarrow \frac{\langle \tilde{f} \tilde{p} \rangle}{\hbar\omega}$$

We then of course calculate  $\langle \tilde{f} \tilde{p} \rangle$  as

$$\langle \tilde{f} \tilde{p} \rangle = \text{Tr} \left( \frac{\tilde{f} \tilde{p} e^{-\beta \tilde{H}}}{\text{Tr}(e^{-\beta \tilde{H}})} \right) = -\frac{\partial}{\partial \beta} \log(\text{Tr}(e^{-\beta \tilde{H}}))$$

Carrying this out we find

$$\langle \tilde{f} \tilde{p} \rangle = \frac{1}{2} \hbar\omega \cot(\frac{1}{2}\alpha\beta\hbar\omega)$$

We can calculate this in another way

$$\langle \tilde{H} \rangle = -\frac{\partial}{\partial \beta} \log(\sum_i e^{-\beta E_i})$$

We are interested in determining the number of states per energy interval. For the 1D Harmonic oscillator the energy is calculated with

$$E_n^{\text{1D}} = \hbar\omega \left(n + \frac{1}{2}\right)$$

For the 2D Harmonic oscillator

$$E_n^{\text{2D}} = \hbar\omega (n_x + n_y + 1)$$

where the above can be expanded to 3D.

For a free particle non-relativistic the Kinematic energy is

$$E_{\vec{k}} = \frac{\hbar^2 \vec{k}^2}{2m}$$

We can write a 2D plane wave as

$$\Psi_{\vec{k}}(\vec{x}) = \Psi_k(x) \Psi_k(y)$$

where we have also

$$\Psi_{\vec{k}}(\vec{x}) = \frac{1}{\sqrt{K}} e^{i\vec{k}\vec{x}}$$

Periodic boundary conditions essentially say

$$\Psi_k(x+L) = \Psi_k(x) = e^{i\vec{k}(x+L)} = e^{i\vec{k}x} \Rightarrow e^{i\vec{k}L} = 1$$

where we have

$$k_x = \frac{2\pi n_x}{L}, \quad n_x = 0, \pm 1, \pm 2$$

Our energy then becomes

$$E_{\vec{k}} = \frac{\hbar^2 \vec{k}^2}{2m} = \frac{\hbar^2}{2m} (k_x^2 + k_y^2)$$

We can then further say the energy is

$$E_{\vec{k}} = \frac{\hbar^2}{2m} \left(\frac{2\pi}{L}\right)^2 (n_x^2 + n_y^2)$$

We have exactly one state per  $(\frac{2\pi}{L})^2$ . Up to energy  $E$  we can say the energy is  $\pi n^2$ . We can then say

$$N(E) = \frac{L^2 \pi^2 m E}{(2\pi\hbar)^2} = \frac{\pi m c^2}{(\frac{2\pi}{L})^2}$$

which is our energy per state. Where finally

$$D(E) = \frac{\partial N(E)}{\partial E} = \frac{m L^2}{2\pi\hbar^2}$$

3-21-22

In Quantum Mechanics we have the Eigenvalue equation

$$\hat{H}\psi = E\psi$$

Where our Hamiltonian is (In 2D)

$$\hat{H} = -\frac{\hbar^2}{2m} \left( \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} \right)$$

Using periodic boundary conditions we have a density of states that is calculated with

$$D(E) = \frac{dN(E)}{dE}$$

For the hardwall boundary conditions we will have the same density of states.

We now examine the Hardwall Boundary Condition

$$\Psi(n_x, n_y) = \frac{2}{L} \sin\left(\frac{n_x \pi x}{L}\right) \sin\left(\frac{n_y \pi y}{L}\right) \quad \begin{array}{l} n_x = 1, 2, 3, \dots \\ n_y = 1, 2, 3, \dots \end{array}$$

The energy for our system is then

$$E = \frac{\hbar^2}{2m} \frac{\pi^2}{L^2} (n_x^2 + n_y^2) \quad \begin{array}{l} n_x, n_y = 0, \pm 1, \pm 2, \dots \end{array}$$

The area per state in  $K$ -Space is  $(\frac{\pi}{L})^2$

The density operator

$$\hat{\rho} = \frac{e^{-\beta \hat{H}}}{\text{Tr}(e^{-\beta \hat{H}})} = \frac{e^{-\beta \hat{H}}}{Q(N, V, T)} \Rightarrow \langle \hat{A} \rangle = \text{Tr}[\hat{\rho} \hat{A}]$$

We can then say for the Grand Canonical Ensemble

$$\hat{\rho} = \frac{e^{-\beta(\hat{H}-\mu\hat{N})}}{Q(\mu, \nu, T)} \Rightarrow Q(\mu, \nu, T) = \sum_n e^{-\beta E_n} \text{Tr}(e^{-\beta \hat{H}_n})$$

We can write this density operator as

$$\hat{\rho}_{mc} = \sum_n \frac{1}{\Gamma(E_n)} |\psi_n\rangle \langle \psi_n|$$

We now shift our focus on looking at the entropy Quantum Mechanically

$$S(N, E, V) = k \log(\Gamma(E))$$

Quantum Mechanically our entropy can go to zero as the temperature goes to zero but typically this approaches a very small constant value.

In Many-Body Systems our particles do not act like Bosons or Fermions

Bosons : Integer Spin , Fermions : Half-Integer Spin

### 3-23-22

#### Section 8.5

In this section we will examine non-interacting, non-relativistic, Bose-Einstein and Fermi-Dirac Systems. The distributions of these should follow that of a Boltzmann distribution

#### Exchange Symmetry

We have a wave function of the form

$$\Psi(\vec{q}_1, \vec{q}_2, \dots, \vec{q}_N)$$

Where  $\vec{q}_i$  is a co-ordinate that includes everything  $\vec{r}, \vec{s}$ . When Bosons are exchanged, it is positive. When Fermions are exchanged, the exchange is negative.

Examining Fermions we see

$$\Psi(z_1, z_2) = -\Psi(z_2, z_1)$$

Where we have a spin triplet that looks like

$$\chi = |\uparrow_1, \uparrow_2\rangle$$

We then have magnetic quantum numbers with domain of

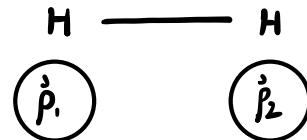
$$m_{s_1} = \pm \frac{1}{2}, m_{s_2} = \pm \frac{1}{2}$$

We then finally have

$$\begin{aligned} X &= | \uparrow \uparrow \rangle \\ X &= \frac{1}{\sqrt{2}} (| \uparrow \downarrow \rangle + | \downarrow \uparrow \rangle) \\ X &= \frac{1}{\sqrt{2}} (| \uparrow \downarrow \rangle - | \downarrow \uparrow \rangle) \\ X &= \frac{1}{\sqrt{2}} (| \uparrow \downarrow \rangle - | \downarrow \uparrow \rangle) \end{aligned} \quad \left. \begin{array}{l} \text{Triplet} \\ \text{Singlet} \end{array} \right\}$$

For Fermions, if one component is symmetric the other must be anti-symmetric due to the total wave function being anti-symmetric for Fermions under particle exchange. Bosons must be symmetric under particle exchange.

We now look at an  $H_2$  molecule



We now want to find the wave function for each Hydrogen atom. We know that the degrees of freedom are

Nuclear (spin), Electronic, Nuclear (Vibration), Nuclear (Rotation)

If we focus only on Nuclear (spin) the wave function is

$$\Psi = X_{\text{Total spin}} Y_{l,m}(\vec{r})$$

If we choose  $l$  to be even, then  $X$  is anti-symmetric and a singlet. If we choose  $l$  to be odd, then  $X$  is symmetric and a triplet.

We choose to work at room temperature where the energy is  $1/40$  eV. If we look at the energy scales

rotational < Vibrational < electronic

What is the ratio of molecular para-hydrogen composition to molecular ortho-hydrogen.

para-hydrogen :  $l = \text{even}$ , ortho-hydrogen :  $l = \text{odd}$

If we now only take into account the rotational degrees of freedom

$$Q_{\text{rot,para}} = \sum_j e^{-\beta E_j} = \sum_{l,\text{even}} (2l+1) e^{-\beta l(l+1) \frac{\hbar^2}{2J}}$$

The ortho-hydrogen is then

$$Q_{\text{rot, ortho}} = \sum_j e^{-\beta E_j} = \sum_{l, \text{odd}} (2l+1) e^{-\beta l(l+1) \frac{\hbar^2}{2J}}$$

We then find the ratios of these to be

$$\frac{N_{\text{para}}}{N_{\text{ortho}}} = \frac{\text{① } Q_{\text{rot, Para}}}{\text{③ } Q_{\text{rot, ortho}}} \quad \begin{array}{l} \xrightarrow{\text{Spin Singlet}} \\ \xleftarrow{\text{Spin triplet}} \end{array}$$

We choose to work with a non-relativistic ideal gas. The Hamiltonian is

$$\tilde{H} = \sum_{j=1}^N \frac{\tilde{p}_j^2}{2m}$$

Where our energy exists in the domain  $[E, E + \Delta]$ . Our single particle energy is simply

$$\epsilon_{\vec{k}} = \frac{\hbar^2 \vec{k}^2}{2m} \quad \text{with} \quad \vec{k} = \frac{2\pi}{L} \hat{n}$$

The total energy of our system is

$$E = \sum_{\vec{k}} \epsilon_{\vec{k}} n_{\vec{k}} \quad \text{with} \quad N = \sum_{\vec{k}} n_{\vec{k}}$$

We then say

$$dk_x = \frac{2\pi}{L} dx, \quad dx = 1 \Rightarrow 1 = \frac{dk_x}{2\pi/L}$$

3-28-22

Let us define a quantity ( $n_{\vec{k}}$ ) called the occupation number for particles of momentum  $\hbar \vec{k}$

For Bosons, Fermions, and Boltzmann particles we find

$$n_{\vec{k}} = 0, 1, 2, \dots, \quad n_{\vec{k}} = 0, 1, \quad n_{\vec{k}} = 0, 1, 2, \dots$$

Under particle exchange Bosons are Symmetric, Fermions are anti-Symmetric, and Boltzmann particles are Bosons but they are distinguishable.

Looking at an example

$$\Phi_1(x_1)\Phi_1(x_2) \Rightarrow n_1=2, n_2=0$$

which tells us that there are two particles occupying state  $n_1$ . Conversely, we can also have something like

$$\Psi_1(x_2)\Psi_2(x_1) \Rightarrow n_1 = 1, n_2 = 0$$

which tells us that there is a particle occupying the  $n_1$  and  $n_2$  state.

We wish to generalize this for  $N$ -particle Bosons. How many terms will we have if we define a symmetrizing / anti-symmetrizing defined as

$$S = \frac{1}{\sqrt{2}}(1 \pm P_{12})$$

Where the above is of course only for two identical particles.

We want to expand this to  $N$  number of particles. We define a total quantity called  $N$ , that is calculated with

$$N = \sum_{\vec{k}} n_{\vec{k}}$$

Where we can also write our total energy in terms of  $E_{\vec{k}}$  and  $n_{\vec{k}}$ . This is then

$$E = \sum_{\vec{k}} E_{\vec{k}} n_{\vec{k}}$$

We can then calculate the number of states in our system with set  $\{n_i\}$  with

$$\Gamma(E) = \sum_{\{n_i\}} W\{n_i\}$$

where  $\{n_i\}$  are the set of occupation numbers for a given total energy  $E$ .

Let's look at Identical Bosons,

$$i^{\text{th}} \text{ cell} \Rightarrow \begin{array}{|c|c|c|} \hline \text{Sub} & \text{Sub} & \dots \dots \\ \hline \text{cell 1} & \text{cell 2} & \\ \hline \end{array}$$

Where our cells are small divisions of a single particles energy. This means if we say

$$g: \text{energy level} \rightarrow g_i: 1 \text{ partition}$$

The number of microstates for a given energy  $E$  is

$$W\{n_i\} = \prod_i W_i \Rightarrow W_i = \frac{(n_i + (g_i - 1))!}{n_i! (g_i - 1)!}$$

Going through the math for this specific example we find

$$W_i = 7$$

We can also write the quantity  $w_i$  as

Identical Fermions :

$$\prod_i w_i = \frac{g_i!}{n_i!(g_i - n_i)!}$$

Boltzmann:

$$W\{\bar{n}_i\} = \prod_i \frac{g_i^{\bar{n}_i}}{\bar{n}_i!}$$

If we look at  $W$  for the three different particles we are working with we find

$$W_{\text{Boltzmann}} \gg W_{\text{Bosons}} \gg W_{\text{Fermions}}$$

With the above micro states, the entropy is then simply

$$S = k \log \left( \sum_{\{\bar{n}_i\}} W\{\bar{n}_i\} \right)$$

We then ask what are the  $\{\bar{n}_i\}$ ? Looking at  $S$  we have

$$S = k \log (W\{\bar{n}_i\})$$

where we say that  $\{\bar{n}_i\}$  are the most probable. If we then vary the log term we see

$$\delta \log W\{\bar{n}_i\} - \left[ \alpha \sum_i \delta_{n_i} + \beta \sum_i \epsilon_i \delta_{n_i} \right] \stackrel{!}{=} 0$$

We then find by doing a lot of algebra, the most probable occupation number is

$$\bar{n}_i = g_i \frac{1}{Z^{-1} e^{\beta \epsilon_i} - 1} \Rightarrow \text{Bosons}$$

$$\bar{n}_i = g_i \frac{1}{Z^{-1} e^{\beta \epsilon_i} + 1} \Rightarrow \text{Fermions}$$

$$\bar{n}_i = g_i \frac{1}{Z^{-1} e^{\beta \epsilon_i}} \Rightarrow \text{Boltzmann}$$

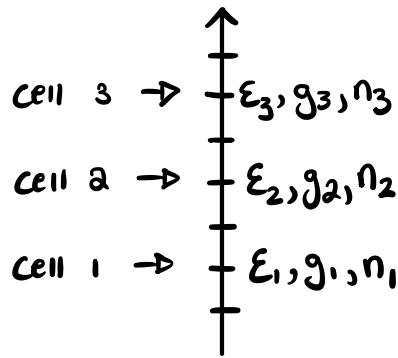
### 3-30-22

We have the microstate equation

$$\Gamma(E) = \sum_{\{\bar{n}_i\}} W\{\bar{n}_i\}$$

Where  $\{\bar{n}_i\}$  are all the allowed sets and  $W\{\bar{n}_i\}$  are the number of states associated with set  $\{\bar{n}_i\}$

We are looking at energy distribution like



where  $g_i \gg 1$ . Knowing this we then make the substitution  $W = \prod_i w_i$ , our equation for our number of microstates is then

$$\Gamma(E) = \sum_{\{n_i\}} \prod_i w_i \{n_i\}$$

where  $w_i$  is directly related to the spin degeneracy. Explicitly,  $w_i$  is how many  $n_i$  particles can be put into a state with degeneracy  $g_i$ .

Knowing all of this, we now wish to look at our entropy

$$S = k \log(\Gamma(E)) = k \log\left(\sum_{\{n_i\}} W \{n_i\}\right) = k \log\left(\sum_{\{n_i\}} \prod_i w_i \{n_i\}\right)$$

Because once we know our entropy we can do Thermodynamics. We now write out our entropy with Lagrange multipliers

$$\delta \log(W \{\bar{n}_i\}) - [\alpha \sum_i \delta \bar{n}_i + \beta \sum_i \epsilon_i \delta \bar{n}_i] = 0$$

↳ "Energy  $E_\Sigma$ "  
↳ " $N E_\Sigma$ "

For different particles we have

$$\alpha = -1 \quad \text{for Bosons}$$

$$\alpha = +1 \quad \text{for Fermions}$$

$$\alpha = 0 \quad \text{for Boltzmann}$$

where we can find  $\bar{n}_i$  to be

$$\bar{n}_i = g_i \frac{1}{Z^{-1} e^{\beta \epsilon_i} + \alpha}$$

We now wish to look at an example for a Boltzmann Gas

We first start with the number equation,

$$N = \sum_i n_i = Z \sum_i g_i e^{-\beta E_i} = Z \sum_k e^{-\beta E_k} = Z \frac{V}{(2\pi)^3} 4\pi \int_0^\infty e^{-\beta \frac{\hbar^2 k^2}{2m}} k^2 dk = \frac{ZV}{\lambda^3}$$

We can then say

$$N = \frac{ZV}{\lambda^3} \Rightarrow Z = \frac{N\lambda^3}{V} = \frac{\lambda^3}{V}$$

The energy can then be written as

$$E = \sum_i n_i \epsilon_i = Z \sum_i g_i \epsilon_i e^{-\beta \epsilon_i} = Z \sum_k \epsilon_k e^{-\beta \frac{\hbar^2 k^2}{2m}} = \frac{3}{2} NkT$$

Now that we have looked at the Micro-canonical ensemble, we want to look at the grand-canonical ensemble.

### 8.6 Grand Canonical Ensemble

We first start in the canonical ensemble. The partition function is of course

$$Q_N(T, V) = \sum_{\text{Ensembles}} g\{n_k\} e^{-\beta E\{n_k\}}$$

We have the "Eigen-value" equation

$$E\{n_k\} = \sum_k n_k \epsilon_k$$

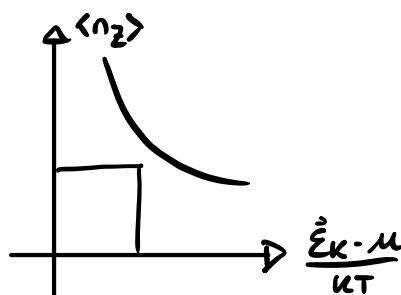
The ensemble average is then

$$\langle n_k \rangle = \frac{1}{Z} e^{\beta \epsilon_k + \alpha}$$

The energy for the ensemble average is

$$E = \frac{1}{e^{(\epsilon_k - \mu)/kT} + \alpha}, \quad \mu = \sum_k \epsilon_k \langle n_k \rangle$$

Choosing to plot this we have



4-4-22

From the previous class we determined the Quantum Partition function in the Grand Canonical Ensemble was

$$Q_n(z, T, V) = \prod_k \sum_n (ze^{-\beta E_k})^n$$

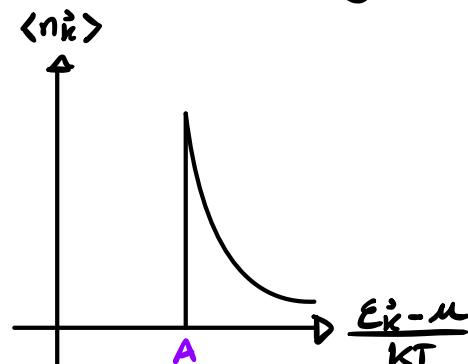
where for Bosons and Fermions we then have

$$Q(z, T, V) = \begin{cases} \log\left(\frac{\prod_k}{k!} \frac{1}{1-ze^{-\beta E_k}}\right) & \text{for identical Bosons} \\ \log\left(\frac{\prod_k}{k!} (1+ze^{-\beta E_k})\right) & \text{for identical Fermions} \end{cases}$$

From all of this we can also say,

$$\langle n_k \rangle \geq 0$$

We can extrapolate this further with a graph

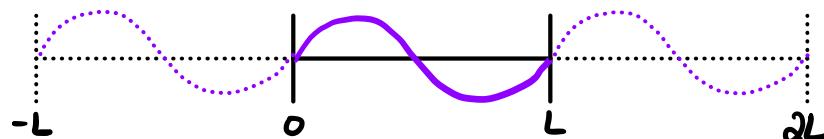


Where at point A we have a macroscopic occupation  $E_0$ , the absolute smallest value of  $E_k$ .

Taking another look at  $\langle n_k \rangle$  for Fermions we have

$$\langle n_k \rangle = \frac{1}{z^{-1} e^{\beta E_k} + 1} = \frac{ze^{-\beta E_k}}{1 + ze^{-\beta E_k}} = -\frac{1}{\beta} \frac{\partial}{\partial E_k} \log(Q_n(z, T, V))$$

Reviewing periodic Boundary Conditions, looking at a single particle in a 1D "box". This looks like



Where periodic boundary conditions is essentially saying we can shift our boundaries and have the same wavefunction.