Course Syllabus and Plan

Statistical Physics: Micro-Canonical, Canonical and Grand Canonical ensembles; Corresponding Partition Functions and their relations to thermodynamic potentials MB, BE and FD Statistical distribution laws; Introduction to White dwarf and Black hole.

Reading:

There are many good books on Statistical Physics. Here is a list.

♣ Fundamentals of Statistical and Thermal Physics by F. Reif

♣ Statistical Physics by Franz Mendl

♣ An Introduction to Statistical Mechanics and Thermodynamics by Robert H. Swendsen

♣ An Introductory Course of Statistical Mechanics by Palash B. Pal

♣ Statistical Physics (University of Cambridge Part II Mathematical Tripos) by David Tong
  You can access this document here: Click Here

Disclaimer: This is not a text book. Rather, these lecture notes are written by **Dr. Ritwik Mondal**, and edited by Dr. Tusharkanti Dey, Department of Physics, IIT (ISM) Dhanbad. The contents are taken from several text books. Please read the above books for your reference. If you find any mistakes or typos, please report to Dr. Tusharkanti Dey.
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Introduction to Statistical Physics

THERMODYNAMICS AND STATISTICAL MECHANICS

1.1 INTRODUCTION: THERMODYNAMICS AND STATISTICAL MECHANICS OF THE PERFECT GAS

Ludwig Boltzmann, who spent much of his life studying statistical mechanics, died in 1906, by his own hand. Paul Ehrenfest, carrying on the work, died similarly in 1933. Now it is our turn to study statistical mechanics.

Perhaps it will be wise to approach the subject cautiously. We will begin by considering the simplest meaningful example, the perfect gas, in order to get the central concepts sorted out. In Chap. 2 we will return to complete the solution of that problem, and the results will provide the foundation of much of the rest of the book.

Figure 1: The opening sentences of an excellent textbook "States of Matter" (1975), by David L. Goodstein.

Ludwig Boltzmann was an Austrian mathematician who made important advances in electromagnetism and thermodynamics. His theories connected the properties and behavior of atoms and molecules with the large scale properties and behavior of the substances of which they were the building blocks.

Boltzmann obtained the Maxwell-Boltzmann distribution in 1871, namely the average energy of motion of a molecule is the same for each direction. He was one of the first to recognise the importance of Maxwell's electromagnetic theory.

Boltzmann worked on statistical mechanics using probability to describe how the properties of atoms determine the properties of matter. In particular his work relates to the Second Law of Thermodynamics which he derived from the principles of mechanics in the 1890s.

Boltzmann's ideas were not accepted by many scientists. In 1904 Boltzmann visited the World's Fair in St Louis, USA. He lectured on applied mathematics and then went on to visit Berkeley and Stanford. Unfortunately he failed to realize that the

new discoveries concerning radiation that he learned about on this visit were about to prove his theories correct.

Boltzmann continued to defend his belief in atomic structure and statistical mechanics proposed by him. However, attacks on his work continued and he began to feel that his life's work was about to collapse despite his defence of his theories. In 1906, depressed and in bad health, Boltzmann committed suicide just before experiment verified his work.

Paul Erenfest was a PhD student of Ludwig Boltzmann. Boltzmann killed himself just two short years after Ehrenfest earned his doctoral degree. Erenfest continued the work of Boltzmann. But, his son had down syndrome and and the Nazi party had seized power earlier that year in 1933. After arriving at the institute, Ehrenfest met his son in the waiting room. There he shot his son Wassik in the head with a pistol, and then he killed himself. It was an unfathomable end - an inconceivable act that betrayed a meaningful life.

It is our turn to understand the statistical mechanics!

In the last few lectures we have covered the topics in thermodynamics which deals with the macroscopic properties of system such as pressure, temperature, volume, entropy. We can study the overall system as a single system with thermodynamics - bulk or macroscopic properties. However, in reality any macroscopic system is composed of microscopic entities like atomic and subatomic particles. For example any liquid, gas or solid system contains many particles in terms of molecules, atoms, electrons etc. In order to understand the microscopic properties of a system, the study of thermodynamics is not enough. In fact a system of gas has 10^{23} molecules. Therefore, if we would like to describe the microscopic properties, we would require to write down the classical mechanical Newton's law for each of these gas molecules. Therefore, you will have to solve a huge numbers of Newton's law that is practically impossible. You are required to know the position and momentum of individual gas molecules which is impractical as well. Hence, one needs to use statistical distribution of position and momentum. As there are huge numbers of gas molecules in the system, the distribution function has less variance. Therefore, the statistical treatment of large number of particles is almost an exact theory.

The macroscopic (bulk) properties of a system are governed by the microscopic (e.g., electrons) properties. The statistical physics calculates the microscopic prop-

erties of a system.

Macrostate

We have so far talked about the macrostates defining a thermodynamical processes. A macrostate can be defined by the set of state functions e.g., pressure, temperature, energy, no. of particles etc. For example, let us consider an ideal gas in an isolated cylinder where the pressure and temperature are constant. In this case if the gas is in equilibrium (uniform distribution of gas molecules) such an equilibrium can be represented by a set $\{E, V, N\}$, where E is the total energy, V is the volume of the gas and N are the no of gas molecules. This constitutes the macrostate of a gas in equilibrium. The equilibrium density of gas molecules can be obtained by $\rho = N/V$ that is constant throughout the gas volume. However, if the gas is not in equilibrium (non-uniform distribution of gas molecules), we need to introduce other macroscopic quantities. In the case of gas, we must introduce the particle (gas molecule) density at a time t and position r. If the nonequilibrium particle density is represented by α (for many density we introduce α_1, α_2, ...). Therefore, the macrostate can be represented by the set $\{E, V, N, \alpha\}$.

Microstate

The macrostates are composed by the microstates. In general 10^{23} particles are involved in a system of gas. Thus, a complete description of microstates are rather complicated. But, we are safe here because equilibrium statistical physics tells us that we do not require a detailed knowledge of all the microstates. Rather, we would like to know how many microstates correspond to a macrostate. The general idea is rather simple. Let us take a simple example for understanding of macrostates and microstates in flipping of a coin. If we flip a coin twice, the outcome has many probabilities. The outcomes could be one of the following: (H,H), (T,T), (H,T), (T,H). These are microstates which takes care of ordering e.g. (H,T) and (T,H). But, the macrostate does not depend on such ordering. You can see that the microstates comes with the probablity factor as well. Therefore, the number of microstates have some weights in terms of their probabilities.
Let us take another example of identical particles. Assume that there are 5 boxes and two balls. You want to find the every possible ways to put 2 balls in 5 boxes.
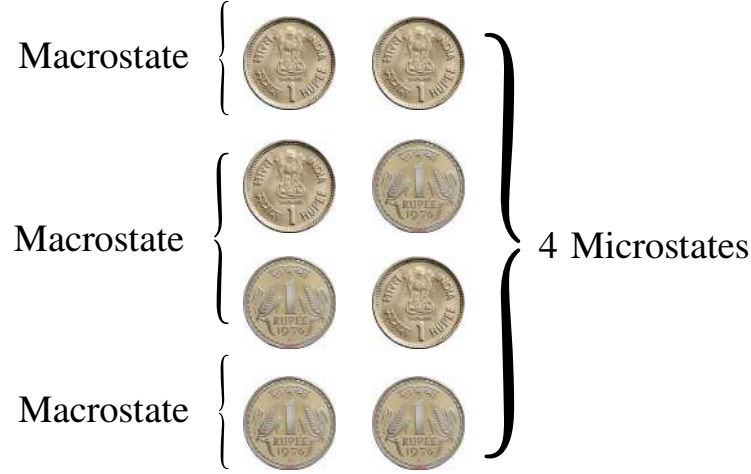
Figure 2: Macrostates and microstates of a coin flipped twice.

The no. of microstates can be calculated by

$$^{n}C_{r} = {}^{5}C_{2} = \frac{5!}{3!\,2!} = 10 \tag{1}$$

Therefore, there are 10 microstates possible.

In a cylinder of gas, there are N no. of gas molecules, where N is very very large! The microstate will be determined by specifying $6N$ variables. There are $3N$ position coordinates $\boldsymbol{q}_1, \boldsymbol{q}_2, \boldsymbol{q}_3, \ldots, \boldsymbol{q}_N$ and other $3N$ momentum variables $\boldsymbol{p}_1, \boldsymbol{p}_2, \boldsymbol{p}_3, \ldots, \boldsymbol{p}_N$. These $6N$ numbers constitute a "phase-space". Now, you have studied Hamilton's equation in classical mechanics. If the Hamiltonian describing the system is $\mathcal{H}(\boldsymbol{q}_i, \boldsymbol{p}_i)$, we can extract the details of positions and momentums by solving the following

$$\dot{\boldsymbol{q}}_i = \frac{\partial \mathcal{H}}{\partial \boldsymbol{p}_i} \tag{2}$$

$$\dot{\boldsymbol{p}}_i = -\frac{\partial \mathcal{H}}{\partial \boldsymbol{q}_i} \tag{3}$$

Unfortunately, we never have exact details of all the microstates. This is where quantum mechanics can become important! Even though we are arguing it for now. According to quantum mechanics, any microstate at a given time can be described by its wave function of the following kind

$$\psi\left(\boldsymbol{q}_1, \boldsymbol{q}_2, \boldsymbol{q}_3, \ldots, \boldsymbol{p}_1, \boldsymbol{p}_2, \boldsymbol{p}_3, \ldots, t\right) \tag{4}$$

Now one could express the position and momentum in terms of angular momentum via $\boldsymbol{l}_i = \boldsymbol{r}_i \times \boldsymbol{p}_i$ where $\times$ indicates a vector cross product. To this end one can have
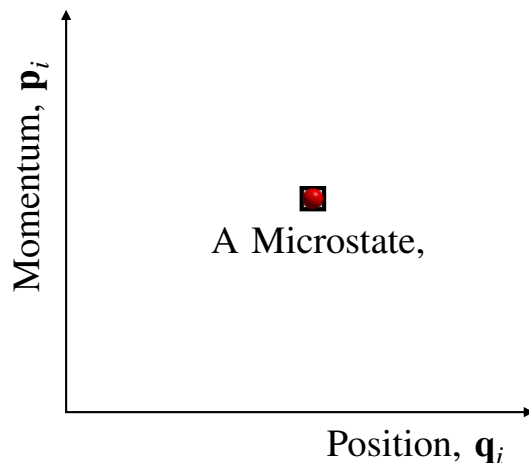
Figure 3: An example of phase-space. The phase-space consists of position and momentum.

a wave function which can be expressed as

$$\psi\left(\boldsymbol{l}_1, \boldsymbol{l}_2, \boldsymbol{l}_3, \ldots, t\right) \tag{5}$$

where all the $\boldsymbol{l}_i$ defines all the quantum numbers necessary to describe the microstate.

For a macrostate defined by a set $\{E, V, N\}$, the accessible microstates are those which are consistent with the fixed values of E, V, N. Remember that we have already talked about the "Equilibrium" in thermodynamics, however, let us understand the meaning of equilibrium in terms of microstates. Suppose that at $t = 0$ the probability of finding any accessible microstate is equal. That is, every accessible microstate occurs with equal probability. Now let the laws of mechanics evolve each microstate forward in time. Our claim is that: at later times $(t > 0)$, every accessible microstate still occurs with equal probability.

If an isolated system is found with equal probability in each accessible microstate, then it is in equilibrium.

Review of Probability distributions:

In order to deal with microstates, a review of probability theory is necessary. Let us consider a set of discrete random variables $\{x|x_1, x_2, x_3, \ldots x_i, \ldots\}$. The probability of obtaining $x = x_i$ is $P(x_i)$ can be called as probability distribution of x. The normalization of the probability tells us that the finding of x must result in any one

of x_i such that

$$\sum_i P(x_i) = 1 \tag{6}$$

The mean value of x can be calculated using the probability distribution as

$$\langle x \rangle = \sum_i x_i P(x_i) \tag{7}$$

The mean square can similarly be calculated as

$$\langle x^2 \rangle = \sum_i x_i^2 P(x_i) \tag{8}$$

The variance is obtained as

$$\sigma^2 = \langle (x - \langle x \rangle)^2 \rangle = \langle (x^2 - 2x\langle x \rangle + \langle x \rangle^2) \rangle = \langle x^2 \rangle - \langle x \rangle^2 \tag{9}$$

The standard deviation is calculated from the variance as $\sqrt{\sigma^2}$.

Binomial Distribution

A particularly important case is that of N independent, identically distributed random numbers that can each take on the value 1 with probability p and 0 with probability 1 - p. Now, the probability of a specific subset of n random variables taking on the value 1, while the remaining $N - n$ random variables that take on the value 0 is easily seen to be

$$p^n (1 - p)^{N-n} \tag{10}$$

The probabilty distribution also depends on the number of permutations of having n subsets from a huge random numbers N. Thus the binomial probability distribution is

$$P(n|N) = \frac{N!}{(N - n)!} p^n (1 - p)^{N-n} \tag{11}$$

Striling's Approximation:

As mentioned above, a difficulty in using the binomial distribution is that $N!$ becomes enormously large when N is even moderately large. For $N = 25$, $N! \approx 1.6 \times 10^{25}$, and we need to consider values of N of 10^{23} and higher. The problem is solved by Stirling's approximation, which is valid for large numbers-exactly the case in which we are interested.

Consider approximating $\ln N!$ in the simplest possible way

$$\ln N! = \ln \left(\prod_{n=1}^{n=N} n \right) = \sum_n \ln n \approx \int_1^N \ln x \, dx = N \ln N - N + 1 \tag{12}$$

Derivation of Equipartition theorem

Generally we talk about energy in physics which has quadratic dependence. For example, the kinetic energy of any particle with a mass m and velocity v can be written as

$$E_{\text{KE}} = \frac{1}{2} m v^2 \tag{13}$$

Similarly, the potential energy of a mass m suspended at one end of a spring and displaced by a small distance y is written as

$$E_{\text{PE}} = \frac{1}{2} k y^2 \tag{14}$$

where k is the spring constant. Therefore, be it kinetic energy or potential energy, these are quadratic in nature. At the moment, we consider the energy to be quadratic such that

$$E = \alpha x^2 \tag{15}$$

where now x is any variable (position, velocity etc.). As we are dealing with equilibrium, all the accessible microstates should have equal probability meaning that x could take any value with equal probability. Now the probability of a system having a particular energy $E = \alpha x^2$ is proportional to the Boltzmann factor $e^{-\beta E}$ where $\beta = 1/k_B T$. The equal probability is then

$$P(x) = \frac{e^{-\alpha \beta x^2}}{\displaystyle\int_{-\infty}^{\infty} e^{-\alpha \beta x^2} \, dx} \tag{16}$$

So the mean energy is

$$\langle E \rangle = \int_{-\infty}^{\infty} EP(x)dx$$

$$= \frac{\displaystyle\int_{-\infty}^{\infty} \alpha x^2 e^{-\alpha\beta x^2}dx}{\displaystyle\int_{-\infty}^{\infty} e^{-\alpha\beta x^2}dx}$$

$$= \frac{\displaystyle\int_{0}^{\infty} \alpha x^2 e^{-\alpha\beta x^2}dx}{\displaystyle\int_{0}^{\infty} e^{-\alpha\beta x^2}dx} \tag{17}$$

To integrate we can consider $z = \alpha\beta x^2$ such that $x = \sqrt{z/\alpha\beta}$ and $dz = 2\alpha\beta xdx$. We transform the integration

$$\langle E \rangle = \frac{\displaystyle\int_{0}^{\infty} \frac{z}{\beta} e^{-z} \frac{dz}{2\alpha\beta}\sqrt{\frac{\alpha\beta}{z}}}{\displaystyle\int_{0}^{\infty} e^{-z} \frac{dz}{2\alpha\beta}\sqrt{\frac{\alpha\beta}{z}}}$$

$$= \frac{1}{\beta} \frac{\displaystyle\int_{0}^{\infty} z^{\frac{1}{2}} e^{-z}dz}{\displaystyle\int_{0}^{\infty} z^{-\frac{1}{2}} e^{-z}dz} \tag{18}$$

We introduce the Gamma function such that

$$\Gamma(n) = \int_{0}^{\infty} z^{n-1} e^{-z}dz \tag{19}$$

Also, $\Gamma(n+1) = n\Gamma(n)$, and $\Gamma(\frac{1}{2}) = (\pi)^{\frac{1}{2}}$

The mean energy can thus be expressed in terms of Gamma function

$$\langle E \rangle = \frac{1}{\beta} \frac{\Gamma\left(\frac{3}{2}\right)}{\Gamma\left(\frac{1}{2}\right)} = \frac{1}{\beta} \frac{\frac{1}{2}\Gamma\left(\frac{1}{2}\right)}{\Gamma\left(\frac{1}{2}\right)} = \frac{1}{2\beta} = \frac{1}{2}k_B T \tag{20}$$

Boltzmann's Entropy:
Boltzmann calculated the entropy from the number of microstates as
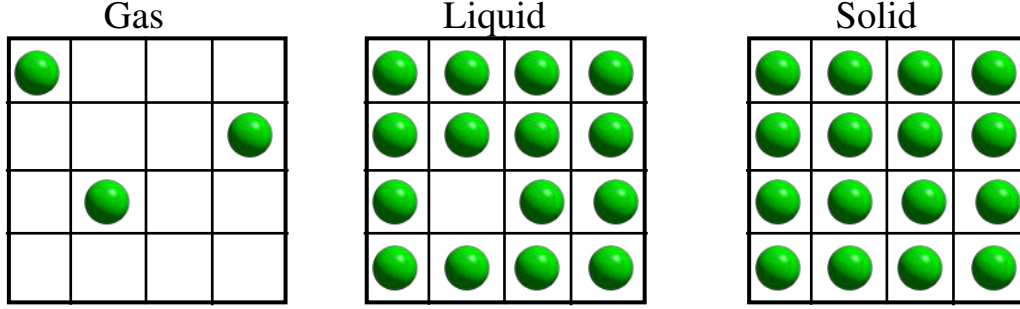
$$S = k_B \ln \Omega \tag{21}$$

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Figure 4: A simple picture of gas, liquid and solid for calculation of microstates.

where Ω is the no of microstates. Even though Max Planck was the first to derive the above expression, but Max Planck followed Boltzmann's idea and named this as Boltzmann's entropy.

From a macroscopic thermodynamical point of view, it is not possible to calculate the entropy of a system of gas or liquid or solids. Even though Boltzmann first calculated the entropy for gases, we can extend his theory for liquids and solids as well. According to Boltzmann, all we need is to calculate the number of microstates.

Before going to the actual calculation, can we guess which system should have higher entropy? Well, from second law of thermodynamics, we know that entropy of the universe is always increasing. This means that entropy somehow measures the randomness or disorder. If we talk about gas, the randomness of the gas molecules are much more than in a liquid or solid. From this simple observation, we can say that the entropy of a gas must be higher.

Okay! Let us calculate the positional microstates in each case as in Fig. 4. There are 16 boxes. For a system of gas, there are only three molecules. This is because gas do not have a proper structure. The possible microstates of having 3 molecules in 16 boxes are

$$\Omega_{\text{Gas}} = \frac{16!}{13!\,3!} = 560 \tag{22}$$

The entropy for this gas

$$S_{\text{Gas}} = k_B \ln \Omega_{\text{Gas}} = k_B \ln 560 \approx 6.33 k_B \tag{23}$$

Of course we would like to compare not the entropy of the whole system, but the

entropy per molecules. For gas the entropy per molecules

$$\frac{S_{\text{Gas}}}{N} \approx \frac{6.33 k_B}{3} = 2.11 k_B \tag{24}$$

For a liquid, there is no definite structure, however, the liquid is more dense than gas. Let us assume that there are 15 liquid molecules that has to be kept in 16 boxes. The possible number of microstates similarly can be calculated

$$\Omega_{\text{Liquid}} = \frac{16!}{15! \, 1!} = 16 \tag{25}$$

The entropy of the liquid

$$S_{\text{Liquid}} = k_B \ln \Omega_{\text{Liquid}} = k_B \ln 16 \approx 2.77 k_B \tag{26}$$

Entropy per molecule for liquid

$$\frac{S_{\text{Liquid}}}{N} \approx \frac{2.77 k_B}{15} \approx 0.185 k_B \tag{27}$$

A solid on the other hand has a definite structure. This means solid is more dense than liquid and gases. There would be 16 "solid molecules" in the 16 boxes. Now if you name the molecules according to their positions then there is only one microstates. Thus, the entropy of a solid is zero.

$$\frac{S_{\text{Solid}}}{N} = 0 \tag{28}$$

Now, you can see that as you had guessed before that the entropy of a gas is always higher than liquid and solid. This is also the reason why we always refer to a system of gases while studying thermodynamics and statistical physics.

Why do we need Ensemble?

Consider a system with a collection of N interacting or non-interacting atoms or molecules or any other particles and we are interested in finding an observable quantity like temperature which is the effect of the motion of these particles. Temperature can be determined by performing the average over the time trajectory of each particle, and then average over all the particles at equilibrium. Time average of velocity is defined for a particle as

$$\langle v \rangle = \lim_{T_t \to \infty} \frac{1}{T_t} \int_0^{T_t} v(t) dt \tag{29}$$

We also know that according to the equipartition theorem the energy can be calculated as

$$E = \frac{1}{2} m v^2 = \frac{3}{2} k_B T \tag{30}$$

Therefore, for N particles (N is huge!) the macroscopic quantity temperature T can be calculated from the microscopic states as

$$T = \frac{m}{3k_B} \frac{1}{N} \sum_{i=1}^{i=N} \lim_{T_t \to \infty} \frac{1}{T_t} \int_0^{T_t} v^2(t) dt \tag{31}$$

where T_t represents time. Understand that the individual particle velocity is required to calculate the temperature of a system.

Let us find how the temperature of a system of harmonic oscillators is obtained. The differential equation for an one-dimensional harmonic oscillator is

$$\frac{d^2 y}{dt^2} + \omega^2 y = 0 \tag{32}$$

where $y(t)$ is the displacement and ω is the angular frequency of the oscillator. The general solution of the above equation is

$$y(t) = a \sin \omega t + b \cos \omega t \tag{33}$$

The velocity can easily be calculated

$$v(t) = \frac{dy}{dt} = \omega(a \cos \omega t - b \sin \omega t) \tag{34}$$

To find out the values of a and b, we must use initial conditions. Let us assume that at $t = 0$, $y(t = 0) = y_0$ and $v(t = 0) = v_0$. We then find $b = y_0$ and $a = v_0/\omega$. Therefore the velocity can be expressed as

$$v(t) = \omega \left(\frac{v_0}{\omega} \cos \omega t - y_0 \sin \omega t \right) \tag{35}$$

We substitute this in the calculation of temperature

$$T = \frac{m\omega^2}{3Nk_B} \sum_{i=1}^{i=N} \lim_{T_t \to \infty} \frac{1}{T_t} \int_0^{T_t} \left(\frac{v_{i0}}{\omega} \cos \omega t - y_{i0} \sin \omega t \right)^2 dt$$

$$= \frac{m\omega^2}{3Nk_B} \sum_{i=1}^{i=N} \left(\frac{v_{i0}^2}{\omega^2} + y_{i0}^2 \right) \tag{36}$$

Can we get this temperature by substituting the unknown values? Look at the unknowns v_0 and y_0, they are the velocity and displacement for each particle and there are N particles with different values of amplitudes and velocities. Thus it is, practically impossible to generate a long time trajectory of a macroscopic system consisting of a large number of atoms or molecules.

Richard Feynmann said on this difficulties:

"Anyone who wants to analyze the properties of matter in a real problem might want to start by writing down the fundamental equations and then try to solve them mathematically. Although there are people who try to use such an approach, these people are the failures in this field ... "

Therefore, we move to the notion of **ensembles**. In thermodynamics, the universe is always divided into a system and its surroundings. The behavior of the system depends on how the system can interact with its surroundings: for example, can it exchange heat or other forms of energy? Can it exchange particles with the surroundings?

The concept of ensemble is the collection of systems that have achieved equilibrium in the same state. In other words, an ensemble is a set of large number of copies of a given macrostate described by different microstates satisfying all the general conditions of the specific macrostate.

If we know the no of microstates, we can compute the probability of having a microstate. Thereby, we can calculate the average of any physical quantity in the question. The computation of microstates can be three ways. Therefore, there are three different ensembles possible.

- ♣ Micro Canonical Ensemble → the macrostate is defined by $\{E, V, N\}$

- ♣ Canonical Ensemble→ the macrostate is defined by $\{T, V, N\}$

- ♣ Grand Canonical Ensemble → the macrostate is defined by $\{T, V, \mu\}$, where μ is the chemical potential.
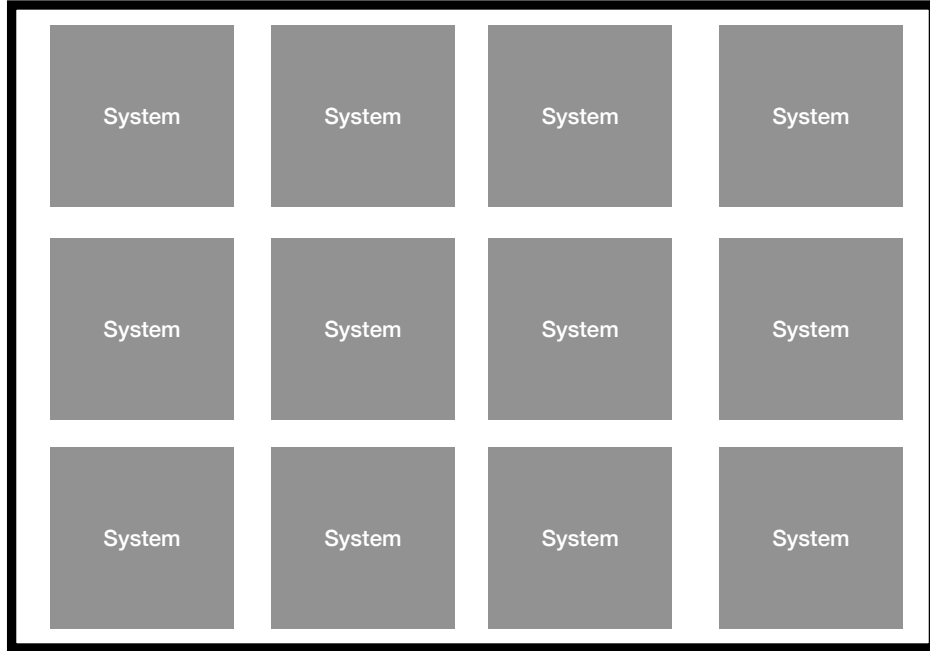
Figure 5: A general definition of an ensemble. The ensemble consists of systems of same macrostates characterised by the microstates.

Micro Canonical Ensemble

The microstates of a micro canonical ensemble correspond to a microstate with fixed energy E, fixed volume V and fixed no. of particles N. The macrostate is thus defined by the set $\{E, V, N\}$. To keep the fixed energy of the macrostate, the system has to be isolated from the surroundings i.e., rest of the universe. Thus, an insulation is used in Fig. 6 for micro canonical ensemble such that the system cannot exchange any energy with the surroundings. Conservation of energy will guarantee that the energy of the macrostate is independent of time.

Let us first analyse the equilibrium properties in micro canonical ensemble. We will use the fundamental postulate of equilibrium statistical physics:

An isolated system is in equilibrium iff all accessible microstates are equally probable.

In other words, there is no preference of any particular microstate. All the microstates can occur with same probability. If the number of microstates are Ω rep-
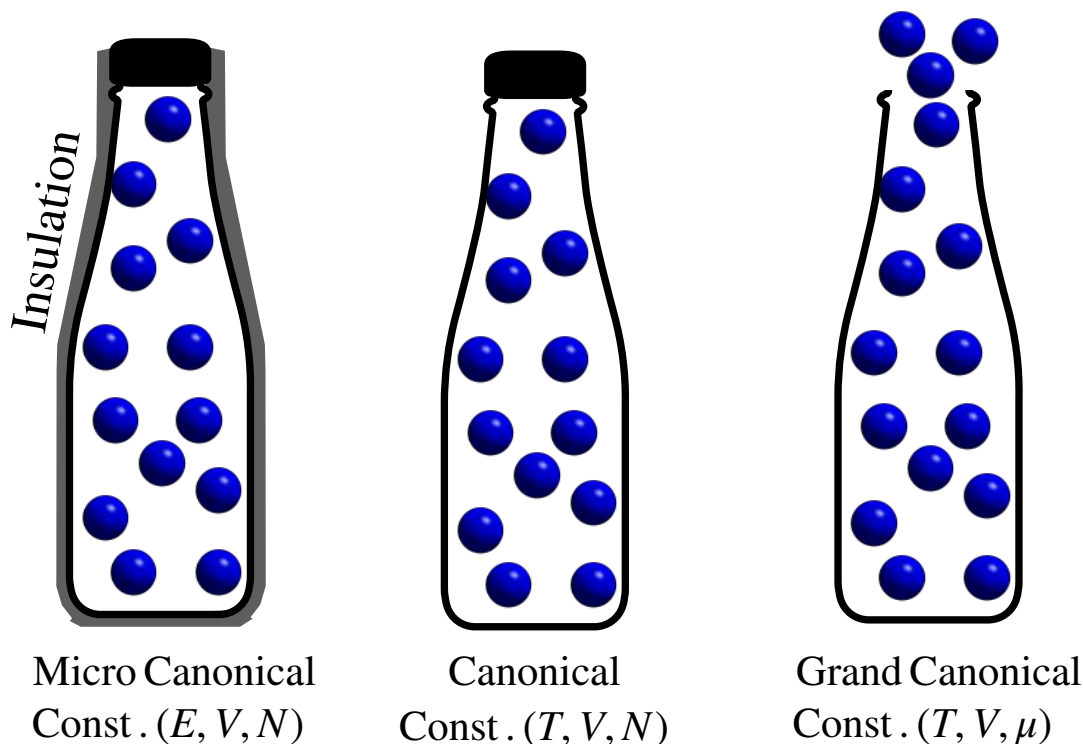
Figure 6: The three different ensembles. Microcanonical ensembles correspond to a macrostate with constant energy E, volume V and no. of particle N. Canonical ensembles correspond to the fixed temperature T, volume V and no. of particles N. Grandcanonical ensemble corresponds to macrostate with fixed temperature T, volume V and chemical potential μ.

resenting the macrostate $\{E, V, N\}$, the probability of occuring each microstate is

$$p(E) = \frac{1}{\Omega(E, V, N)} \tag{37}$$

where $\Omega(E, V, N)$ defines the total number of accessible microstates corresponding to a macrostate $\{E, V, N\}$. The total number of microstates $\Omega(E, V, N)$ can sometimes be called as **Partition Function** for micro canonical ensemble. Although Partition Function is strictly applicable to canonocal and grand canonical ensemble. Our intention is to calculate several thermodynamic state functions using the microstates.
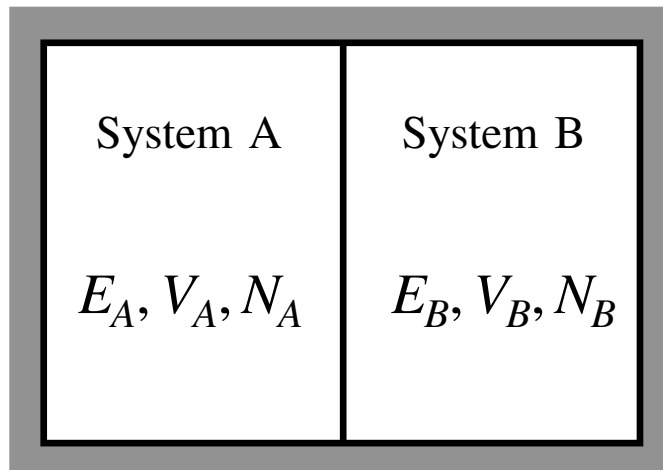
Figure 7: Caption

Consider an isolated system with a macrostate defined by fixed $\{E, V, N\}$. Now we divide the isolated system into two parts say A and B. The individual macrostates are now characterized by the sets $\{E_A, V_A, N_A\}$ for sub system A and $\{E_B, V_B, N_B\}$ for sub system B. As the walls are fixed, no work is done in this case. We find the following equations

$$E_A + E_B = E \tag{38}$$

$$V_A + V_B = V \tag{39}$$

$$N_A + N_B = N \tag{40}$$

Using the fundamental postulate of microstates, we find that the probability that subsystem A has energy E_A and subsystem B has energy E_B is calculated as

$$
\begin{aligned}
p(E_A) &= \frac{\text{Total no of microstates of A having energy E}_A \text{ and B having energy E}_B}{\text{Total number of microstates without the wall}} \\
&= \frac{\Omega_A(E_A)\Omega_B(E_B)}{\Omega(E)} \\
&= \frac{\Omega_A(E_A)\Omega_B(E - E_A)}{\Omega(E)}
\end{aligned}
\tag{41}
$$

The reason is that the energies E_A and E_B are related as the subsystems A and B can exchange some heat between them, however, the total energy E must be conserved.

Of course there are large numbers of microstates correspond to a macrostate. Now the question is which of these microstates will appear in the equilibrium? The an-

swer of this question cannot be given in terms of no. of microstates Ω, but in terms of probability. The equilibrium must correspond to the maximized probability meaning that the lowest no. of microstates. So, the macrostate $\{E, V, N\}$ must correspond to maximize the probability $p(E_A)$ such that

$$\frac{\partial p(E_A)}{\partial E_A} = 0 \tag{42}$$

We know that the no. of microstates is a huge number in any system. Therefore, it is always better to work with the $\ln p(E_A)$ because the function $\ln$ brings an exponential function to a monotonic function. In this case, we find

$$\frac{\partial \ln p(E_A)}{\partial E_A} = 0$$

$$\Rightarrow \frac{\partial}{\partial E_A} \left[\ln \Omega_A(E_A) + \ln \Omega_B(E_B) - \ln \Omega(E) \right] = 0$$

$$\Rightarrow \frac{\partial \ln \Omega_A(E_A)}{\partial E_A} + \frac{\partial \ln \Omega_B(E_B)}{\partial E_A} = 0 \tag{43}$$

Now we know that the total energy is constant $E_A + E_B = E \Rightarrow \partial E_A + \partial E_B = 0 \Rightarrow \partial E_A = -\partial E_B$. Using this relation, we can write Eq. (43) as

$$\underbrace{\frac{\partial \ln \Omega_A(E_A)}{\partial E_A}}_{\text{Property of system A only}} = \underbrace{\frac{\partial \ln \Omega_B(E_B)}{\partial E_B}}_{\text{Property of system B only}} \tag{44}$$

These are characteristics of the subsystems A and B such that the value of $\frac{\partial \ln \Omega_A(E_A)}{\partial E_A}$ should be equal to $\frac{\partial \ln \Omega_A(E_B)}{\partial E_B}$ when the total system $A + B$ is in thermal equilibrium. From thermodynamics we know that this must be related to the temperature T. Now, we know that $\frac{\partial \ln \Omega_A(E_A)}{\partial E_A}$ has a dimension of inverse energy. Therefore, at equilibrium of the total system at temperature T we must have

$$\frac{\partial \ln \Omega_A(E_A)}{\partial E_A} = \frac{1}{k_B T_A} = \frac{\partial \ln \Omega_B(E_B)}{\partial E_B} = \frac{1}{k_B T_B} \tag{45}$$

where k_B is Boltzmann's constant. This above relation is also consistent with the zeroth law of thermodynamics.

For the total system having energy E and temperature T we define

$$\frac{\partial \ln \Omega(E)}{\partial E} = \frac{1}{k_B T}$$

$$\Rightarrow \frac{\partial \left[k_B \ln \Omega(E) \right]}{\partial E} = \frac{1}{T} \tag{46}$$

In this respect, we also introduce a parameter $\beta = 1/k_B T$. Now, we remember the first and second law of thermodynamics

$$dU = TdS - PdV \tag{47}$$

where U is the internal energy which is here defined as E. We know that

$$T = \left(\frac{\partial U}{\partial S}\right)_V \Rightarrow \frac{\partial S}{\partial U} = \frac{1}{T} \tag{48}$$

Note that Eq. (46) has also been obtained with constant volume V such that no work is done! Comparing Eqs. (46) with (48) we obtain the famous Boltzmann entropy

$$S = k_B \ln \Omega(E) \tag{49}$$

Now, see an interesting result. This exactly connects the thermodynamical quantities to the statistical ensembles. If we know the number of microstates, we can predict the entropy of a given thermodynamical system.

In fact, once we know the entropy of a system using the microstates, we can calculate any thermodynamical quantity pressure P, temperature T and others. But the most difficult part in all this is the counting of microstates Ω.

From Eq. (49), we can also write down the no of microstates as

$$\Omega(E) = e^{\frac{S}{k_B}} \tag{50}$$

Later we will see that a similar thing will be called as partition function.

Canonical Ensemble

Even though we have studied micro canonical ensemble in the previous section, that is only valid in an isolated system where no energy is exchanged between the system with the surroundings. In contrary, most of the thermodynamic processes occur where the exchange of energy happens between system and surroundings. In these processes we require to consider canonical ensemble.

While the exchange of energy is possible, we can still keep the temperature of the macrostate constant. Therefore, the canonical distribution describes a system kept at a constant temperature T, with a given volume V and no of particles N. The macrostate will thus be determined by the set $\{T, V, N\}$.

Canonical ensemble consists of a system and a heat reservoir (resource of heat) that keeps a constant temperature. The composite system of the system and heat reservoir can be taken as an isolated system. Let us consider the total energy of the composite is fixed as it is isolated. The total energy isolated composite system is

$$E_{\mathrm{T}} = E + E_{\mathrm{R}} \tag{51}$$

The energy of the system is E and the energy of the reservoir is E_{R} As we have done in previous section, we want to calculate the probability finding the composite system where the system has energy E and reservoir has energy E_{R}

$$
\begin{aligned}
P(E) &= \frac{\text{No of microstates of Sys having energy E and Rev having energy E}_{\mathrm{R}}}{\text{Total number of microstates without the wall}} \\
&= \frac{\Omega(E)\Omega_R(E_R)}{\Omega_T(E_T)} \\
&= \frac{\Omega(E)\Omega_R(E_T - E)}{\Omega_T(E_T)}
\end{aligned}
\tag{52}
$$

We also note that reservoir has infinite amount of energy such that any small amount of heat taken by the system does not change the temperature of the reservoir. Therefore, $E_{\mathrm{T}} >> E$ and $E_{\mathrm{R}} >> E$. As the no. of microstates are huge numbers, we must use the logarithmic function to calculate the probability.

$$\ln P(E) = \ln \Omega(E) + \ln \Omega_{\mathrm{R}}(E_{\mathrm{T}} - E) - \ln \Omega_{\mathrm{T}}(E_{\mathrm{T}}) \tag{53}$$

We can expand the term $\ln \Omega_{\mathrm{R}}(E_{\mathrm{T}} - E)$ around E_{T} as $E_{\mathrm{T}} >> E$:

$$\ln P(E) = \ln \Omega(E) + \ln \Omega_{\mathrm{R}}(E_{\mathrm{T}}) - E \frac{\partial \ln \Omega_{\mathrm{R}}(E_{\mathrm{T}})}{\partial E}\bigg|_{E=E_{\mathrm{T}}} - \ln \Omega_{\mathrm{T}}(E_{\mathrm{T}}) + \mathcal{O}(E^2) \tag{54}$$

We have only kept up to first order terms and the other higher-order terms $\mathcal{O}(E^2)$ have been neglected!

Since the system and the reservoir must have same temperature at equilibrium, we have

$$T = T_{\mathrm{R}} \tag{55}$$

We also know from micro canonical ensemble Eq. (45) that

$$\left. \frac{\partial \ln \Omega_{\mathrm{R}}(E_{\mathrm{T}})}{\partial E} \right|_{E=E_{\mathrm{T}}} = \frac{1}{k_B T} = \beta \tag{56}$$

Due to the fact that the total energy E_{T} is constant, we anticipate that the two terms $\ln \Omega_{\mathrm{R}}(E_{\mathrm{T}})$ and $\ln \Omega_{\mathrm{T}}(E_{\mathrm{T}})$ are also constant at equilibrium. Consider that

$$\ln \Omega_{\mathrm{R}}(E_{\mathrm{T}}) - \ln \Omega_{\mathrm{T}}(E_{\mathrm{T}}) = - \ln Z \tag{57}$$

where Z is constant. From Eq. (54), we insert Eq. (57) and find

$$\ln P(E) = \ln \Omega(E) - \beta E - \ln Z$$
$$\Rightarrow P(E) = \frac{\Omega(E)e^{-\beta E}}{Z} \tag{58}$$

Notice that Z becomes simply a normalization constant in the probability distribution. Z remains constant due to the fact that it does not depend on the energy E, however, it does depend on the other parameters T, V, N which are kept constant in this calculation. If one has discrete energy values, we can use the normalization such that

$$\sum_i P(E_i) = 1$$
$$\Rightarrow Z = \sum_i \Omega(E_i)e^{-\beta E_i} \tag{59}$$

where $\Omega(E_i)$ are the statistical weight of the distribution.

Of course, if the energy is continuous as it does in classcial physics, then the normalization of the probability distributions denotes

$$Z(T, V, N) = \int_0^\infty \Omega(E)e^{-\beta E} dE \tag{60}$$

Z is very special and important in statistical physics and it is called partition function. The universal use of the letter Z comes from a german name *Zustandssumme*.

The word *Zustand* means states; thus the meaning of *Zustandssumme* is that sum over all the states. Therefore, the probability distribution for canonical ensemble with discrete energy levels E_i is

$$P(E_i) = \frac{\Omega(E_i)e^{-\beta E_i}}{\sum_i \Omega(E_i)e^{-\beta E_i}} \tag{61}$$

Thermodynamic Relations:

Average Energy: The great importance of having the partition function Z is that we can calculate many thermodynamic potentials. Let us first calculate the average energy in canonical ensemble

$$\begin{aligned} \langle E \rangle &= \sum_i E_i P(E_i) \\ &= \frac{\sum_i E_i \Omega(E_i)e^{-\beta E_i}}{\sum_i \Omega(E_i)e^{-\beta E_i}} \end{aligned} \tag{62}$$

For the moment we keep this in mind. Now we know the following deinition of partition function

$$Z = \sum_i \Omega(E_i)e^{-\beta E_i}$$

$$\Rightarrow \frac{\partial \ln Z}{\partial \beta} = \frac{1}{Z}\frac{\partial Z}{\partial \beta} = -\frac{\sum_i E_i \Omega(E_i)e^{-\beta E_i}}{Z} = -\frac{\sum_i E_i \Omega(E_i)e^{-\beta E_i}}{\sum_i \Omega(E_i)e^{-\beta E_i}} \tag{63}$$

Comparing Eq (62) with Eq. (63), we find the following relation

$$\langle E \rangle = -\frac{\partial \ln Z}{\partial \beta} = U \tag{64}$$

If the system is not expeienced by any external field, this is actually the internal energy U of the system as we have studied in thermodynamics. However it has to be remembered that in the more general case where there are external field contributions to the energy we can only write

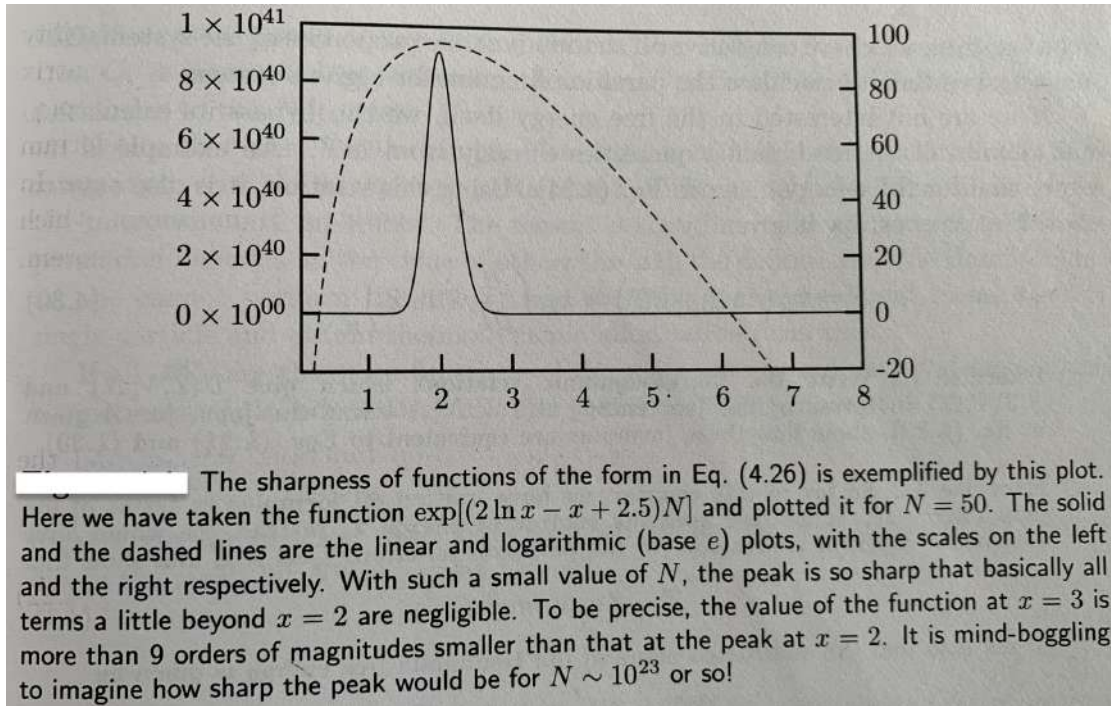$$\langle E \rangle = -\frac{\partial \ln Z}{\partial \beta} \tag{65}$$

Entropy:

We continue to work with the partition function, however, in order to use the no of microstates, we borrow the following formula from micro canonical ensemble

$$\Omega(E) = e^{\frac{S(E)}{k_B}} \tag{66}$$

The partition function can thus be written as

$$Z = \sum_i e^{\frac{S(E_i)}{k_B}} e^{-\beta E_i} = \sum_i \exp\left(\frac{S(E_i)}{k_B} - \beta E_i\right) \tag{67}$$

Notice that the partition function is a product of two factors. Because the tem-

The sharpness of functions of the form in Eq. (4.26) is exemplified by this plot. Here we have taken the function $\exp[(2\ln x - x + 2.5)N]$ and plotted it for $N = 50$. The solid and the dashed lines are the linear and logarithmic (base e) plots, with the scales on the left and the right respectively. With such a small value of N, the peak is so sharp that basically all terms a little beyond $x = 2$ are negligible. To be precise, the value of the function at $x = 3$ is more than 9 orders of magnitudes smaller than that at the peak at $x = 2$. It is mind-boggling to imagine how sharp the peak would be for $N \sim 10^{23}$ or so!

perature must be positive, the factor $S(E_i)$ has to be an increasing function of E_i and its exponential $e^{\frac{S(E_i)}{k_B}}$ has to be an increasing function too. On the other hand, $e^{-\beta E_i}$ is a decreasing function of E_i. The product of such two factors will have a peak at some energy E_i. For a large number of particles, this peak will be very very sharp. Therefore, the sum in Eq. (67) can be replaced by the peak value of E_i. That peak value is the internal energy of the system U we can write

$$Z = \exp\left(\frac{S}{k_B} - \beta U\right) = \exp\left(-\frac{U - TS}{k_B T}\right) \tag{68}$$

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This is an important result because the entropy in canonical ensemble now can be calculated from the above equation

$$\ln Z = -\frac{U - TS}{k_B T}$$

$$\Rightarrow S = k_B \ln Z + \frac{U}{T} \tag{69}$$

However, from thermodynamics we also know that the Helmholtz potential is $F = U - TS$. Thus, we can also calculate the potential from partition function

$$\ln Z = -\frac{F}{k_B T} \Rightarrow F = -k_B T \ln Z \Rightarrow Z = e^{-\beta F} \tag{70}$$

Grand Canonical Ensemble

Even though, the canonical ensemble is the most important one in statistical physics, sometimes the usefulness of other ensemble theory may become convenient. One of them is grand canonical ensemble.

The physical situation described by the grand canonical ensemble is that of a system that can exchange both energy and particles with a reservoir. As usual, we assume that the reservoir is much larger than the system of interest, so that its properties are not significantly affected by relatively small changes in its energy or particle number. Note that the reservoir must have the same type (or types) of particle as the system of interest, which was not a requirement of the reservoir for the canonical ensemble. So far, we have not talked about the no of particles and its connection to the chemical potential. Normally the no. of particles in a system creates a chemical potential that can change if one more particle enters into the system. The chemical potential is denoted by μ. In the grand canonical ensemble the macrostate is defined by constant temperature T, volume V, and chemical potential μ with a set $\{T, V, \mu\}$.

Let us consider the energy and no of particles in the system is denoted by E and N, respectively. The energy and the no of particles in the reservoir are E_R and N_R. For the total composite system, as it is isolated, we must have total energy E_T and total no of particles N_T are constant.

$$E_\mathrm{T} = E + E_\mathrm{R} \tag{71}$$

$$N_\mathrm{T} = N + N_\mathrm{R} \tag{72}$$

The probability distribution of the system having N particles and energy E is

$$P(E, N) = \frac{\Omega(E, N)\Omega_\mathrm{R}(E_\mathrm{R}, N_\mathrm{R})}{\Omega_\mathrm{T}(E_\mathrm{T}, N_\mathrm{T})} = \frac{\Omega(E, N)\Omega_\mathrm{R}(E_\mathrm{T} - E, N_\mathrm{T} - N)}{\Omega_\mathrm{T}(E_\mathrm{T}, N_\mathrm{T})} \tag{73}$$

Following the same procedure as in the case of canonical ensemble, we take the ln which gives

$$\ln P(E, N) = \ln \Omega(E, N) + \ln \Omega_\mathrm{R}(E_\mathrm{T} - E, N_\mathrm{T} - N) - \ln \Omega_\mathrm{T}(E_\mathrm{T}, N_\mathrm{T}) \tag{74}$$

As usual we expand the second term in the vicinity of E_T and N_T:

$$
\begin{aligned}
\ln P(E, N) &= \ln \Omega(E, N) + \ln \Omega_\mathrm{R}(E_\mathrm{T} - E, N_\mathrm{T} - N) - \ln \Omega_\mathrm{T}(E_\mathrm{T}, N_\mathrm{T}) \\
&\approx \ln \Omega(E, N) + \ln \Omega_\mathrm{R}(E_\mathrm{T}, N_\mathrm{T}) - E \frac{\partial \ln \Omega_\mathrm{R}(E_\mathrm{T}, N_\mathrm{T})}{\partial E}\bigg|_{E=E_\mathrm{T}} \\
&\quad - N \frac{\partial \ln \Omega_\mathrm{R}(E_\mathrm{T}, N_\mathrm{T})}{\partial N}\bigg|_{N=N_\mathrm{T}} + \mathcal{O}(E^2, N^2) - \ln \Omega_\mathrm{T}(E_\mathrm{T}, N_\mathrm{T}) \qquad (75)
\end{aligned}
$$

Once again, we already have seen that

$$
\frac{\partial \Omega_\mathrm{R}(E_\mathrm{T})}{\partial E}\bigg|_{E=E_\mathrm{T}, N_\mathrm{T}} = \frac{1}{k_B T} = \beta \tag{76}
$$

We have to calculate the following

$$
\frac{\partial \ln \Omega_\mathrm{R}(E_\mathrm{T}, N_\mathrm{T})}{\partial N}\bigg|_{N=N_\mathrm{T}} \tag{77}
$$

In order to do so, let us go back to thermodynamics but now also taking into effect of chemical potential

$$
dU = TdS - PdV + \mu dN \tag{78}
$$

when the total energy E (U is normally called as E) is fixed, we find the following

$$
\frac{P}{T} = \left(\frac{\partial S}{\partial V}\right)_{E,N}; \qquad -\frac{\mu}{T} = \left(\frac{\partial S}{\partial N}\right)_{E,V} \tag{79}
$$

For micro canonical ensemble, the entropy is

$$
S = k_B \ln \Omega \tag{80}
$$

Thus, using Eq. (79) we have

$$
-\frac{\mu}{T} = \frac{\partial \left[k_B \ln \Omega\right]}{\partial N} \Rightarrow -\frac{\mu}{k_B T} = \frac{\partial \ln \Omega}{\partial N} \Rightarrow -\beta\mu = \frac{\partial \ln \Omega}{\partial N} \tag{81}
$$

Inserting Eqs. (76) and (81) into the grand canonical probability distribution of Eq. (75)

$$
\ln P(E, N) \approx \ln \Omega(E, N) + \ln \Omega_\mathrm{R}(E_\mathrm{T}, N_\mathrm{T}) - \beta E + \beta\mu N - \ln \Omega_\mathrm{T}(E_\mathrm{T}, N_\mathrm{T}) \tag{82}
$$

As usual we keep the total energy E_T and total number of particles N_T constant. Thus, we define $\ln \Omega_R(E_T, N_T) - \ln \Omega_T(E_T, N_T) = -\ln \mathcal{Z}$ that is a constant. The previous equation can be written as

$$\ln P(E, N) \approx \ln \Omega(E, N) - \beta E + \beta \mu N - \ln \mathcal{Z}$$
$$\Rightarrow P(E, N) \approx \frac{\Omega(E, N)e^{-\beta(E-\mu N)}}{\mathcal{Z}} \tag{83}$$

For the discrete energy values, the normalization demands

$$\sum_i \sum_{N_i=0}^{N_i=\infty} P(E_i, N_i) = 1 \tag{84}$$

The grand partition function can thus be written as

$$\mathcal{Z} = \sum_i \sum_{N_i=0}^{N_i=\infty} \Omega(E_i, N_i)e^{-\beta(E_i-\mu N_i)} \tag{85}$$

The probability distribution thus can be written as

$$P(E_i, N_i) = \frac{\Omega(E_i, N_i)e^{-\beta(E_i-\mu N_i)}}{\mathcal{Z}} \tag{86}$$

For continuous energy values though the grand canonical partition function can be written as

$$\mathcal{Z} = \sum_{N=0}^{N=\infty} \int_0^\infty dE\,\Omega(E, N)e^{-\beta(E-\mu N)} \tag{87}$$

We can also replace the canonical partition function from Eq. (149)

$$\mathcal{Z}(T, V, \mu) = \sum_{N=0}^{N=\infty} \underbrace{\int_0^\infty dE\,\Omega(E, N)e^{-\beta E}}_{Z(T,V,N)} e^{\beta\mu N} = \sum_{N=0}^{N=\infty} Z(T, V, N)e^{\beta\mu N} \tag{88}$$

Using the grand canonical ensemble, we can now calculate the average energy and average no of particles.
The average no. of particles can be calculated as

$$\langle N \rangle = \sum_i N_i P(E_i, N_i) \tag{89}$$

Now, we see that

$$\frac{\partial \ln \mathcal{Z}}{\partial \mu} = \frac{1}{\mathcal{Z}} \frac{\partial \mathcal{Z}}{\partial \mu} = \frac{1}{\mathcal{Z}} \frac{\partial}{\partial \mu} \left[\sum_i \sum_{N_i=0}^{N_i=\infty} \Omega(E_i, N_i) e^{-\beta(E_i - \mu N_i)} \right]$$

$$= \beta \frac{\sum_i \sum_{N_i=0}^{N_i=\infty} N_i \Omega(E_i, N_i) e^{-\beta(E_i - \mu N_i)}}{\mathcal{Z}}$$

$$= \beta \sum_i N_i P(E_i, N_i) = \beta \langle N \rangle$$

$$\Rightarrow \langle N \rangle = \frac{1}{\beta} \frac{\partial \ln \mathcal{Z}}{\partial \mu} \tag{90}$$

Following the same procedure, one can find that the average energy is calculated as

$$\langle E \rangle = \sum_i E_i P(E_i, N_i) \tag{91}$$

We calculate

$$\frac{\partial \ln \mathcal{Z}}{\partial \beta} = \frac{1}{\mathcal{Z}} \frac{\partial \mathcal{Z}}{\partial \beta} = \frac{1}{\mathcal{Z}} \frac{\partial}{\partial \beta} \left[\sum_i \sum_{N_i=0}^{N_i=\infty} \Omega(E_i, N_i) e^{-\beta(E_i - \mu N_i)} \right]$$

$$= -\frac{\sum_i \sum_{N_i=0}^{N_i=\infty} E_i \Omega(E_i, N_i) e^{-\beta(E_i - \mu N_i)}}{\mathcal{Z}} + \mu \frac{\sum_i \sum_{N_i=0}^{N_i=\infty} N_i \Omega(E_i, N_i) e^{-\beta(E_i - \mu N_i)}}{\mathcal{Z}}$$

$$= -\sum_i E_i P(E_i, N_i) + \mu \sum_i N_i P(E_i, N_i)$$

$$= -\langle E \rangle + \mu \langle N \rangle$$

$$\Rightarrow \langle E \rangle = -\frac{\partial \ln \mathcal{Z}}{\partial \beta} + \mu \langle N \rangle \tag{92}$$

Entropy

The grand canonical partition function can be written as

$$\mathcal{Z} = \sum_i \sum_{N_i=0}^{N_i=\infty} \Omega(E_i, N_i) e^{-\beta(E_i - \mu N_i)}$$

$$= \sum_i \sum_{N_i=0}^{N_i=\infty} e^{\frac{S(E_i, N_i)}{k_B}} e^{-\beta(E_i - \mu N_i)}$$

$$= \sum_i \sum_{N_i=0}^{N_i=\infty} \exp \left(\frac{S(E_i, N_i)}{k_B} - \beta E_i + \beta \mu N_i \right) \tag{93}$$

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As we argued in the case of canonical ensemble, we find the sum will simply be re-placed by the peak values of energy and no of particles. These peak values are also the average values.

$$\mathcal{Z} = \exp\left(\frac{S}{k_B} - \beta\langle E\rangle + \beta\mu\langle N\rangle\right)$$

$$\Rightarrow S = k_B \ln \mathcal{Z} + \frac{\langle E\rangle}{T} - \frac{\mu\langle N\rangle}{T} = k_B \ln \mathcal{Z} + \frac{U}{T} - \frac{\mu\langle N\rangle}{T} \qquad (94)$$

Normally as there is no external energy provided in an isolated system, we have $\langle E\rangle = U$. We could define a function

$$\Phi = U - TS - \mu\langle N\rangle \qquad (95)$$

Now replace the entropy from Eq. (94) and we get

$$\Phi = U - T\left[k_B \ln \mathcal{Z} + \frac{U}{T} - \frac{\mu\langle N\rangle}{T}\right] - \mu\langle N\rangle$$

$$= -k_B T \ln \mathcal{Z} = -\frac{\ln \mathcal{Z}}{\beta}$$

$$\Rightarrow \mathcal{Z} = e^{-\beta\Phi} \qquad (96)$$

When we should use Quantum Mechanics?

In the black-body radiation, we have studied the energy can be calculated using the wavelength λ as

$$E = \frac{hc}{\lambda} \tag{97}$$

For photons, as their velocity is same as the speed of light, the energy can similarly be represented as

$$E = pc \tag{98}$$

Equating these two relations obtains the de-Broglie wavelength

$$\lambda = \frac{h}{p} \tag{99}$$

This is valid for particles moving at a speed of light c. However, particles can have velocity v which is comparable to the speed of light $v < c$. These particles become relativistic. In this case, the de-Broglie wavelength is

$$\lambda = \frac{h}{p} \quad \text{where } p = \frac{mv}{\sqrt{1 - \frac{v^2}{c^2}}} \tag{100}$$

If the particle velocity is much smaller than the speed of light $v << c$, the particles become non-relativistic. In this case, the de-Broglie wavelength is

$$\lambda = \frac{h}{mv} \tag{101}$$

Quantum statistics are important when the de Broglie wavelength is of order or larger than the interparticle spacing in a system.

Quantum Statistical Physics

The main two agenda in statistical physics that we have learned so far are:

1. Calculate the no of microstates for a given system using appropriate ensemble theory (Micro Canonical, Canonical, Grand Canonical etc.) and calculate the number of microstates and partition function.

2. Calculate the thermodynamics properties from the relations of partition function with entropy, energies etc.

Remember that the above two steps are applicable for not only classical systems, but also, for quantum systems. The quantum systems, however, are different than the classical ones. In the next lecture, we mostly will learn the calculations of microstates and partition function in quantum systems.

Before pondering over the quantum mechanics, let us just remind here what happens in **classical** case. In this case, the particles are considered to be **distinguishable** and any number of particles can be in the same state (later we specify these as quantum state). As the particles are distinguishable, there is no symmetry requirement on the wave function (again quantum mechanics!) when any two particles are interchanged. Such description are known as classical Maxwell-Boltzmann (MB) statistics. We will come back to this in details later! This description is not correct quantum mechanically, however, back in the days MB statistics was useful in explaining the black-body radiation.

Quantum Mechanics:
Consider a gas of N identical particles enclosed within a container of volume V. For a i-th particle the position and momentum coordinates are $\boldsymbol{q}_i$ and $\boldsymbol{p}_i$. The quantum state of this single particle i is denoted by s_i (this includes the angular momentum quantum numbers and also the quantum spin). The quantum state of the whole gas consists of N particles can be described by the following quantum set

$$\{s_1, s_2, s_3, \ldots, s_i, \ldots, s_N\} \tag{102}$$

The quantum wavefunction of the gas in this state can be represented by

$$\Psi = \Psi_{\{s_1, s_2, s_3, \ldots, s_i, \ldots, s_N\}} \left(\boldsymbol{q}_1, \boldsymbol{q}_2, \boldsymbol{q}_3, \ldots, \boldsymbol{q}_N, \boldsymbol{p}_1, \boldsymbol{p}_2, \boldsymbol{p}_3, \ldots, \boldsymbol{p}_N\right) \tag{103}$$

In such context, quantum mechanics brings mainly three important aspects:

♣ **Uncertainty:** We already know that wave function in quantum mechanics depends on the position and momentum. But the fundamental postulates of quantum mechanics tells us that the position and momentum cannot be measured at the same time because they do not commute with each other. In fact the uncertainty principle says that the uncertainty in position Δq and the same in momentum Δp must follow $\Delta q \Delta p \geq \frac{\hbar}{2}$. Therefore, the finding of microstates within a phase space is not valid anymore.

♣ **Identical Particles:** Quantum particles are identical in all aspects e.g., electrons. You can distinguish two classical gas molecules by following their trajectories for a longer period of time. Due to the uncertainty in position and momentum, the trajectory of a quantum particle is absurd. Thus, it is impossible to distinguish two electrons. When quantum mechanics is applied to identical particles, it imposes definite symmetry requirements on the wavefunction Ψ under the interchange of any two identical particles.

♣ **Quantum Spin:** Spin is a fundamental property of identical particles in quantum mechanics. While dealing with identical particles, the wave function also depends on the spin. Spin is a vector in quantum mechanics $\vec{s} = \{s_x, s_y, s_z\}$. However, it is normally described by its magnitude $s = m_s \hbar$ where m_s can be an integer or a half-integer. The $z-$component of the spin has positive and negative values and they are defined by their spin-angular momentum which can take discrete values e.g., $s_z = -m_s\hbar, -(m_s-1)\hbar, \ldots, (m_s-1)\hbar, m_s\hbar$. The spins can be of integer type e.g., $0, \hbar, 2\hbar$, and so on. There are also half-integer spins, e.g., $\frac{\hbar}{2}, \frac{3\hbar}{2}, \frac{5\hbar}{2}$ and so on. For example, an electron has a half-integer spin $\frac{\hbar}{2}$, while a photon has an integer spin 0.

Depending on the symmetry of the wavefunction Ψ and spin, there exist two types of quantum particles (a) **Fermions** (with half-integer spins) and (b) **Bosons** (with integer spins). They obey different statistics. While Fermions obey **Fermi-Dirac statistics**, Bosons obey **Bose-Einstein statistics**. In the classical limit, both these statistics, however, lead to the Maxwell-Boltzmann statistics.

Symmetry Analysis:
To understand the symmetry, let us consider two identical quantum particles A and B. The wavefucntion of the overall system is

$$\Psi = \Psi(q_A, s_A; q_B, s_B) \tag{104}$$

with q_A, s_A are the position and spin of particle A, while q_B, s_B are the position and spin of particle B. Note that we have used one dimensional position co-ordinates q_A and q_A. The other quantum numbers such as angular momentum are suppressed here for convenience! Nevertheless, the wavefunction in quantum mechanics in itself does not have a physical significance. However, the square of the wavefunction tells us the probability of finding a particle. Since we have two particles and

both of them are identical, the probability of finding particle A at position q_A with spin s_A and particle B at position q_B with spin s_B must be exactly the same to the probability of finding particle A at position q_B with spin s_B and particle B at position q_A with spin s_A. The above situation the same as particle exchange between A and B. The probability implies that

$$\left| \Psi(q_A, s_A; q_B, s_B) \right|^2 = \left| \Psi(q_B, s_B; q_A, s_A) \right|^2$$
$$\Rightarrow \Psi(q_A, s_A; q_B, s_B) = \eta \Psi(q_B, s_B; q_A, s_A) \tag{105}$$

where $\eta = \pm 1$ is a phase factor. Therefore, the symmetry of the wavefunction has two possibilities. Either the wavefunction is **symmetric** ($\eta = +1$) under particle exchange $A \leftrightarrow B$ such that

$$\Psi(q_A, s_A; q_B, s_B) = \Psi(q_B, s_B; q_A, s_A) \tag{106}$$

Such particles are called **Bosons**.
The other possibility is that the wavefunction is **anti-symmetric** ($\eta = -1$) under particle exchange $A \leftrightarrow B$

$$\Psi(q_A, s_A; q_B, s_B) = -\Psi(q_B, s_B; q_A, s_A) \tag{107}$$

Such particles are called **Fermions**. Fermions immediately obey Pauli-Exclusion principle which states that
Two fermions cannot occupy the same single-particle quantum state.
Such principle is only valid for Fermions, however, not for the bosons. Let us now try to understand why fermions should obey the Pauli-Exclusion principle. Consider two single particle states K and L for two particles A and B as $\psi_K(q_A, s_A)$ and $\psi_L(q_B, s_B)$. For fermions, the total wavefunction should be anti-symmetric meaning that the total wavefunction should be written as

$$
\begin{aligned}
\Psi(q_A, s_A; q_B, s_B) &= \frac{1}{\sqrt{2}} \left[\psi_K(q_A, s_A)\psi_L(q_B, s_B) - \psi_L(q_A, s_A)\psi_K(q_B, s_B) \right] \\
&= \frac{1}{\sqrt{2}} \left[\psi_K(q_B, s_B)\psi_L(q_A, s_A) - \psi_L(q_B, s_B)\psi_K(q_A, s_A) \right] \quad \{A \leftrightarrow B\} \\
&= -\frac{1}{\sqrt{2}} \left[\psi_K(q_A, s_A)\psi_L(q_B, s_B) - \psi_L(q_A, s_A)\psi_K(q_B, s_B) \right] \\
&= -\Psi(q_B, s_B; q_A, s_A) \tag{108}
\end{aligned}
$$

The factor $1/\sqrt{2}$ comes due to the normalization. Clearly, we can see that the anti-symmetry condition is satisfied. In the above, we have assumed that the two particles staying in two different single particle states. Now, if the two particles A and B are identical and staying in the same state then $K = L$. And in such case, we find the total wavefunction $\Psi(q_A, s_A; q_B, s_B) = 0$. Thus, two fermions cannot occupy the same single particle states.

For **Bosons**, however, we can construct symmetric wave function while two bosons are in the same single particle state. In fact any number of bosons can be accommodated in any single particle state.

Simple Example to Understand Different Statistics:

Consider a system of only two particles A and B. Assume that each particle can be in one of three possible single-particle quantum states $s = 1, 2, 3$. The question is how can we define the possible states of the whole gas. In other words, how many distinct ways one can put two particles in three single-particle states. The answer can be calculated depending upon the the nature of particles.

♣ **Maxwell-Boltzmann Distribution:** Consider that the particles are classical and distinguishable. In this case, any number of particles can stay in any state. Therefore, the following distribution of particles are possible.

State 1	State 2	State 3
A	B	-
B	A	-
-	A	B
-	B	A
A	-	B
B	-	A
AB	-	-
-	AB	-
-	-	AB

Overall, there are 9 possible states for the whole gas.

♣ **Bose-Einstein Distribution:** The particles are considered to be indistinguishable meaning we should remove the particle label i.e., $A = B$. In this case, any particle can stay in any state. But the distinction between A and B is not possible any more. The following distribution is thus obtained.

State 1	State 2	State 3
A	A	-
-	A	A
A	-	A
AA	-	-
-	AA	-
-	-	AA

♣ **Fermi-Dirac Distribution:** In this case, no more than one particle can be in any one state. Thus we obtain the following distribution.

State 1	State 2	State 3
A	A	-
-	A	A
A	-	A

Statistics of Non-interacting Gas

Let us now move forward and consider the non-interacting gas. One advantage of the non-interacting gas is that we can write down the total energy as a sum of individual single-particle energies that are obtained from solving single-particle Schrödinger equation. Considering a system of particles as non-interacting turns out to be a very good approximation. In fact, for interacting particles, one needs to solve many-particle Schrödinger equation that is very difficult and there are research works going on in such field.

Let us consider the single particle states labeled as $i = 1, 2, 3, \ldots$. The energy of level i is ε_i and number of particles in level i is n_i. For example, a particle in a box of size L has momentum $p_n = \frac{n\pi\hbar}{L}$ and the single-particle energy can similarly be calculated as $\varepsilon_n = \frac{p_n^2}{2m}$. We would like to consider the following problem:
Given a large number of non-interacting particles with single-particle energies ε_i, what is the probability distribution (average number of particles in a state i) of particles in single-particle states?
We move to grand canonical ensemble to answer this above question. The reason is not only the energy changes, but also, the number of particles. The partition function in grand canonical ensemble of the whole system

$$\mathcal{Z} = \sum_{N,E} \Omega(E, N) e^{-\beta(E-\mu N)} \tag{109}$$

with the following facts for single-particle states

$$N = \sum_i n_i \tag{110}$$

$$E = \sum_i n_i \varepsilon_i \tag{111}$$

$\sum_i$ defines the sum over all the single-particle states. The grand partition function can conveniently be written as

$$\mathcal{Z} = \sum_{n_i,\varepsilon_i} \Omega(\varepsilon_i, n_i) e^{-\beta\left(\sum_i n_i \varepsilon_i - \mu \sum_i n_i\right)}$$

$$= \prod_{single-particle\ state\ i} \sum_{n_i,\varepsilon_i} \Omega(\varepsilon_i, n_i) e^{-\beta n_i (\varepsilon_i - \mu)}$$

$$= \prod_{single-particle\ state\ i} \mathcal{Z}_i \tag{112}$$

where the single-particle grand partition function is

$$\mathcal{Z}_i = \sum_{n_i,\varepsilon_i} \Omega(\varepsilon_i, n_i) e^{-\beta n_i(\varepsilon_i - \mu)} \tag{113}$$

Eq. (112) means that the full grand partition function of non-interacting system is a product of the grand partition functions for the separate single-particle states: each degree of freedom can be excited independently. This is very powerful, since it means the probability of finding n_i particles occupying state i is completely independent of whatever else is happening. This won't be the case for interacting particles though.

As we calculated the average number of particles in case of Grand Canonical ensemble [see Eq. (90)], the occupation number in this case will simply be

$$\langle n_i \rangle = \frac{1}{\beta} \frac{\partial \ln \mathcal{Z}_i}{\partial \mu} \tag{114}$$

Now let us apply this powerful tool in two following cases:

♣ Bose-Einstein Distribution

For a Bose system, there can be any number $n_i = 0, 1, 2, \ldots$ of bosons in any given state i. The single-particle state grand-canonical partition function for the state i with energy ε_i can thus be expressed as

$$\begin{aligned} \mathcal{Z}_i &= \sum_{n_i=0}^{n_i=\infty} e^{-\beta n_i(\varepsilon_i - \mu)} \\ &= \sum_{n=0}^{n=\infty} x_i^n \quad \text{where } x_i = e^{-\beta(\varepsilon_i - \mu)} << 1 \end{aligned} \tag{115}$$

This is a sum over infinite series which can be written as following

$$\begin{aligned} \mathcal{Z}_i &= \frac{1}{1 - x_i} \\ &= \frac{1}{1 - e^{-\beta(\varepsilon_i - \mu)}} \end{aligned} \tag{116}$$

The average occupation number can thus be calculated

$$\langle n_i \rangle = \frac{1}{\beta} \frac{\partial \ln \mathcal{Z}_i}{\partial \mu}$$

$$= \frac{1}{\beta} \frac{\partial}{\partial \mu} \left[-\ln \left(1 - e^{-\beta(\varepsilon_i - \mu)} \right) \right]$$

$$= \frac{1}{e^{\beta(\varepsilon_i - \mu)} - 1} \tag{117}$$

This is known as **Bose-Einstein distribution** which we call as $b(\varepsilon)$. Now, recall the Planck's derivation of Black-body radiation. He also obtained a similar distribution function! That was for electromagnetic radiation namely photons and we know photons are bosons as they are spin "0" particles. Note
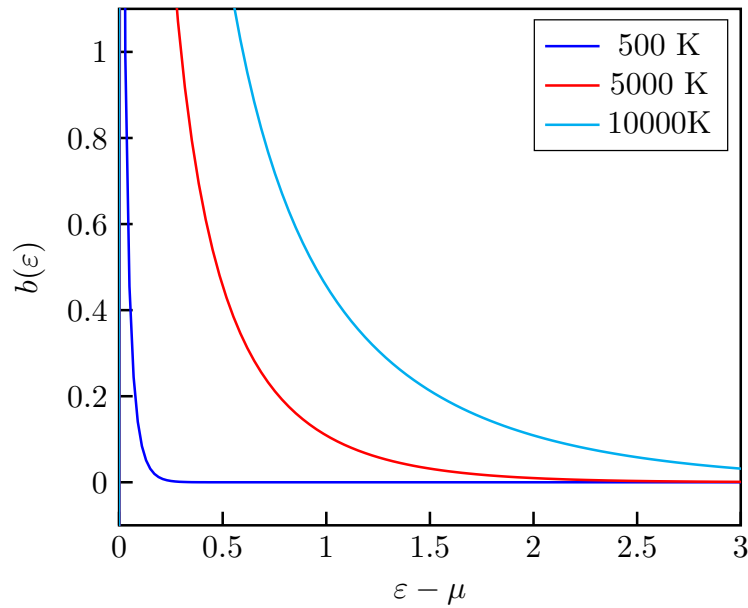

Figure 8: Bose-Einstein distribution function at several temperatures.

that the occupation number in any state i must be positive. To ensure that the following condition must be satisfied

$$e^{\beta(\varepsilon_i - \mu)} \geq 1$$

$$\Rightarrow \beta(\varepsilon_i - \mu) \geq 0$$

$$\varepsilon_i \geq \mu \tag{118}$$

Often we set the ground state energy to zero. In that case, the chemical potential μ is negative.

♣ Fermi-Dirac Distribution

For fermions, no two particles can occupy the same single-particle state. So the single-particle grand- canonical partition function is simply

$$\mathcal{Z}_i = \sum_{n_i=0,1} e^{-\beta n_i(\varepsilon_i-\mu)} = 1 + e^{-\beta(\varepsilon_i-\mu)} \tag{119}$$

Similarly, we can calculate the occupation number as

$$\begin{aligned}
\langle n_i \rangle &= \frac{1}{\beta}\frac{\partial \ln \mathcal{Z}_i}{\partial \mu} \\
&= \frac{1}{\beta}\frac{\partial}{\partial \mu}\left[\ln\left(1 + e^{-\beta(\varepsilon_i-\mu)}\right)\right] \\
&= \frac{1}{e^{\beta(\varepsilon_i-\mu)}+1} \tag{120}
\end{aligned}$$

This is known as **Fermi-Dirac distribution** that is called as $f(\varepsilon)$. An im-
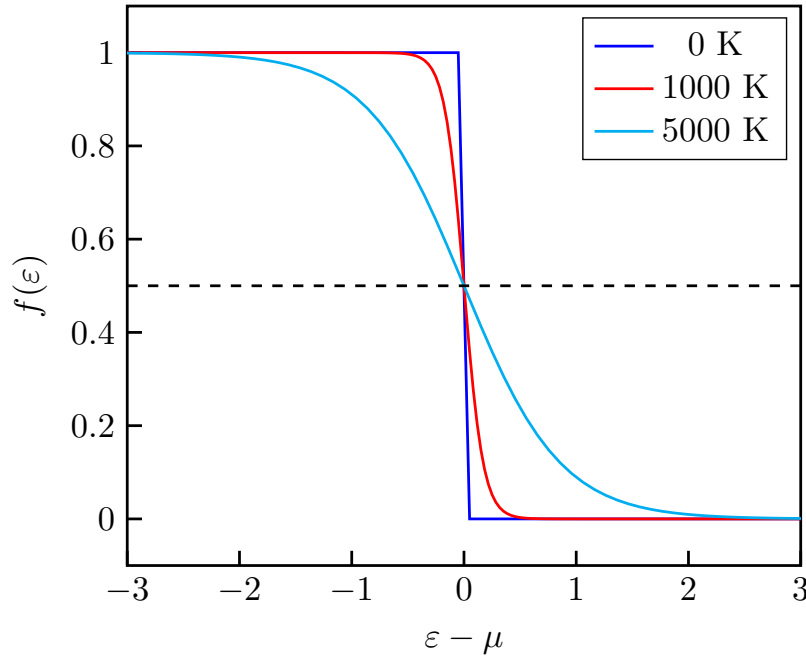

Figure 9: Fermi-Dirac distribution at absolute zero and higher temperatures.

mediate observation from Fermi-Dirac distribution is that at low temperature, the states with energies greater than chemical potential μ are unoccupied and states with energies $\varepsilon < \mu$ are completely filled.

At $T = 0$, the chemical potential is called the **Fermi Energy** $\varepsilon_F = \mu(T = 0)$. This means all the states below Fermi energy are completely occupied, while the states above Fermi energy are completely empty. In fact Fermi energy is very important concept in physics that deals with how electrons are arranged in different solid systems e.g., metals, semiconductors, insulators etc.

Note that unlike BE statistics there is no restriction on the value of chemical potential μ.

Maxwell-Boltzmann Distribution

We have already introduced MB statistics. The classical particles remain distinguishable in this case. However, we can decide if we want to calculate them as distinguishable or indistinguishable particles. It appears that treating the particles indistinguishable is rather easier and known as Maxwell-Boltzmann distribution. Remember that these are classical particles though. For example, consider a system of classical gas. If we assign names to each and individual gas molecules and calculate their trajectories for microstates - the task is super difficult.

For micro canonical ensemble, the number of microstates for indistinguishable particles $\Omega_{\text{indishguishable}}$ can be calculated from the microstates for distinguishable particles $\Omega_{\text{dishguishable}}$ as follows

$$\Omega_{\text{indishguishable}} = \frac{\Omega_{\text{dishguishable}}}{N!} \tag{121}$$

As the particles are indistinguishable, then we need to divide by a factor $N!$ to eliminate the over-counting.

Similarly for canonical ensemble, we introduce partition function and

$$Z_{\text{indishguishable}} = \frac{Z_{\text{dishguishable}}}{N!} \tag{122}$$

However, as always, we deal with grand canonical ensemble and in this case, as we consider the indistinguishable particles, we have

$$\begin{aligned}
\mathcal{Z} &= \sum_{N,E} \Omega(E, N) e^{-\beta(E - \mu N)} \\
&= \sum_N \underbrace{\left(\sum_E \Omega(E, N) e^{-\beta E} \right)}_{Z_N} e^{\beta \mu N} \\
&= \sum_N Z_N e^{\beta \mu N} \tag{123}
\end{aligned}$$

where $Z_N = \sum_E \Omega(E, N)e^{-\beta E}$ is canonical partition function with N indistinguishable particles. Now consider the particles distinguishable such that the partition function is Z'_N. In this case, of course, we have

$$Z_N = \frac{Z'_N}{N!} \tag{124}$$

We have to calculate the partition function for distinguishable particles. To do so, all the particles can contribute independently to the partition function. Therefore, we have to combine all the individual partition functions such that

$$Z'_N = Z_1 \times Z_1 \times Z_1 \times \ldots (N \text{ times}) \qquad\qquad = Z_1^N \tag{125}$$

with Z_1 is the partition function for an individual particles given by

$$Z_1 = \sum_{\varepsilon_i} e^{-\beta \varepsilon_i} \tag{126}$$

Combining Eqs. (124) and (124) and plugging in Eq. (123) we obtain

$$\begin{aligned}
\mathcal{Z} &= \sum_N \frac{e^{\beta \mu N} Z_1^N}{N!} \\
&= \sum_N \frac{\left(Z_1 e^{\beta \mu}\right)^N}{N!} \\
&= \exp(Z_1 e^{\beta \mu}) \\
&= \exp\left(\sum_{\varepsilon_i} e^{-\beta(\varepsilon_i - \mu)}\right) \\
&= \prod_{\varepsilon_i} \exp\left(e^{-\beta(\varepsilon_i - \mu)}\right) = \prod_{\varepsilon_i} \mathcal{Z}_i
\end{aligned} \tag{127}$$

with the fact that the single-particle grand partition function is

$$\mathcal{Z}_i = \exp\left(e^{-\beta(\varepsilon_i - \mu)}\right) \tag{128}$$

We calculate the average number of particles i.e., occupation number as

$$\begin{aligned}
\langle n_i \rangle &= \frac{1}{\beta} \frac{\partial \ln \mathcal{Z}_i}{\partial \mu} \\
&= \frac{1}{\beta} \frac{\partial \left[e^{-\beta(\varepsilon_i - \mu)}\right]}{\partial \mu} \\
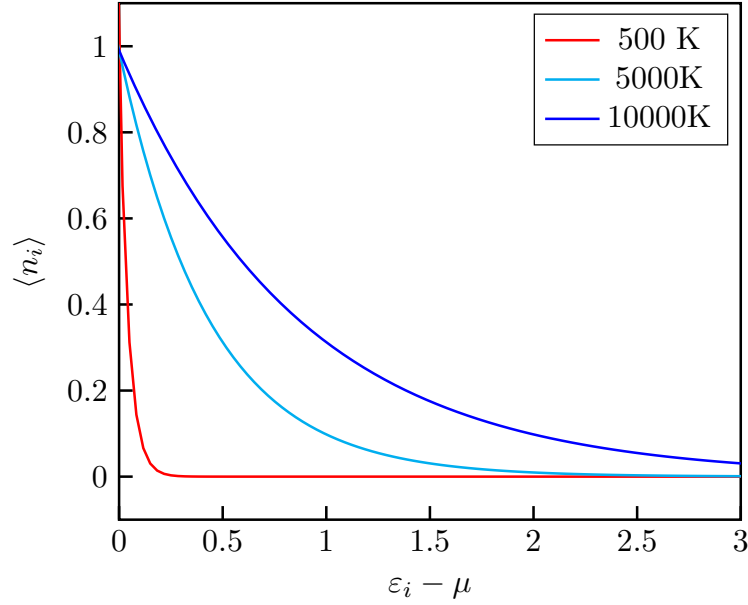&= e^{-\beta(\varepsilon_i - \mu)}
\end{aligned} \tag{129}$$

Figure 10: The Maxwell-Boltzmann statistics plotted.

This is the **Maxwell-Boltzmann** statistics!

Classical Limit of Quantum Statistics

We have obtained the following average occupation numbers for each of the distributions

$$\langle n_i \rangle = \frac{1}{e^{\beta(\varepsilon_i - \mu)} - 1} \qquad \text{BE statistics} \tag{130}$$

$$= \frac{1}{e^{\beta(\varepsilon_i - \mu)} + 1} \qquad \text{FD statistics} \tag{131}$$

$$= \frac{1}{e^{\beta(\varepsilon_i - \mu)}} \qquad \text{MB statistics} \tag{132}$$

Note that all these have the same form

$$\langle n_i \rangle = \frac{1}{e^{\beta(\varepsilon_i - \mu)} + c} \tag{133}$$

where $c = -1, 0$ or $+1$. In the classical limit, the energy values are discontinuous anymore. The energy values reach to the continuum. Therefore, the probability of two particles being in the same state is irrelevant. This limit requires that the aver-

age occupation number is very small i.e., $\langle n_i \rangle << 1$. This leads to the fact that

$$\frac{1}{e^{\beta(\varepsilon_i - \mu)} + c} << 1$$

$$\Rightarrow e^{\beta(\varepsilon_i - \mu)} >> 1 \tag{134}$$

In this respect the factor c is small and can be neglected. Thus, at the claasical limit all the statistics follow MB distribution!
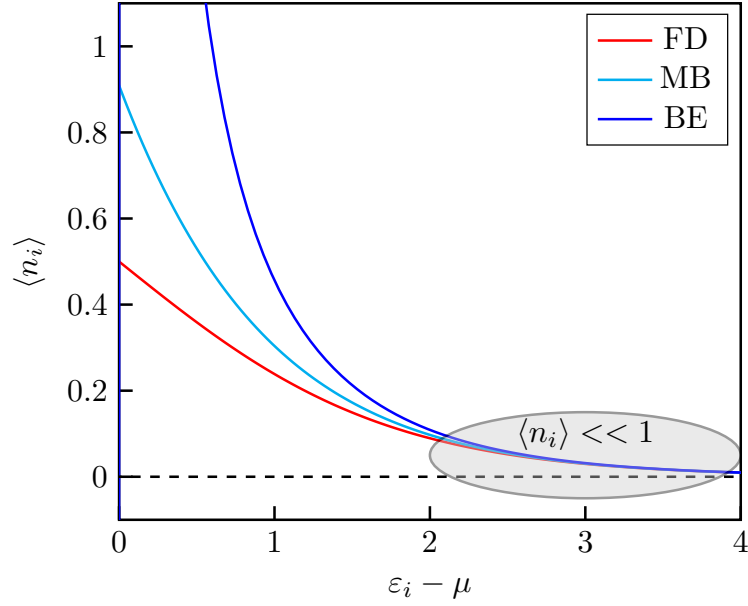

Figure 11: At the classical limit FD and BE statistics follow MB statistics.

Introduction to Steller Objects

Stars are nice laboratories which provide us chances of looking at matter whose composition, temperature and pressure are usually different from those of systems found on earth. Therefore, it is interesting to investigate the stellar objects and their thermodynamical evolution.

Life of a star

Stars form out of gas clouds. A cloud of particles, left to itself, contracts under the gravitational pull between the particles. As it contracts, its temperature rises. Initially, as there is nothing to counter the gravitational pull, the cloud becomes smaller and smaller.

The clouds consist mainly of molecular or atomic hydrogen. As the gravitational contraction continues and temperature rises, the molecular bonds are cut off. At that temperature only the atomic hydrogen exists. At even higher temperature, the atoms are stripped of their electrons. Therefore, the electrons as well as the hydrogen nuclei (which are just protons!) freely move in the clouds. There are other nuclei (from different gas) exist though. Protons have Coulomb repulsion between themselves, so they cannot combine to form heavier nuclei.

When the temperature is very high, the velocity of the particles become higher as well because their energies are higher. The probability of nuclear interaction between two protons increases sharply. A proton can then perform a quantum tunneling through the Coulomb barrier of another proton. At this situation, the nuclear reactions start which produce energy and radiation. The pressure from this radiation counteracts with the gravitational pull and thus the cloud attains an equilibrium state. This is the birth of a star.

In the first stage two protons combine to produce deuteron nucleus

$$p + p \rightarrow \text{H}_2 + e^+ + \nu_e \tag{135}$$

Deuteron is very unstable nucleus because its binding energy is very small. So, it dissociates soon after it forms and following reaction occurs

$$\text{H}_2 + p \rightarrow \text{He}_3 + \gamma \tag{136}$$

$$\text{He}_3 + \text{He}_3 \rightarrow \text{He}_4 + p + p \tag{137}$$

He$_4$ is very stable. **This is how a star is formed**.

During this process, a stage is reached when all the protons in the core region are cooked into helium. Therefore, the nuclear reaction stops. In the absence of any radiation pressure to counter the gravitational pull, the core collapses and heats up, until a temperature is reached where Helium nuclei has enough average energy to overcome the Coulomb barrier between them. At this point, they combine to heavier nuclei mainly to C_{12}. The start would then reach to equilibrium once again until all the Helium fuel is burnt out. If this cycle goes on, at the end iron nuclei will be formed because iron has the highest binding energy among all nuclei. So, further fusion into heavier nuclei is not possible. This is known as **collapse of a star**.

Depending on the mass of the star, the collapse leads to mainly two kinds of steller objects!

♣ **White Dwarf:**

Remember that the core is made of electrons, protons which are fermions! They obey Pauli exclusion principle, meaning one can pack only upto certain number of electrons in a given volume of phase space. If the gravitational pull tries to reduce the volume, the phase space volume also decreases and the Fermions tend to resist that. A stage might be reached when the electron gas is able to resist the gravitational pull. Then the further nuclear reactions are not possible. A white dwarf is created! This is related to the mass of the star because Chandrasekher showed that the white dwarf can only occur if the core has a lesser mass than a certain amount.

Chandrasekher Limit: Chandrasekhar determined what is known as the Chandrasekhar limit—that a star having a mass more than 1.44 times that of the Sun does not form a white dwarf but instead continues to collapse, blows off its gaseous envelope in a supernova explosion, and becomes a neutron star.

♣ **Neutron star:** For the stars having very heavy mass, the nuclear reactions can continue to the end, producing iron nuclei. After that gravitaional contraction in the core might be countered by degeneracy pressure of neutrons and an equilibrium might be achieved. If this happens the core is said to have turned into a neutron star.

♣ **Black Hole:** If the mass of the star is too large, the neutron star cannot be formed. In that case, they turn into black hole.

Tutorials on Statistical Physics

Problem: Calculate the number of macrostates and microstates when three unbiased coins are tossed at the same time.

Solution: When three unbiased coins are tossed together, the macrostates are the following:

- ♣ (H,H,H)

- ♣ (H,H,T)

- ♣ (H,T,T)

- ♣ (T,T,T)

The no. of microstates corresponding to the macrostate (H,H,H) is one because there is only one possibility.

The no. of microstates corresponding to the macrostate (T,T,T) is also one because there is only one possibility.

The no. of microstates corresponding to the macrostate (H,H,T) are 3 as follows:

Coin 1	Coin 2	Coin 3
H	H	T
H	T	H
T	H	H

The no. of microstates corresponding to the macrostate (H,T,T) are 3 as follows:

Coin 1	Coin 2	Coin 3
H	T	T
T	T	H
T	H	T

Problem: Calculate the number of microstates for a single free particle.

Solution: We know that the energy of a free particle is

$$E = \frac{p^2}{2m} \Rightarrow |p| = \sqrt{2mE} \tag{138}$$

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The number of microstates can be calculated from the phase space volume. For a N-particle system the number of microstates can be calculated by

$$
\begin{aligned}
\Omega(E) &= \frac{1}{h^{3N} N!} \int_V d^3 q_1 d^3 q_2 \ldots d^3 q_N \int d^3 p_1 d^3 p_2 \ldots d^3 p_N \\
&= \frac{1}{h^{3N} N!} \int_V \left(d^3 q\right)^N \int \left(d^3 p\right)^N \\
&= \frac{V^N}{h^{3N} N!} \int \left(d^3 p\right)^N
\end{aligned}
\tag{139}
$$

Phase space can be seen as the cells of size h^{3N} because of the uncertainty principle that $\delta q \delta p \sim h$. The factorial $N!$ comes for the fact that we can treat the particles as identical.

Let us now calculate this for only one particle with $N = 1$. In practice you would say that there are infinite number of points in the phase space, right? But, these points are restricted by the energy values of a single particle which is finite and $p = \sqrt{2mE}$. All we need to calculate is the volume element $d^3 p$. We are going to consider the spherical coordinates and calculate the volume element which is exactly $4\pi p^2 dp$. The number of microstates

$$
\begin{aligned}
\Omega(E) &= \frac{V}{h^3} \int_{p=0}^{p=\sqrt{2mE}} 4\pi p^2 dp \\
&= \frac{4\pi V}{h^3} \frac{p^3}{3} \Big|_{p=0}^{p=\sqrt{2mE}} \\
&= \frac{4\pi}{3} \frac{V}{h^3} (2mE)^{\frac{3}{2}}
\end{aligned}
\tag{140}
$$

Problem: Consider a simple two level system in microcanonical ensemble for N particles. The lower energy level is non-degenerate and has zero energy - called ground state. The other energy level at energy ε - excited state that is doubly degenerate meaning two excited states with same energy. If the total number of particles in the excited states is N_{E}, calculate the number of microstates.

Solution: The N_{E} number of particles are in the excited states with energy ε and the $N - N_{\mathrm{E}}$ numbers of particles are in the ground state with energy 0. Total energy of the system is then $E = N_{\mathrm{E}} \varepsilon$.

The question is, how many microstates are available to this energy E? Clearly, we first have to take into account the number of ways that one can select the N_{E} parti-

cles for the excited states among a total number of N particles. This answer is

$$\frac{N!}{N_{\mathrm{E}}!(N - N_{\mathrm{E}})!}$$

Next we need to consider how the N_{E} particles are distributed between the two excited states. Since each particle can be either of the excited states, the total number is $2^{N_{\mathrm{E}}}$. Combining the two factors, the total number of microstates are

$$\Omega = 2^{N_{\mathrm{E}}} \frac{N!}{N_{\mathrm{E}}!(N - N_{\mathrm{E}})!} = \frac{2^{E/\varepsilon} N!}{\left(\frac{E}{\varepsilon}\right)! \left(N - \frac{E}{\varepsilon}\right)!} \tag{141}$$

Problem: Consider a simple two level system in canonical ensemble for N particles. The lower energy level is non-degenerate and has zero energy - called ground state. The other energy level at energy ε - excited state that is doubly degenerate meaning two excited states with same energy. If the total number of particles in the excited states is N_{E}, calculate the partition function and entropy.

Answer: For non-interacting system we already know that the partition function of the total system can be written as a product of the single-particle partition function as follows

$$Z = \prod_i Z_i \tag{142}$$

If there are N number of non-interacting particles and the single particle partition function $Z_i = Q$, then we can write down the product as the power

$$Z = Q^N \tag{143}$$

The one particle canonical partition function is written as

$$Q = \sum_{\varepsilon_i} e^{-\beta \varepsilon_i} \tag{144}$$

In our case, the ground state energy $\varepsilon_0 = 0$ and two excited energies are ε. We find the partition function as

$$Q = e^0 + e^{-\beta \varepsilon} + e^{-\beta \varepsilon} = 1 + 2e^{-\beta \varepsilon} \tag{145}$$

Notice that the factor 2 in the second term on the right hand side. This is purely because of the 2-fold degeneracy of the higher energy level. The partition function of the whole system is then given by

$$Z = \left(1 + 2e^{-\beta \varepsilon}\right)^N \tag{146}$$

First, we calculate the average energy

$$\langle E \rangle = -\frac{\partial}{\partial \beta} \ln Z$$
$$= -\frac{\partial}{\partial \beta} \left[N \ln \left(1 + 2e^{-\beta \varepsilon} \right) \right]$$
$$= \frac{2N\varepsilon e^{-\beta \varepsilon}}{1 + 2e^{-\beta \varepsilon}}$$
$$= \frac{2N\varepsilon}{e^{\beta \varepsilon} + 2} \tag{147}$$

The entropy can be found as

$$S = k_B \ln Z + \frac{\langle E \rangle}{T}$$
$$= N k_B \ln \left(1 + 2e^{-\beta \varepsilon} \right) + \frac{2N\varepsilon}{T \left(e^{\beta \varepsilon} + 2 \right)}$$
$$= N k_B \left[\ln \left(1 + 2e^{-\beta \varepsilon} \right) + \frac{2\beta \varepsilon}{e^{\beta \varepsilon} + 2} \right] \tag{148}$$

Problem: Calculate the partition function for a classical ideal gas of N particles using canonical ensemble.

Answer: We know that the partition function for a classical canonical ensemble is defined as

$$Z(T, V) = \int_0^\infty \Omega(E) e^{-\beta E} dE \tag{149}$$

where $\Omega(E)$ are the number of microstates. We also know that the partition function for the total system of N particles can be written in terms of the single-particle canonical partition function z as

$$Z(T, V, N) = \frac{z^N}{N!} \tag{150}$$

$N!$ arises due to the fact that the particles are indistinguishable.

Therefore, all we have to calculate is the single-particle partition function z. As we have already calculated the number of microstates in Problem 1. The single particle partition function can be written as

$$z = \frac{1}{h^3} \int_{-\infty}^\infty d^3 q \int_{-\infty}^\infty d^3 p \, e^{-\frac{\beta p^2}{2m}}$$
$$= \frac{V}{h^3} \left[\int_{-\infty}^\infty dp \, e^{-\frac{\beta p^2}{2m}} \right]^3 \tag{151}$$

Consider the following:

$$\frac{\beta p^2}{2m} = x \Rightarrow \frac{\beta}{2m} p\, dp = dx \Rightarrow dp = \frac{2m}{\beta}\sqrt{\frac{\beta}{2mx}}\, dx = \sqrt{\frac{2m}{\beta}}\, x^{-\frac{1}{2}}\, dx \quad \text{and } p = \sqrt{\frac{2mx}{\beta}} \tag{152}$$

We continue the calculation of the integration

$$\begin{aligned}
\int_{-\infty}^{\infty} dp\, e^{-\frac{\beta p^2}{2m}} &= \int_{0}^{\infty} \sqrt{\frac{2m}{\beta}}\, x^{-\frac{1}{2}} e^{-x}\, dx \\
&= \sqrt{\frac{2m}{\beta}} \int_{0}^{\infty} x^{\frac{1}{2}-1} e^{-x}\, dx \\
&= \sqrt{2mk_B T}\ \Gamma\left(\frac{1}{2}\right) = \sqrt{2\pi m k_B T} \tag{153}
\end{aligned}$$

Here we have to use the Gamma function definition

$$\Gamma(n) = \int_{0}^{\infty} x^{n-1} e^{-x}\, dx \tag{154}$$

and the calculation of the Gamma function is as follows

$$\Gamma(n) = (n-1)! \quad \text{and } \Gamma(n+1) = n\Gamma(n) \tag{155}$$

For example we can calculate

$$\Gamma\left(\frac{5}{2}\right) = \frac{3}{2}\Gamma\left(\frac{3}{2}\right) = \frac{3}{2} \times \frac{1}{2}\Gamma\left(\frac{1}{2}\right) = \frac{3\sqrt{\pi}}{4} \tag{156}$$

where we have two useful values

$$\Gamma\left(\frac{1}{2}\right) = \sqrt{\pi} \quad \text{and } \Gamma(1) = 1 \tag{157}$$

The single particle partition function can thus be

$$z = \frac{V\,(2\pi m k_B T)^{\frac{3}{2}}}{h^3} = V\left(\frac{2\pi m k_B T}{h^2}\right)^{\frac{3}{2}} \tag{158}$$

The total partition function for N particles can suitably be written in the form

$$Z(T, V, N) = \frac{z^N}{N!} = \frac{V^N}{N!}\left(\frac{2\pi m k_B T}{h^2}\right)^{\frac{3N}{2}} \tag{159}$$

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Problem: Calculate the partition function for a classical ideal gas of N particles using grand canonical ensemble. Calculate the average number of particles and energy.

Answer: In the grand canonical ensemble, the grand partition function $\mathcal{Z}$ has the following form

$$\mathcal{Z}(T,V,\mu) = \sum_{N=0}^{N=\infty} \underbrace{\int_0^\infty dE\,\Omega(E,N)e^{-\beta E}}_{Z(T,V,N)}\,e^{\beta\mu N} = \sum_{N=0}^{N=\infty} Z(T,V,N)e^{\beta\mu N} \qquad (160)$$

We have already calculated the partition function in canonical ensemble $Z(T,V,N)$ in the previous problem. We shall use that in this particular case for grand canonical partition function such that

$$
\begin{aligned}
\mathcal{Z}(T,V,\mu) &= \sum_{N=0}^{N=\infty} \frac{V^N}{N!} \left(\frac{2\pi m k_B T}{h^2}\right)^{\frac{3N}{2}} e^{\beta\mu N} \\
&= \sum_{N=0}^{N=\infty} \frac{\left[V e^{\beta\mu} \left(\frac{2\pi m k_B T}{h^2}\right)^{\frac{3}{2}}\right]^N}{N!} \\
&= \exp\left[V e^{\beta\mu} \left(\frac{2\pi m k_B T}{h^2}\right)^{\frac{3}{2}}\right] \\
&= \exp\left[V e^{\beta\mu} \left(\frac{2\pi m}{\beta h^2}\right)^{\frac{3}{2}}\right] \qquad (161)
\end{aligned}
$$

The average number of particles can be calculated using the following formula

$$
\begin{aligned}
\langle N \rangle &= \frac{1}{\beta}\frac{\partial \ln \mathcal{Z}}{\partial \mu} \\
&= \frac{1}{\beta}\frac{\partial}{\partial \mu}\left[V e^{\beta\mu}\left(\frac{2\pi m k_B T}{h^2}\right)^{\frac{3}{2}}\right] \\
&= V e^{\beta\mu}\left(\frac{2\pi m k_B T}{h^2}\right)^{\frac{3}{2}} = V e^{\beta\mu}\left(\frac{2\pi m}{\beta h^2}\right)^{\frac{3}{2}} \qquad (162)
\end{aligned}
$$

Average energy can similarly be calculated as

$$
\begin{aligned}
\langle E \rangle &= -\frac{\partial \ln \mathcal{Z}}{\partial \beta} + \mu \langle N \rangle \\
&= -\frac{\partial}{\partial \beta} \left[V e^{\beta \mu} \left(\frac{2\pi m}{\beta h^2} \right)^{\frac{3}{2}} \right] + \mu V e^{\beta \mu} \left(\frac{2\pi m}{\beta h^2} \right)^{\frac{3}{2}} \\
&= -\mu V e^{\beta \mu} \left(\frac{2\pi m}{\beta h^2} \right)^{\frac{3}{2}} - V e^{\beta \mu} \left(\frac{2\pi m}{h^2} \right)^{\frac{3}{2}} \frac{\partial}{\partial \beta} \beta^{-\frac{3}{2}} + \mu V e^{\beta \mu} \left(\frac{2\pi m}{\beta h^2} \right)^{\frac{3}{2}} \\
&= -V e^{\beta \mu} \left(\frac{2\pi m}{h^2} \right)^{\frac{3}{2}} \times \left(-\frac{3}{2} \right) \beta^{-\frac{5}{2}} \\
&= \frac{3}{2} \underbrace{V e^{\beta \mu} \left(\frac{2\pi m}{\beta h^2} \right)^{\frac{3}{2}}}_{\langle N \rangle} \frac{1}{\beta} \\
&= \frac{3}{2} \langle N \rangle k_B T
\end{aligned}
\tag{163}
$$

This is exactly the same as we obtained in thermodynamics where the internal energy of an ideal gas $U = \frac{3}{2} N k_B T$ using the equipartition theorem.

Problem: Suppose we have N linear (one-dimensional) harmonic oscillators, with the Hamiltonian given by

$$
\mathcal{H} = \sum_{i=1}^{i=N} \left(\frac{p_i^2}{2m} + \frac{1}{2} m \omega^2 q_i^2 \right)
\tag{164}
$$

calculate the patition function of the whole system using classical approach of canonical ensemble. Calculate the entropy.

Solution: We first find the one-particle partition function as we did earlier. The one-particle canonical partition function can be written as

$$
\begin{aligned}
Q &= \frac{1}{h} \int_{-\infty}^{\infty} dq \, e^{-\frac{\beta m \omega^2 q^2}{2}} \int_{-\infty}^{\infty} dp \, e^{-\frac{\beta p^2}{2m}} \\
&= \frac{2\pi}{\beta h \omega} = \frac{1}{\beta \hbar \omega}
\end{aligned}
\tag{165}
$$

Calculate the integrals using Gamma function!

The partition function for the whole system of N harmonic oscillator is then

$$
Z = Q^N = \left(\frac{1}{\beta \hbar \omega} \right)^N
\tag{166}
$$

The average energy of the harmonic oscillators is

$$\langle E \rangle = -\frac{\partial \ln Z}{\partial \beta} = N \frac{\partial \ln \beta h\omega}{\partial \beta} = \frac{N}{\beta h\omega} \times h\omega = \frac{N}{\beta} = N k_B T \tag{167}$$

The entropy can then be calculated as

$$\begin{aligned}
S &= k_B \ln Z + \frac{\langle E \rangle}{T} \\
&= -N k_B \ln \beta h\omega + N k_B \\
&= N k_B \left(1 - \ln \beta h\omega \right) \\
&= N k_B \left(1 - \ln \left[\frac{h\omega}{k_B T} \right] \right)
\end{aligned} \tag{168}$$

Problem: Suppose we have N linear harmonic oscillators, with the quantum mechanical energy eigen values given by

$$\varepsilon_i = \left(n_i + \frac{1}{2} \right) \hbar\omega \tag{169}$$

where $\hbar = h/2\pi$. Calculate the patition function of the whole system using quantum approach of canonical ensemble. Calculate the entropy. Show that at the classical limit i.e., $\hbar \to 0$ the entropy follows the previous derivation of claasical approach.

Answer: The one-particle partition function can be calculated

$$\begin{aligned}
Q &= \sum_{n_i=0}^{n_i=\infty} e^{-\beta \hbar\omega \left(n_i + \frac{1}{2} \right)} \\
&= e^{-\frac{\beta \hbar\omega}{2}} \sum_{n_i=0}^{n_i=\infty} e^{-\beta \hbar\omega n_i} \\
&= e^{-\frac{\beta \hbar\omega}{2}} \times \frac{1}{1 - e^{-\beta \hbar\omega}}
\end{aligned} \tag{170}$$

The canonical partition function for the total system of N non-interacting particles

$$Z = Q^N = \frac{e^{-\frac{N\beta \hbar\omega}{2}}}{\left(1 - e^{-\beta \hbar\omega} \right)^N} \tag{171}$$

Let us first calculate the average energy

$$
\begin{aligned}
\langle E \rangle &= -\frac{\partial \ln Z}{\partial \beta} \\
&= -\frac{\partial}{\partial \beta}\left[-\frac{N\beta\hbar\omega}{2} - N\ln\left(1 - e^{-\beta\hbar\omega}\right)\right] \\
&= \frac{N\hbar\omega}{2} + \frac{N\hbar\omega e^{-\beta\hbar\omega}}{(1 - e^{-\beta\hbar\omega})} \\
&= \frac{N\hbar\omega}{2} + \frac{N\hbar\omega}{(e^{\beta\hbar\omega} - 1)} \\
&= N\hbar\omega\left(\frac{1}{2} + \frac{1}{e^{\beta\hbar\omega} - 1}\right)
\end{aligned}
\tag{172}
$$

The calculation of entropy is thus simply

$$
\begin{aligned}
S &= k_B \ln Z + \frac{\langle E \rangle}{T} \\
&= k_B\left[-\frac{N\beta\hbar\omega}{2} - N\ln\left(1 - e^{-\beta\hbar\omega}\right)\right] + \frac{N\hbar\omega}{T}\left(\frac{1}{2} + \frac{1}{e^{\beta\hbar\omega} - 1}\right) \\
&= \frac{N\hbar\omega}{T}\frac{1}{e^{\beta\hbar\omega} - 1} - Nk_B \ln\left(1 - e^{-\beta\hbar\omega}\right) \\
&= Nk_B\left[\frac{\beta\hbar\omega}{e^{\beta\hbar\omega} - 1} - \ln\left(1 - e^{-\beta\hbar\omega}\right)\right]
\end{aligned}
\tag{173}
$$

Show the following:

$$
\lim_{\hbar \to 0}\langle E \rangle = Nk_B T
\tag{174}
$$

$$
\lim_{\hbar \to 0} S = Nk_B\left(1 - \ln\left[\frac{\hbar\omega}{k_B T}\right]\right)
\tag{175}
$$

Problem: There are three available states and two particles can be distributed within three states. How many possible ways they can be arranged according to Maxwell-Boltzmann, Bose-Einstein and Fermi-Dirac distribution?

Answer:

♣ **Maxwell-Boltzmann Distribution:** Consider that the particles are classical and distinguishable. In this case, any number of particles can stay in any state. Therefore, the following distribution of particles is possible.

State 1	State 2	State 3
A	B	-
B	A	-
-	A	B
-	B	A
A	-	B
B	-	A
AB	-	-
-	AB	-
-	-	AB

Overall, there are 9 possible states for the whole gas.

♣ **Bose-Einstein Distribution:** The particles are considered indistinguishable meaning we should remove the particle label i.e., $A = B$. In this case, any particle can stay in any state. But the distinction between A and B is not possible anymore. The following distribution is thus obtained.

State 1	State 2	State 3
A	A	-
-	A	A
A	-	A
AA	-	-
-	AA	-
-	-	AA

Overall, there are 6 possible arrangements.

♣ **Fermi-Dirac Distribution:** In this case, no more than one particle can be in any one state. Thus we obtain the following distribution.

State 1	State 2	State 3
A	A	-
-	A	A
A	-	A

Overall, there are 3 possible arrangements.