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1.1   Probability Refresher

Let X be a random variable and $P(X = x)$ the probability of X taking a value x upon measurement. The total probability over all possible values of x must sum up to one, so for discrete number of possible values

$$\sum_i P(X = x_i) = 1$$

this is also called the normalization of the distribution P.
For continuous range of possible values $R(X)$

$$\int_{R(X)} P(X = x)dx = 1$$

The mean is defined as

$$< x >= \sum_i x_i P(X = x_i)$$

for discrete range and

$$< x >= \int_{R(X)} x P(X = x)dx$$

for continuous range. The variance is defined as the mean square distance from possible values of X from the mean, i.e.

$$Var(X) = \sum_i (x_i - < x >)^2 P(X = x_i)$$

for discrete range and

$$Var(X) = \int_{R(X)} (x - < x >)^2 P(X = x)dx$$

for continuous range.
Also, for the mean of a function of a random variable $f(x)$, we have

$$< f(x) >= \sum_i f(x_i)P(f(X) = f(x_i)) = \sum_i f(x_i)P(X = x_i)$$

or, for continuous case

$$< f(x) >= \int_{R(X)} f(x)P(X = x)dx$$

Therefore, we can rewrite the variance relation as

$$Var(x) = \sum_i (x_i - < x >)^2 P(X = x_i) =$$

$$= \sum_i x_i^2 P(X = x_i) - 2 < x > \sum_i x_i P(X = x_i) + < x >^2 \sum_i P(X = x_i)$$

Using the definition of mean and normalization, we have

$$Var(x) = < x^2 > - 2 < x >^2 + < x >^2 = < x^2 > - < x >^2$$

The standard deviation is defined as

$$\sigma_x = \sqrt{Var(x)} = \sqrt{< x^2 > - < x >^2}$$

and it is the measure of the spread of distribution P in the direction of x.

1.1.1 Bernoulli Trial

Consider that the measurement of X can result only in two possible values - 0 with probability $P(X = 0) = q$ (sometimes nicknamed failure) and 1 with probability $P(X = 1) = p$ (success).
Therefore, the distribution is discrete and has following parameters

$$p + q = 1, <x> = 1p + 0q = p, <x^2> = 1^2p + 0^2q = p, \sigma_x = \sqrt{p - p^2} = \sqrt{p(1-p)} = \sqrt{pq}$$

This form of random variable is called the Bernoulli trial. Now, consider that we perform the trial independently n times in a row. Independently means that one trial does not influence the other in any way. Then, the probability of k trials resulting in a "success" is

$$P(n, k) = \left(\begin{array}{c} n \\ k \end{array} \right) p^k q^{n-k}$$

as the trials are perfectly symmetrical and we need to account for interchanging them. This is also a distribution, of a new variable B_n which goes from 0 to n and is called the binomial distribution. It has following properties

$$<k> = np, <k^2> = np(np + q), \sigma_k = \sqrt{npq}$$

Hence, the fractional standard deviation is

$$\frac{\sigma_k}{<k>} = \sqrt{\frac{q}{np}}$$

which decreases as the n increases. Therefore, the distribution becomes relatively narrower as we increase n.

1.1.2 Conditional Probability

The probability of event A happening (event A being a set of values of X that satisfy certain condition) if we know that event B has happened is

$$P(A|B) = \frac{P(A \cap B)}{P(B)}$$

where $P(A \cap B)$ is the probability of A and B both happening simultaneously and $P(B)$ is probability of B happening.
For independent events, it makes sense that $P(A|B) = P(A)$, which leads to

$$P(A \cap B) = P(A)P(B)$$

Also, for independent events, the outcomes are different, hence $A \cap B = \emptyset$.
For either of two events happening, we have

$$P(A \cup B) = P(A) + P(B) - P(A \cap B)$$

And thus for independent events, $P(A \cup B) = P(A) + P(B)$.

1.1.3 Bayes' Theorem

Consider two events, A and B. These events can be partitioned into sets that do not intersect and are thus independent new events as

$$A = (A \cap B) \cup (A \cap B')$$

where S' denotes the complement of set S on some set that includes all possible outcomes. As an event can either occur or not occur, we must have

$$P(S') + P(S) = 1$$

Hence

$$P(S') = 1 - P(S)$$

Since the events $A \cap B$ and $(A \cap B')$ do not share any element, they are independent and thus

$$P(A) = P(A \cap B) + P((A \cap B')) = P(A|B)P(B) + P(A|B')P(B') = P(A|B)P(B) + P(A|B')(1 - P(B))$$

Similarly, we could transform

$$P(B) = P(B|A)P(A) + P(B|A')(1 - P(A))$$

Thus, we can say that probability of B given that A happened is

$$P(B|A) = \frac{P(A \cap B)}{P(A)} = \frac{P(A|B)P(B)}{P(A|B)P(B) + P(A|B')(1 - P(B))}$$

This is called the Bayes' theorem, and enables us to find probabilities with exchanged causality direction.

1.2 Classical Laws of Thermodynamics

Classical laws of thermodynamics in the differential form are as follows. The first law is

$$dU = TdS - pdV \tag{1}$$

where dU is the small change in the internal energy of the system, T is the temperature of the system, dS is the small change in the entropy of the system, p is the pressure in the system and dV is the small change in volume of the system.
The second law is

$$dS \geq 0 \tag{2}$$

The third law is

$$\lim_{T \to 0} S = 0 \tag{3}$$

and applies even inversly

$$\lim_{S \to 0} T = 0$$

The classical thermodynamics tries to make prediction about the system given that it is in thermal equilibrium, but it needs additional definition for this equilibrium (which is the zeroth law of thermodynamics). It usually uses somewhat empirical equations of state to derive system's behaviour, but these equations of state themselves are not derivable using just the thermodynamics methods.
These were some of the reasons why statistical mechanics were developed. Statistical mechanics can derive a reasonable definition of both entropy and thermal equilibrium, and can be used to derive equations of state only from considering the energies of possible states of the system.
The importance of statistical mechanics is further amplified by the fact that it can be used in quantum predictions, as the nature of statistical mechanics is probabilistic.

1.3 Microstates and Macrostates

In statistical mechanics, we usually model the system as a collection of smaller systems which change their states. Then, the ordered set of states for each specific component of the system would be called a microstate of the system. But, we are hardly ever able to measure the properties of each component system. Usually, we can measure only some bulk properties that are created by all the component systems together. Then, all microstates that would lead to the measurement of the same value of the given bulk property are called the macrostate of the system. For big systems, each macrostate corresponds to very big number of possible microstates.
In this module, and in statistical mechanics in general, we are most interested in the macrostates of energy, i.e. the collections of microstates that produce the same overall value of energy of the system.

2 Foundations of Statistical Mechanics

The theory of statistical mechanics is build on several assumptions/laws. First is the definition of thermal equilibrium. The thermal equilibrium occurs if each of the microstates of the system is equally likely.
The second assumption is that the dynamics of the system are such that the microstate of the system is constantly changing.
Final assumption is that if given enough time, the system in thermal equilibrium will at least for some time be in each possible microstate and that the time spent in these microstates is on average equal.
The last assumption is also called the ergodic hypothesis.
The combined consequence of these assumptions is that the macrostate of the system that is represented by more microstates tends to be more probable than one that is represented by less microstates.
In statistical mechanics, three system compositions/situations are usually considered

1. Microcanonical Ensembles

   - Microcanonical ensemble is a set of systems, each of which is isolated from each other

2. Canonical Ensemble

   - Canonical ensemble is a set of systems, each of which can exchange the energy, but not the particles (microstate positions) with some very big reservoir.

3. Grand-Canonical Ensemble

   - Grand-Canonical ensemble is a set of systems that can exchange both energy and particles with a very big reservoir.

2.1 Microcanonical Ensemble

Say that we have three identical quantum harmonical oscillators with natural frequency ω_0. Suppose that we are interested in a macrostate when the total energy of this system is $\frac{5}{2}\hbar\omega_0$. As energy of each oscillator is $E_o = \hbar\omega_0\left(n + \frac{1}{2}\right)$, this means that there is energy $\hbar\omega_0$ that either of the oscillators can have. Therefore, there is a total of three possible microstates - each for one oscillator having energy $\frac{3}{2}\hbar\omega_0$ and the rest having energy $\frac{1}{2}\hbar\omega_0$.

For the general energy $\left(n + \frac{3}{2}\right)\hbar\omega_0$ in the system, we then distribute n $\hbar\omega_0$ energy packets between the three systems. This is identical as permutating 2 system separations and n of these bundles. The total number of microstates corresponding to this is

$$\Omega = \frac{(n+2)!}{n!2!} = \left(\begin{array}{c} n+2 \\ 2 \end{array}\right)$$

where $n! = n \times (n-1) \times ... \times 2 \times 1$ is the factorial operation. Therefore

$$\Omega = \frac{(n+2)(n+1)}{2}$$

Say that we fix the energy as $n = 5$, so $\Omega = 21$. Then, we can define a different macrostates of the system, each corresponding to a different number of oscillators in the ground state. Clearly, the maximum value of this variable is 2, the minimum is 0. But, what are the corresponding numbers of microstates? For 0 oscillators in ground states, we need each oscillator to have at least one energy bundle. Therefore, we are left with $n - 3 = 5 - 3 = 2$ energy bundles that can freely be changed between the three oscillators. The number of microstates is therefore

$$\Omega_0 = \frac{((n-3)+2)!}{(n-3)!2!} = \frac{4!}{4} = 6$$

Now, consider the case when one oscillator is in a ground state. This means that two energy bundles are reserved for the other oscillators. Therefore, for one specific oscillator at a ground state, there is

$$\Omega_{1,1} = \frac{((n-2)+1)!}{(n-2)!1!} = \frac{4!}{3!} = 4$$

microstates for the other two oscillators. But, since it does not matter which oscillator is at the ground state, the total number of microstates corresponding to this setup is

$$\Omega_1 = 3 \times \Omega_{1,1} = 12$$

Finally, for the case of two oscillators in a ground state, there is only one microstate for each oscillator (all energy left is stored in the one remaining oscillator), and therefore

$$\Omega_2 = 3$$

Therefore, if this system was in thermal equilibrium, we would expect that the most probable state would be for 1 oscillator to be in a ground state, with the probability of $\frac{12}{21}$.

2.2 Entropy & Temperature

In thermal equilibrium, we use Boltzmann's definition of entropy

$$S = k_B \ln \Omega \tag{4}$$

where Ω is the number of microstates for a given macrostate of entropy and k_B is the Boltzmann constant, $k_B \approx 1.38 \times 10^{-23}$ J K^{-1}.

From this definition of entropy, it is also clear why the second law of thermodynamics (system reaches the state of maximum entropy, $dS \geq 0$) corresponds to the statistic mechanical rule that the system adopts the macrostate with biggest number of microstates - bigger number of microstates corresponds to bigger entropy.

Consider now two isolated systems, one with total number of microstates Ω_1, the other with number of microstates Ω_2. What is the number of microstates of the combined system? For each microstate in system 2, there is Ω_1 microstates in system 1, and vice-versa (since the systems can change the microstates independently). Therefore, the total number of the microstates of the combined system is

$$\Omega = \Omega_1 \times \Omega_2$$

Hence the total entropy of the combined system is

$$S = k_B \ln \Omega = k_B \ln(\Omega_1 \times \Omega_2) = k_B \ln \Omega_1 + k_B \ln \Omega_2 = S_1 + S_2$$

Thus, for independent systems, the entropy is additive.

2.2.1 Free Expansion

Consider a gas in volume V_0 that is free to expand into another empty volume V_0, so that the total volume after expansion is $2V_0$. What is the change in entropy? For each microstate in the original gas, there is now 2^N microstates in the expanded state, as each of the particles can have exactly the same position and momenutum, but in the second volume instead of the first. Thus, the number of microstates after expansion is $\Omega_0 \times 2^N$, where Ω_0 is the original number of microstates. Therefore, the change in entropy is

$$\Delta S = k_B \ln \left(\Omega_0 \times 2^N \right) - k_B \ln \Omega_0 = k_B \ln 2^N = N k_B \ln 2$$

2.2.2 Definition of Temperature

Now, consider two systems that can exchange energy. Lets say we are measuring the energy macrostate. What is the total number of microstates, corresponding to some total energy E? Let the energy of the first system be E_1 and the energy of the second system E_2. Hence $E = E_2 + E_1$, and more importantly for fixed E

$$0 = dE_2 + dE_1$$

$$dE_1 = -dE_2$$

which just means that all energy lost from system two must be gained by system 1.

On the example of the harmonic oscillators, we have seen that the number of accesible microstates depends on the energy available to the system. Therefore, we can write the number of microstates available in system 1 as

$$\Omega_1 = \Omega_1(E_1)$$

and similarly

$$\Omega_2 = \Omega_2(E_2)$$

The total number of the microstates of the two system is then

$$\Omega = \Omega(E_1)\Omega(E_2)$$

Since we can determine E_2 from E_1 ($E_2 = E - E_1$), to find the maximum of this number (which will correspond to the most probable energy macrostate between these two systems) occurs at

$$\frac{d\Omega}{dE_1} = 0$$

This means that

$$0 = \frac{d\Omega_1\Omega_2}{dE_1} = \Omega_1\frac{d\Omega_2}{dE_1} + \Omega_2\frac{d\Omega_1}{dE_1} = \Omega_1\frac{dE_2}{dE_1}\frac{d\Omega_2}{dE_2} + \Omega_2\frac{d\Omega_1}{dE_1} = \Omega_2\frac{d\Omega_1}{dE_1} - \Omega_1\frac{d\Omega_2}{dE_2}$$

Therefore, at thermal equilibrium

$$\Omega_1\frac{d\Omega_2}{dE_2} = \Omega_2\frac{d\Omega_1}{dE_1}$$

$$\frac{1}{\Omega_2}\frac{d\Omega_2}{dE_2} = \frac{1}{\Omega}\frac{d\Omega_1}{dE_1} \tag{5}$$

Therefore, for a system at thermal equilibrium with its surroundings

$$\frac{1}{\Omega}\frac{d\Omega}{dE} = \beta$$

where β is some constant shared by all systems in equilibrium with the same surroundings. This can be rewritten as

$$\beta = \frac{d\ln\Omega}{dE} = \frac{1}{k_B}\frac{dk_B\ln\Omega}{dE} = \frac{1}{k_B}\frac{dS}{dE}$$

In classical thermodynamics, systems at thermal equilibrium have a common temperature. If we want to define temperature in statistical mechanics so that it behaves in the same way as in classical mechanics, we need to consult the first law of thermodynamics in this context. We know that the systems considered here are fixed in volume (otherwise Ω would depend on the volume of the system as well), hence the first law states

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

For our case, since the S is a function of $U = E$ only and V is always fixed, we can write

$$\frac{1}{T} = \frac{dS}{dE}$$

By comparison with the previous result for C, we find that

$$\beta = \frac{1}{k_B T}$$

And thus, we have our definition of temperature in statistical mechanics, that is defined so that it reduces to classical temperature in classical thermodynamics. The definition is

$$\frac{1}{k_B T} = \frac{d\ln\Omega}{dE} \tag{6}$$

We quite often refer to the constant β directly, instead of reffering to temperature.

2.2.3 Measuring Entropy

Generally speaking, entropy is very hard to measure. Classically, we have relation

$$dU = TdS$$

at fixed volume. We can measure

$$dU = C_V dT$$

where C_V is the heat capacity at fixed volume. Therefore

$$C_V dT = TdS$$

Therefore, the change in entropy (but not its absolute value) can be found as

$$\Delta S = \int_{T_1}^{T_2}\frac{C_V}{T}dT$$

2.2.4 Gibbs Entropy Formula

Gibbs entropy formula defines entropy even for systems out of equilibrium as

$$S = -k_B \sum_i P_i \ln P_i \tag{7}$$

where sum runs over all the microstates of the system and P_i is the probability of the system existing in a given microstate. In a thermal equilibrium,

$$P_i = \frac{1}{\Omega}$$

and thus

$$S = -k_B \sum_i \frac{1}{\Omega} \ln\left(\frac{1}{\Omega}\right) = -k_B \frac{1}{\Omega} \ln\left(\frac{1}{\Omega}\right) \sum_i 1$$

Since the sum runs over all microstates

$$S = -k_B \frac{1}{\Omega} \ln\left(\frac{1}{\Omega}\right) \Omega = -k_B(-\ln\Omega) = k_B \ln\Omega$$

Therefore we see that the Gibbs entropy formula reduces to the Boltzmann entropy formula for systems in equilibrium.

3 Canonical Ensembles

Lets have a collection of systems of fixed number of particles N and fixed volume V. Then, let this ensemble of systems be in a contact with a large reservoir with energy $E - E_i$, where E_i is the energy of the ith macrostate of the ensemble (so that the total energy is $U = E - E_i + E_i = E$).
Now, lets have the system in a thermal equilibrium with the reservoir, where T (and/or β) is fixed both for the ensemble and the reservoir. The ensemble in this state and setup is called the canonical ensemble. Now, we are interested in the probability that the ensemble has energy E_i.
The total number of microstates for both the reservoir and the ensemble is

$$\Omega = \Omega_e(E_i)\Omega_r(E - E_i)$$

where Ω_e is the number of microstates of the ensemble and Ω_r is the number of microstates of the reservoir. The probability of system having energy E_i is then a function of this total number of microstates. Since the reservoir has energy E relatively big and a very big number of possible places for the energy, we can approximate

$$P(E_i) \propto \Omega(E - E_i)$$

So

$$P(E_i) = C\Omega(E - E_i)$$

where C is some constant.
To find $\Omega(E - E_i)$, consider a Taylor expansion of $\ln\Omega(E - E_i)$

$$\ln\Omega(E - E_i) \approx \ln\Omega(E) - \frac{d\ln\Omega(E)}{dE}E_i$$

But, from our definition of temperature

$$\frac{d\ln\Omega(E)}{dE} = \beta$$

Hence

$$\ln\Omega(E - E_i) \approx \ln\Omega(E) - \beta E_i = \ln\left(\Omega(E)e^{-\beta E_i}\right)$$

Dropping the approximation sign

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

Hence, the probability of system having energy E_i is

$$P(E_i) = C\Omega(E)e^{-\beta E_i}$$

Since $C\Omega(E)$ do not depend on the energy of the system E_i, we write them together as a constant $\frac{1}{Z}$ so

$$P(E_i) = \frac{e^{-\beta E_i}}{Z} \tag{8}$$

This is called the Boltzmann distribution, and constant Z is called the partition function.

Since the system has to have some energy (zero energy is still a state, only with $E_i = 0$), the overall probability of system having some energy must be equal to 1, i.e.

$$\sum_i P(E_i) = 1$$

Which means that

$$\sum_i \frac{e^{-\beta E_i}}{Z} = 1$$

and therefore

$$Z = \sum_i e^{-\beta E_i} \tag{9}$$

and thus we have our definition of partition function.

3.1   Two State system

Consider now a system that can exist in tow states of energies - either it has energy ϵ or energy 0. The partition function for this system is

$$Z = e^{-\beta 0} + e^{-\beta \epsilon} = 1 + e^{-\beta \epsilon}$$

And thus the Boltzmann distribution is

$$P(E) = \frac{e^{-\beta E}}{1 + e^{-\beta \epsilon}}$$

The expectation value for the energy of the system is

$$<E> = P(E = 0) \times 0 + P(E = \epsilon)\epsilon = \frac{\epsilon e^{-\beta \epsilon}}{1 + e^{-\beta \epsilon}} = \frac{\epsilon}{1 + e^{\beta \epsilon}}$$

Therefore as $T \to \infty$ (and $\beta \to 0$), $<E> \to \frac{\epsilon}{2}$, which makes sense (the system changes swiftly from energy 0 to ϵ and back). Also, as $T \to 0$, $\beta \to \infty$, $<E> \to 0$, which is also reasonable.

Here, we calculated for the expectation value of $<E>$. Because the reservoir is constantly changing its microstates, we can assume that the observed value of total energy U will be simply

$$U = <E>$$

We could then also calculate the heat capacity

$$C_V = \frac{\partial U}{\partial T} = \frac{d}{dT}\frac{\epsilon}{1 + e^{\beta \epsilon}} = \frac{d\beta}{dT}\frac{d}{d\beta}\frac{\epsilon}{1 + e^{\beta \epsilon}} = -\frac{1}{k_B T^2}\epsilon\left(-\frac{1}{(1 + e^{\beta \epsilon})^2}e^{\beta \epsilon}\epsilon\right) = k_B \beta^2 \left(\frac{\epsilon}{1 + e^{\beta \epsilon}}\right)^2 e^{\beta \epsilon}$$

This can be rewritten in terms of hyperbolic functions as

$$C_V = k_B \beta^2 \epsilon^2 e^{\beta \epsilon}\left(\frac{1}{e^{\frac{\beta \epsilon}{2}}\left(e^{\frac{\beta \epsilon}{2}} + e^{-\frac{\beta \epsilon}{2}}\right)}\right)^2 = k_B \beta^2 \epsilon^2 \frac{e^{\beta \epsilon}}{e^{\beta \epsilon}}\frac{1}{4\cosh^2\left(\frac{\beta \epsilon}{2}\right)} = \frac{k_B \beta^2 \epsilon^2}{4\cosh^2\left(\frac{\beta \epsilon}{2}\right)}$$

Since β^2 initially increases faster than $\cosh\left(\frac{\beta \epsilon}{2}\right)$, there exists a peak of maximum heat capacity. This is called the Schottky anomaly.

3.2   Equipartition Theorem

Equipartition theorem states that for system where energy states are near continuous (which is usually close to the high temperature classical limit of thermodynamics) and where the energy of the states depends on a square of some variable taking any value from $-\infty$ to ∞, the average energy of the system is independent of the specific state and only depends on the temperature.

For example, imagine a classical monatomic gas. Each molecule in such gas has only the kinetic energy, which is

$$T = \frac{1}{2}m(v_x^2 + v_y^2 + v_z^2)$$

where m is the mass of the atom of the gas and $v_{x/y/z}$ are the different components of speed, each of which can go from $-\infty$ to ∞.

Similarly, the potential energy of a harmonic oscillator in 1D goes as

$$V = \frac{1}{2}kx^2$$

where k is the spring constant and x is the displacement from the equilibrium position, again going from $-\infty$ to ∞.

Therefore, we see that setup of the equipartition theorem is quite a common situation. Now, we need to employ the methods of statistical mechanics to progress.

Lets say that the energy of a part of the system depends on n independent variables as

$$E = \alpha_1 x_1^2 + \alpha_2 x_2^2 + ... + \alpha_n x_n^2$$

Therefore, the partition function is obtained by summing together values for each possible value of each variable, which can be achieved by integral

$$Z = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} ... \int_{-\infty}^{\infty} e^{-\beta \sum_{i=1}^{n} \alpha_i x_i^2} dx_1 dx_2 ... dx_n$$

The exponential function can be split into products as

$$Z = \int_{-\infty}^{\infty} ... \int_{-\infty}^{\infty} \prod_{i=1}^{n} e^{-\beta \alpha_i x_i^2} dx_1 ... dx_n$$

This means that the integral can be factorised as

$$Z = \prod_{i=1}^{n} \int_{-\infty}^{\infty} e^{-\beta \alpha_i x_i^2} dx_i$$

Now, we can solve just the one integral as

$$I_i = \int_{-\infty}^{\infty} e^{-\beta \alpha_i x_i^2} dx_i$$

Substituting $y_i = \sqrt{\beta \alpha_i} x_i$

$$I_i = \frac{1}{\sqrt{\beta \alpha_i}} \int_{-\infty}^{\infty} e^{-y_i^2} dy_i$$

$$I_i^2 = \frac{1}{\beta \alpha_i} \int_{-\infty}^{\infty} e^{-y_i^2} dy_i \int_{-\infty}^{\infty} e^{-z_i^2} dz_i = \frac{1}{\beta \alpha_i} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} e^{-(y_i^2 + z_i^2)} dy_i dz_i$$

Changing the coordinates to planar polar

$$I_i^2 = \frac{1}{\beta \alpha_i} \int_{0}^{\infty} \int_{0}^{2\pi} e^{-r_i^2} r_i d\phi_i dr_i = \frac{2\pi}{\beta \alpha_i} \int_{0}^{\infty} r_i e^{-r_i^2} dr_i = \frac{2\pi}{\beta \alpha_i} \left[-\frac{1}{2} e^{-r_i^2} \right]_0^{\infty} = \frac{\pi}{\beta \alpha_i}$$

Therefore

$$I_i = \sqrt{\frac{\pi}{\beta \alpha_i}}$$

Therefore

$$Z = \prod_{i=1}^{n} \sqrt{\frac{\pi}{\beta \alpha_i}} = \left(\frac{\pi}{\beta}\right)^{\frac{n}{2}} \prod_{i=1}^{n} \frac{1}{\sqrt{\alpha_i}} \tag{10}$$

The probability of system being in an energy state with energy E as defined above is then given by Boltzmann distribution

$$P(E) = \frac{e^{-\beta E}}{Z} = \frac{e^{-\beta \sum_{i=1}^{n} \alpha_i x_i^2}}{Z} = \frac{\prod_{i=1}^{n} e^{-\beta \alpha_i x_i^2}}{Z}$$

And the total energy of the system (which is the expectation value of the energy - the mean of energy) is then

$$U = \int_{-\infty}^{\infty} ... \int_{-\infty}^{\infty} EP(E)dx_1...dx_n = \int_{-\infty}^{\infty} ... \int_{-\infty}^{\infty} \left(\sum_{j=1}^{n} \alpha_j x_j^2 \right) \frac{1}{Z} \prod_{i=1}^{n} e^{-\beta \alpha_i^2} dx_1...dx_n$$

Each of the $\alpha_j x_j^2$ terms in the sum is only integrated in one integral, and therefore we can factorize the integral as

$$U = \frac{1}{Z} \sum_{j=1}^{n} \int_{-\infty}^{\infty} \alpha_j x_j^2 e^{-\beta \alpha_j x_j^2} dx_j \prod_{i=1,i\neq j}^{n} \int_{-\infty}^{\infty} e^{-\beta \alpha_i x_i^2} dx_i$$

We have already done the second integral, but we have to do the first one.

$$J_i = \int_{-\infty}^{\infty} \alpha_i x_i^2 e^{-\beta \alpha_i x_i^2} dx_i = \alpha_i \int_{-\infty}^{\infty} x_i \left(x_i e^{-\beta \alpha_i x_i^2} \right) dx_i =$$

$$= \alpha_i \left[x_i \left(-\frac{1}{2\beta \alpha_i} e^{-\beta \alpha_i x_i^2} \right) \right]_{-\infty}^{\infty} + \frac{1}{2\beta} \int_{-\infty}^{\infty} e^{-\beta \alpha_i x_i^2} dx_i$$

We can see that the bracketed term goes to zero, as $e^{-\beta \alpha_i x_i^2}$ goes to zero much faster than x_i diverges. The second integral we already calculated as I_i, so we are left with

$$J_i = \frac{1}{2\beta} \sqrt{\frac{\pi}{\beta \alpha_i}}$$

Therefore, we have

$$U = \frac{1}{Z} \sum_{j=1}^{n} \frac{1}{2\beta} \sqrt{\frac{\pi}{\beta \alpha_j}} \prod_{i=1,i\neq j}^{n} \sqrt{\frac{\pi}{\beta \alpha_i}} = \frac{1}{2\beta Z} \sum_{j=1}^{n} \prod_{i=1}^{n} \sqrt{\frac{\pi}{\beta \alpha_i}} = \frac{n}{2\beta Z} \prod_{i=1}^{n} \sqrt{\frac{\pi}{\beta \alpha_i}}$$

We can see that the last product expression is nothing else but the partition function Z, and therefore

$$U = \frac{n}{2\beta Z} Z = \frac{n}{2\beta} = \frac{n}{2} k_B T \tag{11}$$

This is a major result, because we discovered that the total energy of the system does not depend on the exact nature of the energy (we do not need to know each α_i to determine the energy of the system).
Therefore, we can make some predictions about the total energy of the system without the exact knowledge of the system.
It should be noted that for a system of N, particles, each of which has n quadratic energy terms, there is total of Nn quadratic energy terms for the whole system, and thus

$$U = N \frac{n}{2} k_B T$$

and therefore we see that this total energy is classicaly extensive.
It should be noted however that Z is not a proper partition function, as it has dimensions - a proper partition function needs to be dimensionless. This is particularly seen when trying to calculate other values from this partition function (see later).

3.2.1 Gases

Gases can usually quite well fulfill the assumptions of equipartition theorem (there is almost no interaction between the molecules/atoms of the gas, and the kinetic energy is quadratic with velocity). For monatomic gas, we expect three quadratic energy modes (translation in three different directions), and therefore we expect energy $\frac{3}{2} k_B T$ per particle of the gas. Hence, the molar heat capacity of monatomic gas is expected to be (at constant volume)

$$C_V = N_A \frac{3}{2} k_B = \frac{3}{2} R$$

where $R = 8.314$ J mol^{-1}K^{-1} is the molar gas constant.

For diatomic gas, we also expect additional two vibrational modes (velocity and potential vibrational energies) and three rotational modes. But, the rotational motion around the axis of the molecule is forbidden for reasons from quantum mechanics, and the vibrational modes only start to excite at about 4000 K (because the ground state energy of the oscillations is otherwise lower than the energy from equipartition). Similarly, the rotation around the centre of the molecule only becomes available above about 250 K. Therefore, for less than 250 K, the molar heat capacity of diatomic gas is $\frac{3}{2}R$, for 250 - 4000 K, the molar heat capacity is $\frac{5}{2}k_B T$ (the two additional rotational modes are available) and after that $\frac{7}{2}k_B T$ (vibrational modes).

For gases with more atoms, the vibrational modes are again supressed, but from the turn on point three rotational modes are available, so for common range of temperatures, the molar heat capacity is $3R$.

3.2.2 Metals

We can imagine an atom of metals as a particle sitting in a harmonic potential centered on its place in the crystal lattice. There are 6 total energy modes - three translational and three rotational. Therefore, we expect the molar heat capacity to be $3R$.

3.3 Partition Function

So far, we only used the basic derivations of statistical mechanics, but the methods were essentially classical. But, we can completly reformulate the thermodynamics using pretty much only the partition function. To do this, we first need to remember the basic functions of state for a thermodynamical system

3.3.1 Classical Functions of State

Since for canonical ensemble T and V are fixed, they are effectively not a functions of state, but only the variables. Also, since particles are not exchanged, the number of particles N is also only a variable and not a function of state.

The classical functions of state are then internal energy U, entropy S, pressure p, Helmholtz free energy F, enthalpy H and Gibbs free energy G. The internal energy is defined by statistical mechanics as

$$U = \sum_i E_i P_i$$

where E_i is the energy of ith microstate and P_i is probability of system being in this microstate.

The entropy is defined by Gibbs formula

$$S = -k_B \sum_i P_i \ln P_i$$

Helmholtz free energy is defined as

$$F = U - TS \tag{12}$$

Pressure is classically defined from the first law of thermodynamics

$$dU = TdS - pdV$$

and change in Helmholtz free energy

$$dF = d(U - TS) = dU - TdS - SdT = TdS - pdV - TdS - SdT = -pdV - SdT$$

which leads to

$$p = -\left(\frac{\partial F}{\partial V}\right)_T$$

The enthalpy is defined as

$$H = U + pV \tag{13}$$

The Gibbs free energy is defined as

$$G = H - TS \tag{14}$$

3.3.2   Partition Function Formulation

For canonical ensemble, we had

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

Applying a derivative with respect to β

$$\frac{dZ}{d\beta} = \sum_i (-E_i) e^{-\beta E_i} = -\sum_i E_i e^{-\beta E_i}$$

Comparing this to the definition of internal energy for canonical ensemble

$$U = \sum_i E_i P_i = \sum_i E_i e^{-\beta E_i} \frac{1}{Z}$$

we then have

$$\frac{dZ}{d\beta} = -ZU$$

and thus

$$U = -\frac{1}{Z}\frac{dZ}{d\beta} = -\frac{d(\ln Z)}{d\beta} \tag{15}$$

Thus, we can determine the internal energy directly from the partition function.
We can try to do the same for the rest of the state functions. For entropy, we can use Gibbs definition of entropy and Boltzmann distribution

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

$$= \frac{k_B}{Z}\sum_i \beta E_i e^{-\beta E_i} + \frac{k_B}{Z}\ln Z \sum_i e^{-\beta E_i} = k_B \beta U + k_B \ln Z$$

So, we have

$$S = k_B \ln Z - \frac{1}{T}\frac{d\ln Z}{d\beta} \tag{16}$$

Therefore, the Helmholtz free energy is

$$F = U - TS = U - T(k_B\beta U + k_B \ln Z) = U - k_B T\frac{1}{k_B T}U - k_B T \ln Z$$

And therefore

$$F = -k_B T \ln Z \tag{17}$$

Sometimes, it is therefore easier to calculate the entropy from the definition of Helmholtz free energy as

$$S = \frac{U - F}{T}$$

Using the expression for pressure, we have

$$p = -\left(\frac{\partial F}{\partial V}\right)_T = -\left(\frac{\partial(-k_B T \ln Z)}{\partial V}\right)_T = k_B T\left(\frac{\partial \ln Z}{\partial V}\right)_T$$

Thus the enthalpy is

$$H = U + pV = k_B T V\left(\frac{\partial \ln Z}{\partial V}\right)_T - \frac{d\ln Z}{d\beta} = k_B T\left[V\left(\frac{\partial \ln Z}{\partial V}\right)_T + T\frac{d\ln Z}{dT}\right]$$

And Gibbs free energy

$$G = F + pV = -k_B T \ln Z + k_B T V\left(\frac{\partial \ln Z}{\partial V}\right)_T = k_B T\left[V\left(\frac{\partial \ln Z}{\partial V}\right)_T - \ln Z\right]$$

3.3.3 Equipartition Revised

We have shown that the equipartition partition function was

$$Z = \left(\frac{\pi}{\beta}\right)^{\frac{n}{2}} \prod_{i=1}^{n} \frac{1}{\sqrt{\alpha_i}}$$

Therefore

$$\ln Z = \frac{n}{2}\left(\ln \pi - \ln \beta\right) - \frac{1}{2}\sum_{i=1}^{n}\ln \alpha_i$$

and

$$U = -\frac{d\ln Z}{d\beta} = \frac{n}{2}\frac{d\ln \beta}{d\beta} = \frac{n}{2\beta} = \frac{n}{2}k_B T$$

which is the same result as before, but obtained on three lines of almost trivial calculation. But, the results for other variables are not very useful, because the Z constructed for equipartition is not dimensionless.

3.4 1D Harmonic Oscillator

The energy of a 1D quantum harmonic oscillator is given as

$$E_n = \left(n + \frac{1}{2}\right)\hbar\omega_0$$

where ω_0 is the natural frequency of the oscillator.
Therefore, the partition function is

$$Z = \sum_{n=0}^{\infty} e^{-\beta E_n} = \sum_{n=0}^{\infty} e^{-\beta n\hbar\omega_0 - \frac{\beta}{2}\hbar\omega_0} = e^{-\frac{\beta}{2}\hbar\omega_0}\sum_{n=0}^{\infty}\left(e^{-\beta\hbar\omega_0}\right)^n$$

We can recognize that the sum is the geometric series with ration $e^{-\beta\hbar\omega_0}$ Therefore

$$\sum_{n=0}^{\infty} e^{-\beta\hbar\omega_0 n} = \frac{1}{1 - e^{-\beta\hbar\omega_0}}\left(1 - \lim_{n\to\infty} e^{-\beta\hbar\omega(n+1)}\right)$$

But, the limit goes to zero, so

$$Z = e^{-\frac{1}{2}\beta\hbar\omega_0}\frac{1}{1 - e^{-\beta\hbar\omega_0}} = \frac{e^{-\frac{1}{2}\beta\hbar\omega_0}}{1 - e^{-\beta\hbar\omega_0}} \tag{18}$$

The internal energy than can be derived as

$$\ln Z = -\frac{\beta\hbar\omega_0}{2} - \ln\left(1 - e^{-\beta\hbar\omega_0}\right)$$

$$U = -\frac{d\ln Z}{d\beta} = \frac{\hbar\omega_0}{2} + \frac{1}{1 - e^{-\beta\hbar\omega_0}}\left(-e^{-\beta\hbar\omega_0}\right)\left(-\hbar\omega_0\right) = \hbar\omega_0\left[\frac{1}{2} + \frac{e^{-\beta\hbar\omega_0}}{1 - e^{-\beta\hbar\omega_0}}\right]$$

Hence the heat capacity

$$C_V = \frac{\partial U}{\partial T} = \hbar\omega_0\frac{-\hbar\omega_0 e^{-\beta\hbar\omega_0}\frac{d\beta}{dT}\left(1 - e^{-\beta\hbar\omega}\right) - e^{-\beta\hbar\omega_0}\left(-e^{-\beta\hbar\omega_0}\right)\left(-\hbar\omega_0\right)\frac{d\beta}{dT}}{\left(1 - e^{-\beta\hbar\omega_0}\right)^2} =$$

$$= -\hbar^2\omega_0^2 e^{-\beta\hbar\omega_0}\frac{d\beta}{dT}\frac{\left(1 - e^{-\beta\hbar\omega_0}\right) + e^{-\beta\hbar\omega_0}}{\left(1 - e^{-\beta\hbar\omega_0}\right)^2} = -\hbar^2\omega_0^2 e^{-\beta\hbar\omega_0}(-k_B\beta^2)\frac{1}{\left(1 - e^{-\beta\hbar\omega_0}\right)^2}$$

So, we have

$$C_V = k_B(\beta\hbar\omega_0)^2\frac{e^{-\beta\hbar\omega_0}}{\left(1 - e^{-\beta\hbar\omega_0}\right)^2}$$

For a large temperature, $\beta \to 0$, so

$$C_V \to k_B(\beta\hbar\omega_0)^2\frac{(1 - \beta\hbar\omega_0)}{(1 - (1 - \beta\hbar\omega_0))^2} = k_B(\beta\hbar\omega_0)^2\frac{(1 - \beta\hbar\omega_0)}{(\beta\hbar\omega_0)^2} \to k_B$$

which is the same result as we would obtain by equipartition.

3.5 Degeneracy

In case that a state with the same energy can be occupied in multiple degenerate setups, then we need to reflect this in the partition function - as the temperature rises, the states become all equally probable, and thus more degenerate states will be likely more occupied than low degeneracy states.

This can be accounted for simply by treating each of the degenerate states as a state on its own (unless the states are indistinguishable, which will be discussed later), so the partition function becomes

$$Z = \sum_i g_i e^{-\beta E_i} \tag{19}$$

where g_i is the number of degenerate states with energy E_i.

3.5.1 Degenerate 2-state System

Consider a two state system, with energies 0 and Δ. But this time, the energy level 0 has degeneracy g_1 and energy level Δ has degeneracy g_2. The partition function is

$$Z = g_1 e^{-\beta 0} + g_2 e^{-\beta \Delta} = g_1 + g_2 e^{-\beta \Delta}$$

The internal energy is now

$$U = -\frac{1}{Z}\frac{dZ}{d\beta} = \frac{-1}{g_1 + g_2 e^{-\beta\Delta}} g_2 e^{-\beta\Delta}(-\Delta) = \frac{g_2 \Delta e^{-\beta\Delta}}{g_1 + g_2 e^{-\beta\Delta}} = \frac{\Delta}{1 + \frac{g_1}{g_2}e^{\beta\Delta}}$$

In high temperature limit $(\beta \to 0)$

$$U \to \frac{\Delta}{1 + \frac{g_1}{g_2}(1 + \beta\Delta)} \to \frac{\Delta}{1 + \frac{g_1}{g_2}}$$

Hence, if $g_2 >> g_1$, then $U \to \Delta$. This can be explained by considering that at high temperature, any state is approximately equally probable. But, if there is much more states with energy Δ ($g_2 >> g_1$), then the average state is basically state 2 and thus the average enery is its energy, which is Δ.

3.6 Combining Systems

In thermodynamics, we usually deal with big systems consisting of many individual smaller systems. In order to be able to create these combinations, we need to know how to combine the partition functions of systems.

Lets number states of system 1 by i and states of system 2 by j. Hence, the state of the combination of the two systems can be expressed as state i, j. The energy of this state is simply

$$E_{i,j} = E_{1i} + E_{2j}$$

where E_{1i} is the energy of the state i in the system 1, and analogously E_{2j} is energy of state j in system 2. The partition function then is

$$Z = \sum_i \sum_j e^{-\beta E_{i,j}} = \sum_i \sum_j e^{-\beta(E_{1i}+E_{2j})} = \sum_i \sum_j e^{-\beta E_{1i}} e^{-\beta E_{2j}} = \left(\sum_i e^{-\beta E_{1i}}\right)\left(\sum_j e^{-\beta E_{2j}}\right)$$

But, we can recognize the bracketed expressions as partition functions of the component systems. Therefore

$$Z = Z_1 Z_2 \tag{20}$$

The combined partition function is therefore the product of the partition functions of the composite systems. Similarly we see that any function of state that depends on $\ln Z$ (such as energy, Helmholtz free energy, entropy, pressure, etc.) is additively extensive (combined function of state is the sum of the composite functions of state - for energy, this was effectively our assumption, so it should not be too surprising)

3.6.1 Indistinguishibility

In the above derivation, we suggested that each combination of states (i, j) is distinguishable from each other. This could apply even if the energy of some pair of states, say (i, j), was the same as energy of other pair of states, say (k, l), as long as there is some property (such as spin) that differentiates the states from each other. Then, this simply comes up as a degeneracy factor.

But sometimes some pairs of states are virtually indistinguishable. This tends to happen especially if we combine identical systems, for example when modelling behaviour of N identical particles, each with partition function Z_1. Then, any specific state combination $(i, j, ...)$ is indistinguishable from any state which is specified by a permutation of indices $i, j, ...$ Since there is N indices (N particles), the number of permutations is $N!$. Since these states are indistinguishable, we must not count them more then once each. Therefore, the combined partition function for such system is

$$Z = \frac{1}{N!} \sum_{i,j,\cdots} e^{-\beta(E_{1i} + E_{2j} + \cdots)} = \frac{Z_1^N}{N!} \tag{21}$$

3.6.2 3D Harmonic Oscillator

The harmonic oscillator in 3D is effectively a combination of three independent harmonic oscillators, each in one perpendicular dimensions. These oscillations are each distinct, so the combined partition function of 3D harmonic oscillator is

$$Z_{3DSHO} = (Z_{1DSHO})^3 = \frac{e^{-\frac{3}{2}\beta\hbar\omega}}{(1 - e^{-\beta\hbar\omega})^3}$$

Hence

$$\ln Z_{3DSHO} = 3 \ln Z_{1DSHO}$$

and therefore $U_{3DSHO} = 3U_{1DSHO}$, as expected, and similarly for all other functions of state.

3.6.3 Spin-half Paramagnet

Imagine an atom with one unpaired electron. This electron has spin angular momentum component in the z direction given as $\hbar s$ where $s = \pm\frac{1}{2}$.

The magnetic moment given by this spin is

$$\mu = -g\mu_B s$$

where g is the gyromagnetic ratio of the electron and $\mu_B = \frac{e\hbar}{2m_e}$ is the Bohr magneton. The minus sign is to account for negative charge of the electron. Since $g \approx 2$, we can simplify this as

$$\mu \approx \mp\mu_B$$

The energy of an electron in a magnetic field B in z direction is

$$E = \mu B = \mp\mu_B B$$

Therefore, this electron in magnetic field forms effectively a two state system.

For a constant volume paramagnet, the first law of thermodynamics is

$$dU = TdS + dE_M$$

where E_M is the total magnetic energy stored in the orientation of electron spins. The macroscopic variable measuring the overall magnetic moment of the paramagnet is magnetisation m, which points in the direction of the magnetic moment. Since for aligned moment the energy is smaller and increasing the field causes bigger energy well for aligned moments m, we have

$$dU = TdS - mdB \tag{22}$$

Therefore, the change in Helmholtz free energy is

$$dF = d(U - TS) = d(U) - TdS - SdT = TdS - mdB - TdS - SdT = -mdB - SdT$$

Therefore for a fixed temperature

$$m = -\left(\frac{\partial F}{\partial B}\right)_T = k_B T \left(\frac{\partial \ln Z}{\partial B}\right)_T$$

Since the paramagnet is a two state system (for one atom that is), the partition function is

$$Z_1 = e^{-\beta\mu_B B} + e^{\beta\mu_B B} = 2\cosh(\beta\mu_B B)$$

In a solid, all atoms sit in a distinct position given by crystallic lattice, and therefore are all distinguishable. Therefore, the combined partition function for all N atoms of the paramagnet is

$$Z = (Z_1)^N$$

And thus the magnetisation of the magnet is

$$m = k_B T \left(\frac{\partial \ln Z}{\partial B}\right)_T = N k_B T \left(\frac{\partial \ln Z_1}{\partial B}\right)_T = \frac{N k_B T}{2\cosh(\beta\mu_B B)} 2\sinh(\beta\mu_B B)\beta\mu_B = N\mu_B \tanh(\beta\mu_B B)$$

3.7 Thermodynamic Potentials

Lets now return to the second law of thermodynamics, that is $dS \geq 0$. This means that at the thermal equilibrium, the entropy of the system is maximized.
The entropy is defined as

$$S = -k_B \sum_i P_i \ln P_i$$

At the maximum value

$$\forall j : \frac{\partial S}{\partial P_j} = 0$$

Using the definition of entropy and assuming that we vary only some P_j and P_k

$$\forall j : 0 = -k_B \left[\frac{\partial P_j}{\partial P_j} \ln P_j + P_j \frac{1}{P_j}\frac{\partial P_j}{\partial P_j} + \frac{\partial P_k}{\partial P_j}\ln P_k + P_k \frac{1}{P_k}\frac{\partial P_k}{\partial P_j}\right]$$

Since

$$1 = \sum_i P_i$$

we can check that if we vary only some specific P_j and P_k, we have

$$\frac{\partial P_j}{\partial P_k} = -1$$

And thus

$$\ln P_j + 1 = \ln P_k + 1$$

or

$$P_j = P_k$$

Therefore, the probability of existing in each microstate is identical in thermal equilibrium. This applies generally for all isolated systems. The case why we have probability distribution in canonical ensemble is because the probability of the microstates of the system with the reservoir together is uniform, but since the reservoir is bigger than the system, several microstates of the system+reservoir correspond to a single microstate of the system only.

3.7.1 Systems with Fixed Temperature and Volume

The first law of thermodynamics for systems with fixed volume and temperature is (at equilibrium)

$$dU = TdS - pdV = TdS$$

The Helmholtz free energy is

$$F = U - TS$$

and its change is (at equilibrium)

$$dF = dU - TdS - SdT = dU - TdS = 0$$

Therefore, the value of Helmhotz free energy is extremal at the equilibrium. To find the nature of this extremum, consider more general form of first law of thermodynamics

$$dU = \dtod Q + \dtod W$$

where $\dtod Q$ is the heat transfered to the system and $\dtod W$ is the work done on the system.
which can be rewritten as

$$\dtod Q \leq dU$$

$$\dtod Q \leq T dS$$

Since the volume is not changing, $\dtod W = 0$, and therefore

$$\dtod Q + \dtod W - T dS = dU - T dS = dF \leq T dS + \dtod W - T dS = 0$$

and we have

$$dF \leq 0$$

Therefore, the Helmholtz free energy reaches its minimum value at equilibrium.
By similar procedure, it can be shown that enthalpy is minimised for fixed S and p and that Gibbs free energy is minimized for fixed T and p.
The functions that are minimized in the equilibrium of a system are called the thermodynamic potentials.

3.7.2   Minimizing F

We can use our definitions of internal energy and entropy to minimise F for constant V and T, finding the minimum in the coordinate space of probabilities of microstates P_i. This can be achieved by using Lagrange multipliers, where our function to be minimized is F

$$F = U - TS = \sum_i E_i P_i + k_B T \sum_i P_i \ln P_i$$

and our constraint is

$$\sum_i P_i = 1$$

Therefore, we have

$$\forall j : \frac{\partial}{\partial j} \left(\sum_i E_i P_i + k_B T \sum_i P_i \ln P_i - \lambda \sum_i P_i \right) = 0$$

where λ is the Lagrange multiplier. This leads to

$$\forall j : E_j + k_B T (\ln P_j + 1) - \lambda = 0$$

$$\forall j : \ln P_j + 1 = \frac{\lambda - E_j}{k_B T}$$

$$\forall j : P_j = e^{\frac{\lambda}{k_B T} - 1} e^{-\frac{E_j}{k_B T}}$$

Since λ is just some constant, we can write $e^{\frac{\lambda}{k_B T} - 1} = A$ and thus

$$P_J = A e^{-\beta E_j}$$

which we recognize as Boltzmann distribution. Therefore, our formalism is fully compatible with the formalism of thermodynamical potentials.

3.8 Fluctuations

We expect the fluctuations in energy to be in order of standard deviation of the energy. As we defined in the beginning, the standard deviation of a random variable is

$$\sigma_x^2 = <x^2> - <x>^2$$

So, for energy

$$\sigma_E^2 = <E^2> - <E>^2$$

We already know that the mean energy is the total internal energy of the system, but we need to determine $<E^2>$. This is defined as

$$<E^2> = \sum_i E_i^2 P_i$$

For canonical ensemble

$$<E^2> = \frac{1}{Z} \sum_i E_i^2 e^{-\beta E_i}$$

But, consider $\frac{d^2 Z}{d\beta^2}$

$$\frac{d^2 Z}{d\beta^2} = \frac{d^2}{d\beta^2} \sum_i e^{-\beta E_i} = \frac{d}{d\beta} \sum_i (-E_i) e^{-\beta E_i} = \sum_i E_i^2 e^{-\beta E_i}$$

Therefore

$$<E^2> = \frac{1}{Z} \frac{d^2 Z}{d\beta^2}$$

and thus

$$\sigma_E^2 = \frac{1}{Z} \frac{d^2 Z}{d\beta^2} - \frac{1}{Z^2} \left(\frac{dZ}{d\beta} \right)$$

But, we can notice one more thing. If we are determining the heat capacity

$$C_V = \frac{dU}{dT} = \frac{d\beta}{dT} \frac{dU}{d\beta} = -k_B \beta^2 \frac{d}{d\beta} \left(-\frac{1}{Z} \frac{dZ}{d\beta} \right) = k_B \beta^2 \left(-\frac{1}{Z^2} \left(\frac{dZ}{d\beta} \right)^2 + \frac{1}{Z} \frac{d^2 Z}{d\beta^2} \right) = k_B \beta^2 \sigma_E^2$$

Therefore

$$\sigma_E = \sqrt{k_B C_V} T \tag{23}$$

Which corresponds to approximate fluctuations magnitude of energy. Similarly, we could derive the fluctuation in other state functions, but these usually depend on the specific energy distribution of E_is. Importantly, if we consider a big system of identical particles with partition function

$$Z = \frac{Z_1^N}{N!}$$

The total energy of the system is

$$U = -\frac{dN \ln Z_1 - \ln N!}{d\beta} = N U_1$$

And thus

$$C_V = \frac{dU}{dT} = N \frac{dU_1}{dT} = N C_{V1}$$

and

$$\sigma = \sqrt{k_B C_V} T = \sqrt{k_B N C_{V1}} T$$

and

$$\frac{\sigma}{U} = \sqrt{\frac{k_B}{C_{V1} N}} T$$

which means that the relative size of the fluctuations decreases as inverse square root of N.

3.9   Ideal Gases

For ideal gases, there is no interaction between the molecules. Therefore, the molecules are free particles, usually enclosed in some volume V. This means that the wavefunctions of the particles are plane waves with wavevector

$$\vec{k} = \left(\frac{2\pi}{L_x} n_x, \frac{2\pi}{L_y} n_y, \frac{2\pi}{L_z} n_z \right)$$

Therefore the volume in k-space corresponding to one state is

$$\Delta V_k = \Delta k_x \Delta k_y \Delta k_z = \frac{(2\pi)^3}{L_x L_y L_z} = \frac{(2\pi)^3}{V}$$

where V is the real volume of the gas.

The energy of the molecule can be expressed as a function of k and is

$$E = \frac{\hbar^2 k^2}{2m^*}$$

where m^* is the effective mass of the molecule. Since here we take only magnitude of the k vector, we expect some degeneracy of states with the same k but different $\vec{k}$. To quantify this degeneracy, we usually use the density of states - we say that the number of states that have energy $\frac{\hbar^2 k^2}{2m^*}$ or close to within small interval dk is

$$g(k)dk$$

where $g(k)$ is the density of states. Density of states is given as a derivative of the number of states that have smaller energy than the one given by k. It can be also derived as follows. Consider a small spherical volume in k-space, with radius from k to dk. The number of states in this volume (and thus our searched number $g(k)dk$) is

$$g(k)dk = 4\pi k^2 dk \frac{1}{\Delta V_k} = \frac{Vk^2}{2\pi^2} dk$$

If there can exist D states with the same momentum, then the volume per state is decreased by a factor of $\frac{1}{D}$ and thus the density of states becomes

$$g(k)dk = D \frac{Vk^2}{2\pi^2} dk$$

Thus, we have the energy of each state and the energy degeneracy of each state. So, the partition function of one molecule of the gas is

$$Z_1 = \int_0^\infty g(k) e^{-\beta \frac{\hbar^2 k^2}{2m^*}} dk$$

where the integral goes from 0 to infinity because k is magnitude, which only takes positive values. Substituting for $g(k)$

$$Z_1 = \int_0^\infty \frac{DVk^2}{2\pi^2} e^{-\beta \frac{\hbar^2 k^2}{2m^*}} dk$$

Substituting $y = \sqrt{\frac{\beta}{2m^*}} \hbar k$, we have

$$Z_1 = \frac{DV}{2\pi^2} \left(\frac{2m^*}{\beta \hbar^2} \right)^{\frac{3}{2}} \int_0^\infty y^2 e^{-y^2} dy$$

The second integral can be calculated similarly as shown before. Start by integration per partes

$$\int_0^\infty y^2 e^{-y^2} dy = \left[-\frac{y}{2} e^{-y^2} \right]_0^\infty + \frac{1}{2} \int_0^\infty e^{-y^2} dy = \frac{1}{2} \int_0^\infty e^{-y^2} dy$$

Denoting

$$I = \int_0^\infty e^{-y^2} dy$$

$$I^2 = \left(\int_0^\infty e^{-y^2} dy \right) \left(\int_0^\infty e^{-x^2} dx \right) = \int_0^\infty \int_0^\infty e^{-(x^2+y^2)} dx dy$$

Changing to polar planar coordinates

$$I^2 = \int_0^\infty \int_0^{\frac{\pi}{2}} e^{-r^2} r d\phi dr = \frac{\pi}{2} \int_0^\infty r e^{-r^2} dr = \frac{\pi}{2} \left[-\frac{1}{2} e^{-r^2} \right]_0^\infty = \frac{\pi}{4}$$

Thus

$$\int_0^\infty y^2 e^{-y^2} dy = \frac{\sqrt{\pi}}{4}$$

and

$$Z_1 = \frac{DV}{2\pi^2} \left(\frac{2m^*}{\beta \hbar^2} \right)^{\frac{3}{2}} \frac{\sqrt{\pi}}{4} = DV \left(\frac{m^* k_B T}{2\pi \hbar^2} \right)^{\frac{3}{2}} = \frac{DV}{\lambda_{th}}$$

where λ_{th} is so called thermal wavelength

$$\lambda_{th} = \sqrt{\frac{2\pi \hbar^2}{m^* k_B T}} = \frac{h}{\sqrt{2\pi m^* k_B T}} \tag{24}$$

Sometimes, we also mark

$$n_Q = \frac{1}{\lambda_{th}^3}$$

where n_Q is the quantum concentration. At this concentration, the thermal wavelengths of the particles start to overlap, and the particles' states start to overlap, which has specific consequences for bosons and fermions separately.

But as long as concentration is significatnly smaller then quantum concentration, the particles states do not overlap as much and we can.

At these concentrations, we also assume that particles are not forced to the same state, and thus we can effectively set $D = 1$, as every state accesible to the particles is occupied by a maximum of 1 particle. Therefore, this semi-classical mode has partition function

$$Z_1 = \frac{V}{\lambda_{th}^3} = V \left(\frac{m^* k_B T}{2\pi \hbar^2} \right)^{\frac{3}{2}} \tag{25}$$

Now we need to combine the partition functions for N particles in the gas. But since these particles are indistinguishable, we write

$$Z = \frac{Z_1^N}{N!}$$

The logarithm of partition function is (using Sterling approximation)

$$\ln Z \approx N \ln Z_1 - N \ln N + N$$

The pressure of the gas is then

$$p = k_B T \left(\frac{\partial \ln Z}{\partial V} \right)_T = k_B T N \frac{\partial \ln Z_1}{\partial V} = k_B T N \frac{\partial \ln V}{\partial V} = \frac{k_B T N}{V}$$

we therefore have our ideal gas equation

$$pV = N k_B T \tag{26}$$

The Helmholtz free energy is

$$F = -k_B T \ln Z = -k_B T N \ln Z_1 + k_B T (N \ln N - N)$$

The internal energy is

$$U = -\frac{d \ln Z}{d\beta} = -N \frac{d \ln Z_1}{d\beta} = -N \frac{3}{2} \frac{1}{T} \frac{dT}{d\beta} = -\frac{3}{2} N \frac{1}{T \frac{d\beta}{dT}} = \frac{3}{2} N k_B T$$

Hence the entropy is

$$S = \frac{U - F}{T} = \frac{3}{2} N k_B + k_B N \ln Z_1 - k_B N \ln N + k_B N = \frac{5}{2} k_B N + k_B N \ln \left(\frac{Z_1}{N} \right)$$

Therefore

$$S = N k_B \left[\frac{5}{2} + \ln \left(\frac{V}{N \lambda_{th}^3} \right) \right] \tag{27}$$

This is called the Sackur-Tetroda equation. It is especially important since it differs from the entropy for the case where the individual particles of the gas are distinguishable. For such case, $Z = Z_1^N$, which does not change U but changes F to

$$F' = -k_B T \ln Z = -N k_B T \ln Z_1$$

So

$$S' = \frac{3}{2} N k_B + N k_B \ln Z_1 = N k_B \left[\frac{3}{2} + \ln \left(\frac{V}{\lambda_{th}^3} \right) \right]$$

3.9.1   Gibbs Paradox

Consider now two situations. In the first situation, we have two volumes of gas, each of volume V, separated by a barrier. Suppose that in one volume, gas A is present, and different gas B is in the other volume. Now, we remove the barrier between the gases. After the gases mix, how does the entropy of the system change? We expect it to grow, as this process is irreversible. To calculate it precisely, first assume that molecules of each gas are distinguishable.
The entropy of gas A before expansion is then

$$S_A' = N_A k_B \left[\frac{3}{2} + \ln \left(\frac{V}{\lambda_A^3} \right) \right]$$

The entropy of gas B before expansion is

$$S_B' = N_B k_B \left[\frac{3}{2} + \ln \left(\frac{V}{\lambda_B^3} \right) \right]$$

The entropy of gas A after expansion is

$$S_{Af}' = N_A k_B \left[\frac{3}{2} + \ln \left(\frac{2V}{\lambda_A^3} \right) \right]$$

The entropy of gas B after expansion is

$$S_{Bf}' = N_B k_B \left[\frac{3}{2} + \ln \left(\frac{2V}{\lambda_B^3} \right) \right]$$

Which means that the change in entropy is

$$\Delta S' = S_{Af}' + S_{Bf}' - S_A' - S_B' = N_A k_B \ln 2 + N_B k_B \ln 2$$

Similarly for indistinguishable molecules of two different gases (indistinguishable for each gas respectively, but molecules of A distinct from those of B)

$$S_A = N_A k_B \left[\frac{5}{2} + \ln \left(\frac{V}{N_A \lambda_A^3} \right) \right]$$

$$S_B = N_B k_B \left[\frac{5}{2} + \ln \left(\frac{V}{N_B \lambda_B^3} \right) \right]$$

$$S_{Af} = N_A k_B \left[\frac{5}{2} + \ln \left(\frac{2V}{N_A \lambda_A^3} \right) \right]$$

$$S_{Bf} = N_B k_B \left[\frac{5}{2} + \ln \left(\frac{2V}{N_B \lambda_B^3} \right) \right]$$

So

$$\Delta S = S_{Af} - S_A + S_{Bf} - S_B = N_A k_B \ln 2 + N_B k_B \ln 2$$

Therefore, in this case, both approaches predict the same result, which is an increase in entropy, which is what we expect.
Now consider a different situation, in with the same setup but now the gas A and gas B are identical in the beginning, lets say that both volumes are filled with gas A. Now, we would expect that removing the

barrier will not change the entropy, because the process should reversible (the gases do not in anyway mix more - they are the same gases) Again, start by considering molecules of A as distinguishable, the initial entropy is

$$S' = 2N_A k_B \left[\frac{3}{2} + \ln \left(\frac{V}{\lambda_A^3} \right) \right]$$

and final entropy is

$$S'_f = 2N_A k_B \left[\frac{3}{2} + \ln \left(\frac{2V}{\lambda_A^3} \right) \right]$$

Therefore there is a change in entropy and it is

$$\Delta S' = 2N_A k_B \ln 2$$

This is very bizzare. Fortunately, the second approach gives a reasonable result. For the particles being indistinguishable

$$S = 2N_A k_B \left[\frac{5}{2} + \ln \left(\frac{V}{N_A \lambda_A^3} \right) \right]$$

But, the entropy after expansion is

$$S_f = 2N_A k_B \left[\frac{5}{2} + \ln \left(\frac{2V}{2N_A \lambda_A^3} \right) \right] = 2N_A k_B \left[\frac{5}{2} + \ln \left(\frac{V}{N_A \lambda_A^3} \right) \right]$$

which predicts expected change in entropy

$$\Delta S = 0$$

Therefore, the particles of a gas must be indistinguishable for this situation to make sense.

4 Grand-Canonical Ensemble

4.1 Chemical Potential

Chemical potential μ is defined as amount of energy generated by adding particles to the system. The first law of thermodynamics with chemical potential becomes

$$dU = TdS - pdV + \mu dN \tag{28}$$

where dN is the change in the number of particles. If there is multiple types of particles that can be added to the system, then they have their respective chemical potentials.
From this definition, we can derive

$$\mu = \left(\frac{\partial U}{\partial N} \right)_{S,V}$$

The change in Helmholtz free energy is

$$dF = dU - TdS - SdT = \mu dN - pdV - SdT$$

Hence

$$\mu = \left(\frac{\partial F}{\partial N} \right)_{V,T}$$

The change in Gibbs free energy is

$$dG = dF + pdV + Vdp = \mu dN + Vdp - SdT$$

Hence

$$\mu = \left(\frac{\partial G}{\partial N} \right)_{p,T}$$

Since $G = U + pV - TS$, for fixed p and T, U, V and S are all extensive with number of particles. So, assume that we have some basic Gibbs energy of one particle G_1. The Gibbs energy of N particles is then

$$G = NG_1$$

And the chemical potential of these particles is

$$\mu = \frac{\partial N G_1}{\partial N} = G_1$$

because G_1 of one individual particle cannot depend on the number of particles N (for non-interacting particles). Reexpressing this in terms of original Gibbs energy

$$\mu = \frac{G}{N} \tag{29}$$

4.1.1 Connected Systems

Consider two connected systems, which can particles, but are otherwise independent and have fixed, even though possibly different, volumes and temperatures.
Also, assume that the total number of particles is fixed. So

$$N_1 + N_2 = N = const.$$

where $N_{1/2}$ is the number of particles in the first/second system. By the second law of thermodynamics

$$dS \geq 0$$

The only thing that can increase the entropy here is the exchange of particles (since the temperature is fixed). Also, because temperature is fixed, the internal energy of the systems is fixed (assuming that they reached equilibrium). Hence

$$dS = \left(\frac{\partial S_1}{\partial N_1}\right)_{U,V} dN_1 + \left(\frac{\partial S_2}{\partial N_2}\right)_{U,V} dN_2 \geq 0$$

For fixed volume and internal energy (temperature), we then have from the first law of thermodynamics

$$dU = 0 = TdS - pdV + \mu dN = TdS + \mu dN$$

$$\frac{\mu}{T} = -\left(\frac{\partial S}{\partial N}\right)_{U,V}$$

Also, since the total number of particles is fixed

$$dN_1 = -dN_2$$

And thus

$$dS = -\frac{\mu_1}{T_1} dN_1 + \frac{\mu_2}{T_2} dN_1 \geq 0$$

$$\left(\frac{\mu_2}{T_2} - \frac{\mu_1}{T_1}\right) dN_1 \geq 0 \tag{30}$$

This means that if $\frac{\mu_1}{T_1} \geq \frac{\mu_2}{T_2}$, then dN_1 has to be negative and thus particles are leaving the system 1 and entering system 2. Similarly, if $\frac{\mu_2}{T_2} \geq \frac{\mu_1}{T_1}$, particles must be entering system 1 and leaving system 2. This continues until the difference of these potentials is set to zero and

$$\frac{\mu_1}{T_1} = \frac{\mu_2}{T_2}$$

4.2 Grand-Partition Function

To derive the form of grand-partition function, consider a system in contact with a large reservoir so that it can exchange energy and particles with the reservoir. The ability to exchange energy leads to the temperature of both the system and the reservoir being fixed at the same value. The fixed temperature together with ability to exchange particles than leads to the chemical potential of both the system and the reservoir to be fixed at a common value.

The entropy of the system then does generally depend on the number of particles in the system N_i and energy of the system E_i. If the total energy and total number of particles is fixed as N and E respectively, the entropy of the reservoir is

$$S = S(E - E_i, N - N_i) \approx S(E, N) - \left(\frac{\partial S}{\partial U}\right)_{V,T,N} E_i - \left(\frac{\partial S}{\partial N}\right)_{V,T,U} N_i$$

The first law of thermodynamics is
$$dU = TdS - pdV + \mu dN$$

For fixed temperature, volume and number of particles
$$dU = TdS$$

$$\left(\frac{\partial S}{\partial U}\right)_{T,V,N} = \frac{1}{T}$$

For fixed temperature, volume and internal energy
$$0 = TdS + \mu dN$$

$$\left(\frac{\partial S}{\partial N}\right)_{T,V,U} = -\frac{\mu}{T}$$

Hence
$$S(E - E_i, N - N_i) \approx S(E, N) - \frac{E_i}{T} + \frac{\mu N_i}{T}$$

Using Boltzmann definition of equilibrium entropy
$$S = k_B \ln \Omega$$

We have

$$\ln \Omega(E - E_i, N - N_i) \approx \ln \Omega(E, N) - \frac{1}{k_B T}(E_i - \mu N_i) = \ln \left(\Omega(E, N) e^{-\beta(E_i - \mu N_i)}\right)$$

$$\Omega(E - E_i, N - N_i) = \Omega(E, N) e^{-\beta(E_i - \mu N_i)}$$

Again, we assume that for big reservoir, the probability of state of the system goes as

$$P(E_i, N_i) \propto \Omega(E - E_i, N - N_i)$$

And thus

$$P(E_i, N_i) = \frac{e^{-\beta(E_i - \mu N_i)}}{\mathscr{Z}} \tag{31}$$

Where the normalization factor z is the grand-partition function

$$\mathscr{Z} = \sum_i e^{-\beta(E_i - \mu N_i)} \tag{32}$$

Similarly with the case of canonical ensemble, where the thermodynamical potentail was the Helmholtz free energy, we introduce the grand-potential, defined as

$$\Phi_G = U - TS - \mu N \tag{33}$$

and is also sometimes called the Landau free energy.
Now, we need to determine the internal energy and expected number of particles from the grand-partition function, similarly as before.
The internal energy is
$$U = \sum_i E_i P_i = \sum_i E_i \frac{e^{-\beta(E_i - \mu N_i)}}{\mathscr{Z}}$$

And the number of particles
$$N = \sum_i N_i P_i = \sum_i N_i \frac{e^{-\beta(E_i - \mu N_i)}}{\mathscr{Z}}$$

Using the Gibbs definition of entropy

$$S = -k_B \sum_i P_i \ln P_i = -k_B \sum_i \frac{e^{-\beta(E_i - \mu N_i)}}{\mathscr{Z}} \left(-\beta(E_i - \mu N_i) - \ln \mathscr{Z}\right)$$

$$S = k_B \sum_i \beta E_i \frac{e^{-\beta(E_i - \mu N_i)}}{\mathscr{Z}} - k_B \sum_i \beta \mu N_i \frac{e^{-\beta(E_i - \mu N_i)}}{\mathscr{Z}} + k_B \ln Z \sum_i \frac{e^{-\beta(E_i - \mu N_i)}}{\mathscr{Z}}$$

Using previously defined relations and definition of grand-partition function

$$S = k_B \beta U - k_B \beta \mu N + k_B \ln \mathscr{Z}$$

Hence

$$TS = k_B T \beta U - k_B T \beta \mu N + k_B T \ln \mathscr{Z} = U - \mu N + k_B T \ln \mathscr{Z}$$

And thus

$$\Phi_G = -k_B T \ln \mathscr{Z} \tag{34}$$

which is exactly analogous to expression for Helmholtz free energy in canonical ensemble, where the Helmholtz free energy was the thermodynamical potential.

One important observation is that when $\mu = 0$, $\mathscr{Z} \to Z$ and $\Phi_G \to F$ and the ensemble becomes described by canonical ensemble formalism, even though the number of particles changes over time.

4.2.1 Grand-Partition Function Formalism

Similarly as before, we are able to derive several functions of state from the partition function. For example, we have

$$\frac{\partial \mathscr{Z}}{\partial \mu} = \sum_i \beta N_i e^{-\beta(E_i - \mu N_i)} = \mathscr{Z} \beta N$$

And thus

$$N = \frac{1}{\beta \mathscr{Z}} \frac{\partial \mathscr{Z}}{\partial \mu} = k_B T \frac{\partial \ln \mathscr{Z}}{\partial \mu} \tag{35}$$

For energy, we can use

$$\frac{\partial \mathscr{Z}}{\partial \beta} = \sum_i -(E_i - \mu N_i) e^{-\beta(E_i - \mu N_i)} = -\sum_i E_i e^{-\beta(E_i - \mu N_i)} + \mu \sum_i N_i e^{-\beta(E_i - \mu N_i)} = -\mathscr{Z}(E - \mu N)$$

Therefore

$$E - \mu N = -\frac{1}{\mathscr{Z}} \frac{\partial \mathscr{Z}}{\partial \beta} = -\frac{\partial \ln \mathscr{Z}}{\partial \beta}$$

And thus

$$E = \mu k_B T \frac{\partial \ln \mathscr{Z}}{\partial \mu} - \frac{\partial \ln \mathscr{Z}}{\partial \beta} \tag{36}$$

4.2.2 One State System

Consider a system in contact with large reservoir which has exactly one state with energy ϵ such that every particle that occupies this state has energy ϵ. Therefore, if there are N particles in the system, the energy of the system is $N\epsilon$. Therefore, the grand-partition function of the system is

$$\mathscr{Z} = \sum_{N=0}^{N_{max}} e^{-\beta(E_N - \mu N)} = \sum_{N=0}^{N_{max}} e^{-\beta N(\epsilon - \mu)}$$

We can recognize this as geometric series, which equal to

$$\mathscr{Z} = \frac{1 - e^{-\beta(\epsilon - \mu)(N_{max}+1)}}{1 - e^{-\beta(\epsilon - \mu)}} \tag{37}$$

Therefore, the average number of particles in the state (the average occupacy of the state) is

$$N = k_B T \frac{\partial \ln \mathscr{Z}}{\partial \mu} = k_B T \left[\frac{-e^{-(N_{max}+1)\beta(\epsilon - \mu)}}{1 - e^{-(N_{max}+1)\beta(\epsilon - \mu)}} ((N_{max}+1)\beta) + \frac{e^{-\beta(\epsilon - \mu)}}{1 - e^{-\beta(\epsilon - \mu)}} \beta \right]$$

$$N = \frac{e^{-\beta(\epsilon - \mu)}}{1 - e^{-\beta(\epsilon - \mu)}} - \frac{(N_{max}+1)e^{-(N_{max}+1)\beta(\epsilon - \mu)}}{1 - e^{-(N_{max}+1)\beta(\epsilon - \mu)}} \tag{38}$$

This will be useful for quantum statistics, which are discussed as last part of this module.

4.3 Particle Conservation Laws

Consider now two special cases. First, a system with fixed temperature and volume where the particles can be created freely. Since the particles can be created in without limitations, at the equilibrium, all functions of state of the system must be independent of the number of particles.
Therefore, for Helmholtz free energy

$$\left(\frac{\partial F}{\partial N}\right)_{T,V} = 0$$

Small change in Helmholtz free energy is

$$dF = dU - TdS - SdT = -pdV + \mu dN - SdT$$

and thus

$$\left(\frac{\partial F}{\partial N}\right)_{T,V} = \mu$$

This means that if the particles can be created without limitiations, the chemical potential in the system must be $\mu = 0$.

Consider now a different situation, where there are two types of particles that can be created, and the difference of number of these particles is kept constant, i.e. particles can be created only in pairs of the two types. This is typical behaviour for example for creation of electron-positron pairs.
Since the difference of the particle number is conserved, if we write the difference of the particle number as a state variable, we have a fixed V, T and N where

$$N = N_+ - N_-$$

is the difference of the particle number, and thus the potential of thus system is the Helmholtz free energy $F(V, T, N)$. At the equilibrium

$$dF = 0$$

$$dU - TdS - SdT = 0$$

$$\mu_+ dN_+ + \mu_- dN_- - pdV - SdT = 0$$

Since V and T are constant

$$\mu_+ \frac{dN_+}{dN_-} + \mu_- = 0$$

But, from the definition of constant N

$$dN = 0 = dN_+ - dN_-$$

$$\frac{dN_+}{dN_-} = 1$$

And thus

$$\mu_+ = -\mu_-$$

5 Quantum Gases

So far, we have only discussed the classical ideal gases. But, methods of statistical physics can be used to described generalized systems of non-interacting particles that follow some creation rules even in the quantum regime. First, we try to derive them in a sort of semi-classical way, in which they were probably first derived.

5.1 Semi-Classical Approach

5.1.1 Photon Gas

Photons are particles of the electromagnetic radiation. Because photons are massless, we can assume they can be created at will. Therefore, they can be described as a canonical ensemble ($\mu = 0$). First attempt at modelling photon gas was to assume that each photon is approximately a 1D harmonic oscillator, oscillating in the direction of its polarisation.

The energy of a harmonic oscillator at frequency ω is

$$U(\omega) = \hbar\omega \left(\frac{1}{2} + \frac{e^{-\beta\hbar\omega}}{1 - e^{-\beta\hbar\omega}} \right) = \hbar\omega \left(\frac{1}{2} + \frac{1}{e^{\beta\hbar\omega} - 1} \right)$$

The wavenumber of a photon is given as

$$k = \frac{\omega}{c}$$

and photons can exist in two polarised states for each wavevector $\vec{k}$. Therefore, the density of states for photons uses $D = 2$ and is

$$g(k)dk = 2\frac{Vk^2}{2\pi^2}dk$$

Hence

$$g(\omega)d\omega = g(k(\omega))dk(\omega)\frac{V\omega^2}{\pi^2 c^2}\frac{d\omega}{c} = \frac{V\omega^2}{\pi^2 c^3}d\omega$$

Then, the total internal energy of the photon gas is

$$E = \int_0^\infty g(\omega)U(\omega)d\omega$$

And the energy density

$$u = \frac{E}{V} = \frac{1}{V}\int_0^\infty \frac{V\omega^2}{\pi^2 c^3}\hbar\omega \left(\frac{1}{2} + \frac{1}{e^{\beta\hbar\omega} - 1} \right)d\omega$$

Planck, who came up with this relationship, then argued that since the photons can be created and anihilated at will, it makes no sense to talk about the zero point energy, and therefore we should neglect the $\frac{1}{2}$ in the bracket (also, the integral diverges if we consider it). Then

$$u = \int_0^\infty \frac{\hbar}{\pi^2 c^3}\frac{\omega^3}{e^{\beta\hbar\omega} - 1}d\omega$$

Substituting $x = \beta\hbar\omega$, we obtain

$$u = \frac{\hbar}{\pi^2 c^3}\int_0^\infty \frac{1}{\beta^3\hbar^3}\frac{x^3}{e^x - 1}\frac{1}{\beta\hbar}dx = u = \frac{1}{\pi^2 c^3\hbar^3\beta^4}\int_0^\infty \frac{x^3}{e^x - 1}dx$$

This integral turns out to be a standard one, and equals $\frac{\pi^4}{15}$. Therefore

$$u = \frac{\pi^2}{15c^3\hbar^3}k_B^4 T^4 = \frac{4\sigma}{c}T^4 \tag{39}$$

where

$$\sigma = \frac{\pi^2 k_B^4}{60c^2\hbar^3} \approx 5.67 \, \text{W K}^{-4}\text{m}^{-2}$$

Is the Stefan-Boltzmann constant.
This then leads to surface intensity

$$I = \sigma T^4$$

and maximum at

$$\lambda_{max}T = b$$

where $b \approx 2.898$ mm K is the Wien's displacement constant.
Historically, this is called the black-body radiation problem and it is one of the problems that lead to the formulation of quantum mechanics. But even today, the same physics is still applied, for example to cosmic microwave background, which is a very good black-body radiation, with temperature 2.726 K.

5.1.2 Einstain Model of Phonon Gas

Phonons are virtual particles that create oscillations in the lattice of solids. Generally, we expect 3 polarizations of phonons per each wavevector of phonon, and we expect that they are free to appear and disappear.

In the Einstain model, we assume that the frequency of all phonons is the same, and therefore the density of states as a function of frequency is

$$g(\omega) = 3N\delta(\omega - \omega_E)$$

where ω_E is the frequency of oscillations (Einstain frequency) and N is the total number of phonons in the system (for each phonon, there is 3 states available).

We model each phonon as a 1D simple harmonic oscillator, again neglecting the zero point energy. Therefore

$$E = \frac{\hbar\omega}{e^{\beta\hbar\omega} - 1}$$

Therefore, the total internal energy is

$$U = \int_0^\infty E(\omega)g(\omega)d\omega = 3NE(\omega_E) = 3N\frac{\hbar\omega_E}{e^{\beta\hbar\omega_E} - 1}$$

We usually substitute $\hbar\omega_E = k_B\theta_E$, where θ_E is the Einstain temperature. Then

$$U = 3N\frac{k_B\theta_E}{e^{\frac{\theta_E}{T}} - 1} \tag{40}$$

We can also determine the heat capacity

$$C_V = \frac{\partial U}{\partial T} = 3N\frac{k_B\theta_E e^{\frac{\theta_E}{T}}}{\left(e^{\frac{\theta_E}{T}} - 1\right)^2}\frac{\theta_E}{T^2} = 3Nk_B\frac{\theta_E^2}{T^2}\frac{e^{\frac{\theta_E}{T}}}{\left(e^{\frac{\theta_E}{T}} - 1\right)^2}$$

This model is reasonably well for high and intermediate temperatures, but is not precise for small temperatures.

5.1.3 Debye Model for Phonon Gas

In the Debye model, phonons follow dispersion relation

$$\omega = vk \tag{41}$$

where v is the speed of sound in the medium. The density of states is

$$g(\omega)d\omega = \frac{3V\omega^2}{2\pi^2 v^3}d\omega$$

The phonons are again modelled as harmonic oscillators with no zero-point energy. The main difference to previous models is that there is some assumed cut-off frequency, called Debye frequency ω_D, which limits the oscillations of atoms. Then the total energy is

$$U = \int_0^{\omega_D} g(\omega)\frac{\hbar\omega}{e^{\beta\hbar\omega} - 1}d\omega$$

The condition on Debye frequency is that the integral of density of states up to Debye frequency includes all accesible states, so

$$\int_0^{\omega_D} g(\omega)d\omega = 3N$$

where N is the number of phonons. Then

$$\frac{3V}{2\pi^2 v^3}\int_0^{\omega_D}\omega^2 d\omega = 3N$$

$$\frac{V\omega_D^3}{2\pi^2 v^3} = 3N$$

$$\omega_D = \sqrt[3]{\frac{6N\pi^2 v^3}{V}} \tag{42}$$

Also

$$g(\omega)d\omega = \frac{9N\omega^2}{\omega_D^3}$$

So, the total energy is

$$U = \frac{9N\hbar}{\omega_D^3}\int_0^{\omega_D}\frac{\omega^3}{e^{\beta\hbar\omega}-1}d\omega$$

Substituting $x = \beta\hbar\omega$

$$U = \frac{9N\hbar}{\omega_D^3}\frac{1}{\beta^4\hbar^4}\int_0^{\frac{x}{\beta\hbar}}\frac{x^3}{e^x-1}dx$$

The heat capacity is

$$C = \frac{\partial U}{\partial T} = \frac{9N\hbar}{\omega_D^3}\int_0^{\omega_D}\frac{\omega^3}{(e^{\beta\hbar\omega}-1)^2}e^{\beta\hbar\omega}\hbar\omega k_B\beta^2 d\omega = \frac{9N\hbar^2 k_B\beta^2}{\omega_D^3}\int_0^{\omega_D}\frac{\omega^4 e^{\beta\hbar\omega}}{(e^{\beta\hbar\omega}-1)^2}d\omega$$

For low T, $\beta \to \infty$ and

$$C \to \frac{9N\hbar^2 k_B\beta^2}{\omega_D^3}\int_0^{\omega_D}\frac{\omega^4}{e^{\beta\hbar\omega}}d\omega = \frac{9N\hbar^2 k_B\beta^2}{\omega_D^3}\int_0^{\omega_D}\omega^4 e^{-\beta\hbar\omega}d\omega$$

This is a standard integral, and the resulting heat capacity is

$$C \to \frac{12\pi^4}{5}Nk_B T^3\frac{k_B^3}{\hbar^3\omega_D^3}$$

with a characteristic T^3 dependence.
For high temperatures

$$C \to 3Nk_B$$

which is the result of equipartition theorem.
In real solid, the dispersion relations can be much more complicated. In fact, there are two distinct types of oscillations - lattice oscillations, which symbolizes movement of the ions in the lattice so that the whole lattice structure oscillates, and so called optical modes, when only ions inside a unit cell oscillate, but centre of mass of the unit cell remains stationary. Usually, the optical modes have quite narrow range of frequencies, and are often well modelled by Einstain model, while the other (also called acoustic modes) are better modelled by the Debye model. Since optical modes are also more energetic, at low energies, these are not excited and the vibrations are purely acoustic, which means that the Debye model is precise.
The Debye model describes the behaviour of heat capacity well until we reach so small temperatures that the addition to heat capacity from electrons around the Fermi surface stops being negligable.
One final note is on the heat expansion - so far, the oscillations we supposed were harmonic, which have overall zero expansion. But, for big expansions, we start to have unharmonic effects, which are responsible for the expansion.

5.2 Quantum Statistics

There are generally two types of quantum particles - fermions and bosons. The main difference is that fermions follow the Pauli exclusion principle and therefore only 1 fermion can exist in a specific state. There is no such limitation for bosons. If we now assume that some system with number of states is connected to a reservoir at constant temperature and can exchange energy and particles with this reservoir, we arrive at two characteristic different behaviours for non-interacting fermions and bosons.

5.2.1 Fermi-Dirac Distribution

Consider some state of the system with energy ϵ. Because of Pauli exclusion principle, there are only two possibilities for the number of fermions in this system - 0 or 1. Using (38) with $N_{max} = 1$, we obtain

$$N = \frac{e^{-\beta(\epsilon-\mu)}}{1-e^{-\beta(\epsilon-\mu)}} - \frac{2e^{-2\beta(\epsilon-\mu)}}{1-e^{-2\beta(\epsilon-\mu)}} = \frac{e^{-\beta(\epsilon-\mu)}(1+e^{-\beta(\epsilon-\mu)})}{(1-e^{-\beta(\epsilon-\mu)(1+e^{-\beta(\epsilon-\mu)})})} - \frac{2e^{-2\beta(\epsilon-\mu)}}{(1-e^{-\beta(\epsilon-\mu)})(1+e^{-\beta(\epsilon-\mu)})} =$$

$$= \frac{e^{-\beta(\epsilon-\mu)} - e^{-2\beta(\epsilon-\mu)}}{(1 - e^{-\beta(\epsilon-\mu)})(1 + e^{-\beta(\epsilon-\mu)})} = \frac{e^{-\beta(\epsilon-\mu)}(1 - e^{-\beta(\epsilon-\mu)})}{(1 - e^{-\beta(\epsilon-\mu)})(1 + e^{-\beta(\epsilon-\mu)})} = \frac{e^{-\beta(\epsilon-\mu)}}{1 + e^{-\beta(\epsilon-\mu)}}$$

Therefore, we have the so called Fermi-Dirac distribution, which gives the average occupacy of a state with energy ϵ, for a system with chemical potential μ as

$$N = f_{FD}(\epsilon, T) = \frac{1}{1 + e^{\frac{\epsilon-\mu}{k_B T}}} \tag{43}$$

We can also determine the grand-partition function as

$$\mathscr{Z} = \sum_{N=0}^{1} e^{-\beta N(\epsilon-\mu)} = 1 + e^{-\beta(\epsilon-\mu)}$$

5.2.2 Bose-Einstain Distribution

Consider the same system as above, but now for bosons. Since there is no limit on how many bosons can be in one state, we use (38), but with $N_{max} \to \infty$ this time. This leads to

$$N \to \frac{e^{-\beta(\epsilon-\mu)}}{1 - e^{-\beta(\epsilon-\mu)}}$$

and therefore we have the Bose-Einstain distribution

$$N = f_{BE}(\epsilon, T) = \frac{1}{e^{\frac{\epsilon-\mu}{k_B T}} - 1} \tag{44}$$

The grand-partition function is

$$\mathscr{Z} = \frac{1}{1 - e^{-\beta(\epsilon-\mu)}}$$

In both cases above, for a system that consists of multiple states with different energies ϵ, the statistics are exactly the same, only the ϵ energy is now a variable.

5.3 Electron Gas

Electrons are fermions, and in the metal, they can be viewed as non-interacting free fermions (interactions are small and effectively come out just as a effective mass of the electron). If we have a solid that is filled with electrons at the temperature $T = 0$, the most energetic electron sits at energy level called the Fermi energy E_f. If we then add another electron, its energy will be this Fermi energy. Therefore, the change in the energy of the system will be

$$dU = E_f = \mu dN$$

As we added one electron, $dN = 1$, and therefore

$$E_f = \mu \tag{45}$$

Therefore, if we connect two metals, their Fermi energies have to be at the same level - they can exchange both energy and electrons.

The electrons are free particles, and they have degeneracy 2 due to their spins. Therefore the density of states is

$$g(k)dk = 2\frac{Vk^2}{2\pi^2} = \frac{Vk^2}{\pi^2}$$

In terms of energy

$$E = \frac{\hbar^2 k^2}{2m^*}$$

$$dE = \frac{\hbar^2}{m^*} k dk = \frac{\hbar^2}{m^*} \sqrt{\frac{2m^* E}{\hbar^2}} dk$$

Hence

$$g(E)dE = \frac{V}{\pi^2} \frac{2m^* E}{\hbar^2} \frac{m^*}{\hbar^2} \sqrt{\frac{\hbar^2}{2m^* E}} dE = \frac{V}{2\pi^2} \left(\frac{2m^*}{\hbar^2}\right)^{\frac{3}{2}} \sqrt{E} dE$$

From the definition of Fermi energy, the total number of electrons in the system is

$$N = \int_0^{E_f} g(E) f_{FD}(E, 0) dE$$

For zero temperature, Fermi-Dirac distribution becomes a step function, with 1 for all $E < \mu = E_f$ and 0 for all greater energies. Therefore

$$N = \int_0^{E_f} g(E) dE = \int_0^{E_f} \frac{V}{2\pi^2} \left(\frac{2m^*}{\hbar^2}\right)^{\frac{3}{2}} \sqrt{E} dE = \frac{V}{2\pi^2} \left(\frac{2m^*}{\hbar^2}\right)^{\frac{3}{2}} \int_0^{E_f} \sqrt{E} dE =$$

$$= \frac{V}{2\pi^2} \left(\frac{2m^*}{\hbar^2}\right)^{\frac{3}{2}} \frac{2}{3} E_f^{\frac{3}{2}} = \frac{V}{3\pi^2} \left(\frac{2m^* E_f}{\hbar^2}\right)^{\frac{3}{2}}$$

This can be rephrased using the Fermi wavevector k_f

$$\frac{\hbar^2 k_f^2}{2m^*} = E_f$$

to be

$$k_f^2 = \left(3\pi^2 \frac{N}{V}\right)^{\frac{2}{3}} \tag{46}$$

and hence

$$E_f = \frac{\hbar^2 k_f^2}{2m^*} = \frac{\hbar^2}{2m^*} \left(3\pi^2 \frac{N}{V}\right)^{\frac{3}{2}}$$

The total energy of the system is

$$U(T) = \int_0^\infty g(E) f_{FD}(E, T) E dE$$

At $T = 0$

$$U(0) = \int_0^{E_f} g(E) E dE = \frac{V}{2\pi^2} \left(\frac{2m^*}{\hbar^2}\right)^{\frac{3}{2}} \int_0^{E_f} E^{\frac{3}{2}} dE = \frac{3}{5} \frac{V}{3\pi^2} \left(\frac{2m^* E_f}{\hbar^2}\right)^{\frac{3}{2}} E_f = \frac{3}{5} N E_f$$

therefore the average energy per electron is

$$< E > = \frac{3}{5} E_f$$

We can also find the pressure response of the system, which is called the degeneracy pressure, as

$$p = -\left(\frac{\partial U}{\partial V}\right)_S = -\frac{3}{5} N \frac{\partial}{\partial V} \frac{\hbar^2}{2m^*} \left(3\pi^2 N\right)^{\frac{2}{3}} V^{-\frac{2}{3}} = \frac{6}{15} N \frac{\hbar^2}{2m^*} \left(3\pi^2 N\right)^{\frac{2}{3}} V^{-\frac{5}{3}} = \frac{2}{5} \frac{\hbar^2}{2m^*} n \left(3\pi^2 n\right)^{\frac{2}{3}}$$

where $n = \frac{N}{V}$ is the number density of the electrons. Or, in terms of Fermi energy

$$p = \frac{2}{5} n E_f \tag{47}$$

5.3.1 Heat Capacity of Electron Gas

Usually, the Fermi energy is a very high value, relative to the thermal energy. Therefore, we can approximate that any thermal excitations that happen do so only very close to the Fermi energy level, and have reach about $k_B T$.

Therefore, the number of electrons involved in these excitatitons is approximately

$$N = g(E) dE \approx g(E_f) k_B T$$

The energy is gained by these electrons, and therefore the total change in internal energy is

$$\Delta U \approx N k_B T \approx g(E_f) k_B^2 T^2 = \frac{V}{2\pi^2} \left(\frac{2m^*}{\hbar^2}\right)^{\frac{3}{2}} \sqrt{E_f} k_B^2 T^2 = \frac{2}{3} \frac{N}{E_f} k_B^2 T^2$$

This is an approximate solution, the exact solution is

$$\Delta U = \frac{\pi^2}{4} \frac{N}{E_f} k_B^2 T^2$$

Hence, the heat capacity

$$C_e = \frac{\partial (U(0) + \Delta U)}{\partial T} = \frac{\pi^2}{2} \frac{N}{E_f} k_B^2 T$$

Therefore, for low values of temperature, the overall heat capacity of a solid is

$$C_T = C_{phonon} + C_e = \alpha \frac{T}{T_F} + \beta \left(\frac{T}{\theta_D} \right)^3$$

where θ_D is the Debye temperature, defined by $k_B \theta_D = \hbar \omega_D$ and T_F is the Fermi temperature, defined by $k_B T_F = E_f$.

5.4 Quantum Gases Revisited

With our quantum particle distributions, we can now reformulate the assumptions for photon and phonon gases. For photon gas, we declare dispersion relation

$$\omega = ck$$

and degeneracy 2 for 2 polarizations. Then, the density of states is

$$g(\omega) d\omega = \frac{V \omega^2}{\pi^2 c^3} d\omega$$

Since the photons can be created at will, $\mu = 0$. Therefore, the total energy of a photon gas is

$$U = \int_0^\infty g(\omega) \hbar \omega f_{BE}(\hbar \omega, T) d\omega = \int_0^\infty \frac{V \omega^2}{\pi^2 c^3} \frac{\hbar \omega}{e^{\beta \hbar \omega} - 1} d\omega$$

We can see that this is the same result as before, but we derived it in a theoretically clear way, without having to neglect any zero point energies. Similarly for phonon gas, we have dispersion relation

$$\omega = vk$$

and degeneracy 3, so

$$g(\omega) d\omega = \frac{3V \omega^2}{2\pi^2 v^3} d\omega$$

And thus

$$U = \int_0^{\omega_D} \hbar \omega g(\omega) f_{BE}(\hbar \omega, T) d\omega = \int_0^{\omega_D} \hbar \omega \frac{3V \omega^2}{2\pi^2 v^3} \frac{1}{e^{\beta \hbar \omega} - 1} d\omega$$

Which is again exactly analogous.

5.5 Bose-Einstain Condensation

For boson gas at some very low temperature, all the bosons tend to be in the ground state of the system. This means that we can no longer describe the distribution of bosons by continuous density of states. The temperature when this occurs is called the critical temperature and the state of matter when nearly all bosons are in the same ground state is called the Bose-Einstain condensate. It can be shown that near the low temperatures, the fraction of bosons in the ground state, $\frac{N_0}{N}$ is

$$\frac{N_0}{N} = 1 - \frac{T^2}{T_C^2}$$

where T_C is the critical temperature of the boson gas.
Since nearly all the particles in the system are in the same state, Bose-Einstain condensate has many perculiar properties, but these are not further explored here.