

# Recapitulation

Last time we covered:

1. Phase Space
2. Gibbs ensemble
3. Statistical Physic Postulate
4. Microcanonical Ensemble

Today, we will finish up Gibbs ensemble by discussing details in canonical ensemble where we will introduce (1) partition function, (2) energy in the canonical ensemble, and (3) relation with other thermodynamic potential. We will also discuss about Grand-Canonical Ensemble and provide a summary for Gibbs ensemble.

Moreover, we will calculate the distribution of particles on different levels of energy. We will introduce three different kinds of statistics, such as

1. Maxwell Boltzmann
2. Fermi-Dirac
3. Bose-Einstein

## Canonical Ensemble

### Partition Function

When the system can exchange heat with a reservoir, but not work and matter, there is a larger number of microstates. We have to account for the microstates  $1 \leq i \leq \Omega(U_j)$  accessible to the system which has a given energy  $U_j$ . This is known as the *canonical ensemble*.

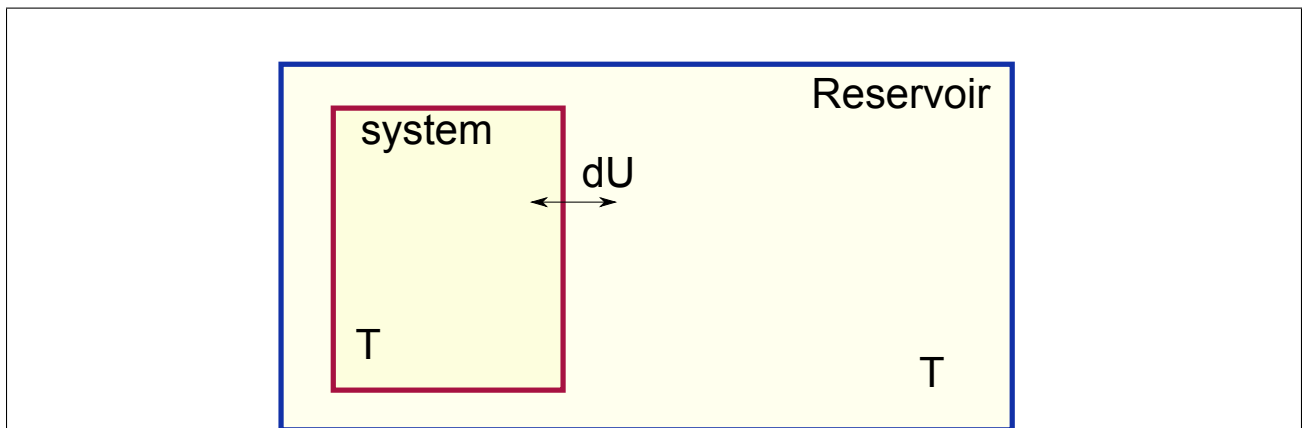


Figure 0-1: The system is in contact with the reservoir. The heat is exchanged between the system and the reservoir.

The reservoir maintains the temperature  $T$  constant and the total energy,  $U_0 = U_j + U_T$ , of the system plus its reservoir is constant. The total number of microstates  $\mathcal{N}$  accessible for the system and the reservoir will be given by

$$\mathcal{N}(U_0) = \Omega(U_j)\Omega_T(U_0 - U_j) \quad (1)$$

which is constant with regard to all the possible variations  $U_j$  because the total energy is constant. The probability  $P_{ij}$  to find the system in the microstate  $i$  of the energy  $U_j$  will be proportional to

$$P_{ij} \propto \frac{1}{\Omega(U_j)} \quad (2)$$

at equilibrium; this probability is also proportional to

$$P_{ij} \propto \Omega_T(U_0 - U_j) \quad (3)$$

e.g., to the number of microstates accessible to the thermostat. The normalization requirement on probabilities leads to

$$P_{ij} = \frac{\Omega_T(U_0 - U_j)}{\sum_j \sum_i \Omega_T(U_0 - U_j)} \quad (4)$$

The thermostat that many more degrees of freedom than the system ( $N_j/N_T \ll 1$ ) as well as  $U_j \ll U_0$ , thus

$$\Omega_T(U_0 - U_j) = \Omega_T(U_0) - \left(\frac{\partial \ln \Omega_T}{\partial U}\right)_{U=U_0} U_j + \dots \quad (5)$$

The partial derivative of the first order is  $1/k_B T$  ( $k_B$  is the Boltzmann constant or  $R/N_{avg}$ ). We have

$$\begin{aligned} \ln \Omega_T(U_0 - U_j) &= \ln \Omega_T(U_0) - \frac{U_j}{k_B T} \\ \Omega_T(U_0 - U_j) &= \Omega_T(U_0) \exp\left(-\frac{U_j}{k_B T}\right) \end{aligned} \quad (6)$$

The probability  $P_{ij}$  of a particular microstate  $ij$  is

$$P_{ij} = \frac{1}{Z} \exp\left(-\frac{U_j}{k_B T}\right) \quad (7)$$

where  $Z$  is the quantity that normalizes the probabilities.  $Z$  is considered the most important quantity in statistical thermodynamics, because it can be used to derive so many quantities.

$$Z = \sum_j \sum_i \exp\left(-\frac{U_j}{k_B T}\right) \quad (8)$$

This function is called *partition function*. It is a function of  $T$ ,  $V$ , and  $N$ . *This function plays a very important role.*

In the *canonical ensemble*, there is a statistical weight associated at each microstate. This statistical weight is the exponential of the internal energy normalized by the thermal agitation  $k_B T$ . This last term is the energy term associated with the *Boltzmann constant*,  $k_B$ . We may note that at high temperature, all the microstates have the same probability of occurrence whatever the energy of these configurations. At low temperatures, the states with low energy are favored. *This result should be familiar: nature prefers that a system minimize its energy at low temperatures, and maximize its entropy at high temperatures.*

## Energy in the canonical ensemble

The partition function  $Z$  allows to calculate the average energy  $\langle U \rangle$  of the system—the average is given by

$$\langle U \rangle = \sum_j \sum_i P_{ij} U_j \quad (9)$$

Using the Boltzmann factor and by normalizing by  $Z$ , we have

$$\langle U \rangle = \frac{1}{Z} \sum_j \sum_i U_j \exp(-\beta U_j) \quad (10)$$

It is traditional to introduce a thermodynamic scale for energy:  $\beta \equiv E_{char}/E_i$  where  $E_{char}$  is the characteristic thermal energy  $k_B T$ . **The symbol  $\beta$  plays the role of an ‘inverse’ temperature in expressions like  $\exp(-\beta E) \equiv \exp(-E/k_B T)$**  This expression can be written as

$$\langle U \rangle = \frac{1}{Z} \sum_j \sum_i \frac{\partial}{\partial \beta} [\exp(-\beta U_j)] \quad (11)$$

By extracting the derivative operator of the sum, we obtain

$$\begin{aligned} \langle U \rangle &= -\frac{1}{Z} \frac{\partial Z}{\partial \beta} \\ \langle U \rangle &= k_B T^2 \left( \frac{\partial \ln Z}{\partial T} \right) \end{aligned} \quad (12)$$

We can also estimate the fluctuations of energy  $(\Delta U)^2 = \langle U^2 \rangle - \langle U \rangle^2$

$$\begin{aligned} \langle U^2 \rangle &= \frac{1}{Z} \sum_j \sum_i U_j^2 \exp(-\beta U_j) \\ \langle U^2 \rangle &= \frac{1}{Z} \frac{\partial^2 Z}{\partial \beta^2} = \frac{\partial^2 \ln Z}{\partial \beta^2} + \langle U \rangle^2 \end{aligned} \quad (13)$$

We finally obtain that:

$$(\Delta U)^2 = \langle U^2 \rangle - \langle U \rangle^2 = k_B T^2 \left( \frac{\partial \langle U \rangle}{\partial T} \right) = k_B T^2 C_v \quad (14)$$

We then can describe the system and their fluctuations around the equilibrium. Besides, the fluctuations of energy are linked to the heat capacity  $C_v$  of the system. For a perfect gas, we have  $\langle U \rangle = \frac{3}{2} N k_B T$  and the relative fluctuations of energy are

$$\frac{\Delta U}{\langle U \rangle} = \sqrt{\frac{2}{3N}} \quad (15)$$

These fluctuations are low because the number of particles are generally higher than  $10^{23}$ .

## Relation with other thermodynamic potentials

In the canonical ensemble, that are the variables  $T$ ,  $V$ , and  $N$  that are pertinent. The free energy  $F(T, V, N)$  is then the accurate thermodynamic potential to describe the system. The different microstates of the canonical ensemble are characterized by the same free energy. All the thermodynamics of the system will be obtained from the relation:

$$Z = \exp\left(-\frac{F}{k_B T}\right) \quad (16)$$

By the way, the relation

$$\langle U \rangle = F + TS = F - T\left(\frac{\partial F}{\partial T}\right)_{V,N} \quad (17)$$

is well defined when  $F = -k_B T \ln Z$ . We can also derive the entropy

$$S = -\left(\frac{\partial F}{\partial T}\right)_{N,V} = k_B \ln Z - \frac{k_B T}{Z} \left(\frac{\partial Z}{\partial T}\right)_{N,V} \quad (18)$$

## Grand Canonical Ensemble

In the grand canonical ensemble, we consider the microstates for which the system can exchange both heat and particles with the reservoir.

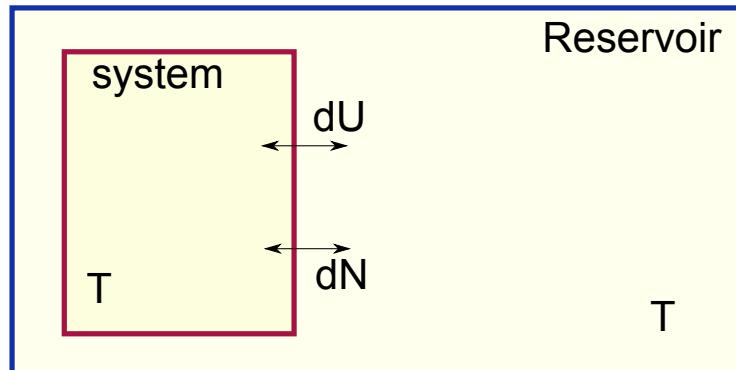


Figure 0-2: The system is in contact with the reservoir. Both heat and particles are exchanged between the system and the reservoir.

In this ensemble, we generalize the case of the canonical ensemble with a variable number of particles. The reservoir maintains a temperature  $T$  constant. The total energy  $U_0 = U_j + U_T$  and the total number of particles  $N_0 = N + N_T$  are also constant. The probability  $P_{ijN}$  to find the system in the microstate  $i$  of  $N$  particles and at the energy  $U_j$  will be proportional to

$$\Omega_T(U_0 - U_j, N_0 - N) \quad (19)$$

e.g., tot he number of microstate accessible to the thermostat. The condition of normalization of probabilities leads to

$$P_{ijN} = \frac{\Omega_T(U_0 - U_j, N_0 - N)}{\sum_N \sum_j \sum_i \Omega_T(U_0 - U_j, N_0 - N)} \quad (20)$$

We will use a thermostat that has a number of degree of freedom much higher than the system and we also have  $U_j \ll U_0$  as well as  $N_j \ll N_0$ . We can then perform a limited development around  $\Omega_T(U_0, N_0)$

$$\ln \Omega_T(U_0 - U_j, N_0 - N) = \ln \Omega_T(U_0, N_0) - \left(\frac{\partial \ln \Omega_T}{\partial U}\right)_{U=U_0} U_j - \left(\frac{\partial \ln \Omega_T}{\partial N}\right)_{N=U_0} N + \dots \quad (21)$$

We can evaluate up to first-order term and ignore other higher order terms. Both partial derivatives of the first order term corresponding to

$$\begin{aligned} \left(\frac{\partial \ln \Omega_T}{\partial U}\right)_{U=U_0} &= \frac{1}{k_B T} = \beta \\ \left(\frac{\partial \ln \Omega_T}{\partial N}\right)_{N=U_0} &= -\frac{\mu}{k_B T} = -\beta\mu \\ \ln \Omega_T(U_0 - U_j, N_0 - N) &= \ln \Omega_T(U_0, N_0) - \frac{U_j}{k_B T} + \frac{\mu N}{k_B T} \\ \Omega_T(U_0 - U_j, N_0 - N) &= \Omega_T(U_0, N_0) \exp(-\beta U_j + \beta\mu N) \end{aligned} \quad (22)$$

Then the probability  $P_{ijN}$  becomes

$$P_{ijN} = \frac{1}{Q} \exp(\beta\mu N - \beta U_j) \quad (23)$$

with the grand canonical partition function  $Q$  which represents the normalization of all the probabilities, we have

$$Q(T, V, \mu) = \sum_N \sum_j \sum_i \exp(\beta\mu N - \beta U_j) \quad (24)$$

It is a function of  $T$ ,  $V$ , and  $\mu$  which generalize  $Z$  whatever the number of particles via

$$Q(T, V, \mu) = \sum_N \exp(\beta\mu N) Z(T, V, N) \quad (25)$$

The thermodynamic potential corresponding to their variables is the grand potential  $\mathcal{J}(T, V, \mu)$  constructed from the Legendre transformation following

$$\mathcal{J} = F - \mu N \quad (26)$$

where the three equations of states are respectively

$$N = -\left(\frac{\partial \mathcal{J}}{\partial \mu}\right)_{T, V} \quad S = -\left(\frac{\partial \mathcal{J}}{\partial T}\right)_{V, \mu} \quad \mathcal{P} = -\left(\frac{\partial \mathcal{J}}{\partial V}\right)_{T, \mu} \quad (27)$$

The average number of particles  $\langle N \rangle$  that can be associated to the first equation of state is given by

$$\begin{aligned} \langle N \rangle &= \frac{1}{Q} \sum_{N=0}^{\infty} N \exp(\beta\mu N) Z(T, V, N) \\ \langle N \rangle &= k_B T \frac{\partial}{\partial \mu} \ln Q \end{aligned} \quad (28)$$

It is the number of particles at equilibrium. Hence, we associate the grand potential to  $\mathcal{J} = -k_B T \ln Q$ . We can also show that the average energy in the grand canonical ensemble is given by

$$\begin{aligned}\langle U \rangle &= \frac{1}{Q} \sum_N \sum_j \sum_i U_j \exp(\beta \mu N - \beta U_j) \\ \langle U \rangle &= -\frac{\partial}{\partial \beta} \ln Q\end{aligned}\tag{29}$$

The grand canonical partition function  $Q$  also allows to calculate the fluctuation of the number of particles around the thermodynamic equilibrium. For example, we can demonstrate that

$$(\Delta N)^2 = \langle N^2 \rangle - \langle N \rangle^2 = k_B T \frac{\partial}{\partial \mu} \langle N \rangle\tag{30}$$

## Summary

The table below summarize the domain of application and the properties of the three partition functions  $\Omega$ ,  $Z$ ,  $Q$ .

Ensemble	Variable	Exchanges	Partition Function	Potential
Microcanonical	$U, V, N$	-	$\Omega = \sum_i 1$	$S = k_B \ln \Omega$
Canonical	$T, V, N$	$U$	$Z = \sum_j \sum_i \exp(-\frac{U_j}{k_B T})$	$F = -k_B T \ln Z$
Grand canonical	$T, V, \mu$	$U, N$	$Q = \sum_N \exp(\frac{N\mu}{k_B T}) Z$	$\mathcal{J} = -k_B T \ln Q$

## Distribution

The calculation of a partition function allows to estimate the probability to observe a system at a given total energy. This calculation considers the Boltzmann factor of the total energy. In numerous cases, the different microscopic entities are the same and occupy different levels of energy. It could be useful to calculate the most probable number of entities occupying a chosen level of energy or to calculate the distribution of particles on different levels of energy. We can distinguish three different kinds of statistics, those which come or doesn't come from quantum effects:

1. Maxwell Boltzmann Distribution
2. Fermi-Dirac Distribution
3. Bose-Einstein Distribution

## Maxwell Boltzmann Distribution

The system is composed of  $N$  identical and distinguishable particles, which occupy  $K$  different levels of energy  $\epsilon_i$ . We can find  $n_i$  particles on the level of energy  $\epsilon_i$  for a total energy  $U$  and a

number of particle  $N$ , we have the following relations:

$$\begin{aligned} \sum_{i=1}^K n_i \epsilon_i &= U \\ \sum_{i=1}^K n_i &= N \end{aligned} \quad (31)$$

As these quantities are assumed to be constant, the system is entirely determined by the distribution  $\{n_i\}$  of particles on the  $K$  levels. The space phase is a space at  $K$  dimensions:

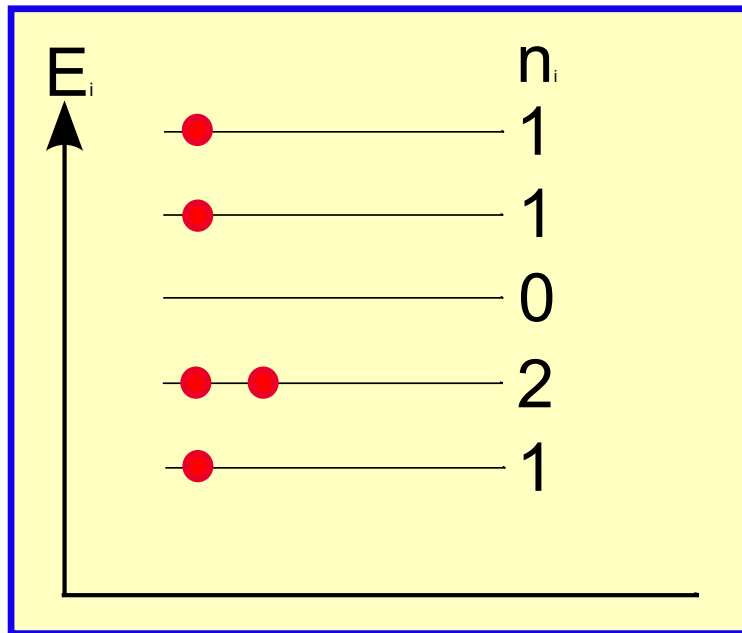


Figure 0-3: The different level of energy  $\epsilon_i$  is determined by the distribution of  $\{n_i\}$  of particles.

The system being completely isolated, we work in the microcanonical ensemble. As the particles are distinguishable, it resists a high number  $\Omega$  of possible microscopic configurations that are compatible with the distinguishable  $\{n_i\}$ :

$$\Omega\{n_i\} = \frac{N!}{n_1! n_2! \dots n_K!} \quad (32)$$

Nevertheless, we have neglected the possible degeneracy of levels. If there are  $g_i$  under-levels, where the energy equals to  $\epsilon_i$ , the previous relation can be rewritten as

$$\Omega\{n_i\} = N! \frac{g_1^{n_1} g_2^{n_2} \dots g_K^{n_K}}{n_1! n_2! \dots n_K!} \quad (33)$$

We want the most probable distinguishable  $\bar{n}_i$ , that is, the distribution which maximizes the volume  $\Omega\{n_i\}$  of the accessible area by the system in the space phase. To determine this

extremum  $\bar{n}_i$ , we will find the maximum of  $\ln \Omega\{n_i\}$ , e.g., the maximum of entropy. This distribution of  $\bar{n}_i$  corresponds to a thermodynamic equilibrium:

$$\ln \Omega\{n_i\} = \ln N! + n_1 \ln g_1 + n_2 \ln g_2 + \dots + n_K \ln g_K - \ln n_1! - \ln n_2! - \dots - \ln n_K! \quad (34)$$

Using the Stirling formula  $\ln n! \approx n \ln n - n$ , we have

$$\begin{aligned} \ln \Omega\{n_i\} &= N \ln N - N + n_1 \ln g_1 + n_2 \ln g_2 + \dots + n_K \ln g_K \\ &\quad - (n_1 \ln n_1 - n_1) - (n_2 \ln n_2 - n_2) - \dots - (n_K \ln n_K - n_K) \\ \ln \Omega\{n_i\} &= N \ln N - \sum_i n_i \ln \frac{n_i}{g_i} \end{aligned} \quad (35)$$

To determine the extremum of  $\ln \Omega$ , we will differentiate the expression taking into account that  $dN = 0$ . We have

$$\begin{aligned} d(\ln \Omega) &= - \sum_i (dn_i) \ln \frac{n_i}{g_i} - \sum_i n_i d(\ln \frac{n_i}{g_i}) \\ &= - \sum_i (dn_i) \ln \frac{n_i}{g_i} - \sum_i dn_i \\ &= - \sum_i (dn_i) \ln \frac{n_i}{g_i} \end{aligned} \quad (36)$$

This differentiated expression of  $\ln \Omega$  equals to 0 at its extremum:

$$- d(\ln \Omega) = \sum_i (dn_i) \ln \frac{n_i}{g_i} = 0 \quad (37)$$

There are two additional condition imposed to the system:

**The conservation of the number of particle  $N$ .**

**The conservation of the total energy  $U$ .**

Under the differential forms, we have:

$$\begin{aligned} \sum_i dn_i &= 0 \\ \sum_i \epsilon_i dn_i &= 0 \end{aligned} \quad (38)$$

To find the extrema for the specified fixed constraint, we use Lagrange multipliers. This is a method that permits us to find stationary points of differentiable functions of one or many variables. (Note the similarity between a Lagrange multiplier and a Legendre transformation.) The distribution is then given by:

$$\sum_i \left[ \ln \frac{n_i}{g_i} + \alpha + \beta \epsilon_i \right] dn_i = 0 \quad (39)$$

When the number of level  $K$  is high, we can consider that the fluctuations  $dn_i$  are independent. Hence, we have

$$\ln \frac{\bar{n}_i}{g_i} + \alpha + \beta \epsilon_i = 0 \quad \text{or} \quad \boxed{\bar{n}_i = g_i \exp(-\alpha - \beta \epsilon_i)} \quad (40)$$



which is the distribution of Maxwell-Boltzmann with the coefficients  $\alpha$  and  $\beta$  determined respectively from the conditions  $\sum_{i=1}^K n_i = N$  and  $\sum_{i=1}^K n_i \epsilon_i = U$  (eqn (31)).

The coefficient  $\beta$  is easier to understand than the coefficient  $\alpha$ . Using the first condition, we have

$$\begin{aligned} N &= \sum_i \bar{n}_i = \sum_i g_i \exp(-\alpha - \beta \epsilon_i) \\ N &= \exp(-\alpha) \left( \sum_i g_i \exp(-\beta \epsilon_i) \right) = \exp(-\alpha) Z_1 \end{aligned} \quad (41)$$

Using the second condition

$$\begin{aligned} U &= \sum_i \bar{n}_i \epsilon_i = \frac{N}{Z_1} \sum_i g_i \epsilon_i \exp(-\beta \epsilon_i) \\ U &= -N \frac{\partial \ln Z_1}{\partial \beta} \end{aligned} \quad (42)$$

We can note that if we associate  $\beta$  to the temperature via  $\beta = 1/(k_B T)$ . We define the canonical partition function  $Z_1$  of a single particle that can be placed on  $K$  degenerated level. The  $N - 1$  other particles play the role of the reservoir.

The coefficient  $\beta$  is the one we have defined previously. The coefficient  $\alpha$  is linked to the chemical potential  $\mu$  but its value is determined according to each different case. We finally obtain

$$\bar{n}_i = \frac{g_i}{\exp(\alpha) \exp\left(\frac{\epsilon_i}{k_B T}\right)} \quad (43)$$

The Boltzmann distribution is an important result and is the basis for understanding many microscopic phenomena. Its interpretation is perhaps useful to state in words: *When a system has different energy states available, the occupation of each state is given by an exponential distribution proportional to (minus) the energy of that state.* The energy is divided by a thermal energy (as it must to make the units work out), and therefore *The low energy states tend to have higher occupancy.* Because the proportionality goes like  $1/T$ , the differences in occupation probability decrease with increasing temperature. *Low energy states are densely occupied at low temperature; as the temperature increases the distribution becomes more uniform as the higher energy states become occupied.*

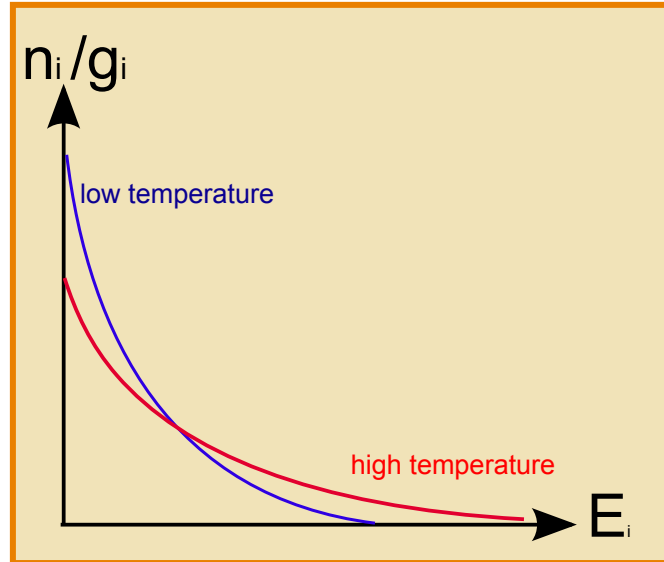


Figure 0-4: Maxwell-Boltzmann distribution under different temperatures.

## Fermi-Dirac Distribution

It describes quantum systems composed of fermions. This system is composed of  $N$  indistinguishable particles which can be located on  $K$  levels of energy  $\epsilon_i$ . Each level of energy  $\epsilon_i$  is degenerated  $g_i$  times. Two particles called fermions can't be in the same quantity state. It is the exclusion principle of Pauli. Hence the number of microstates is simply given by:

$$\Omega\{n_i\} = \prod_i C_{g_i}^{n_i} = \prod_i \frac{g_i!}{n_i!(g_i - n_i)!} \quad (44)$$

and the Fermi-Dirac Distribution is given by

$$\bar{n}_i = \frac{g_i}{\exp(\alpha + \beta\epsilon_i) + 1} \quad (45)$$

We can note that this distribution is the same as the one of Maxwell-Boltzmann for high energy.  $\beta$  plays the same role as the one in the distribution of Maxwell-Boltzmann and is linked to the temperature.

The parameter  $\alpha$  is linked to the Fermi level. At  $T = 0K$ , fermions occupy the levels of energy until the level  $\epsilon_F$ . When the temperature increases, the superior levels are occupied and the distribution spread over the fermi level.

The distribution of Fermi Dirac can then be rewritten as:

$$\bar{n}_i = \frac{g_i}{\exp\left(\frac{\epsilon_i - \epsilon_F}{k_B T}\right) + 1} \quad (46)$$

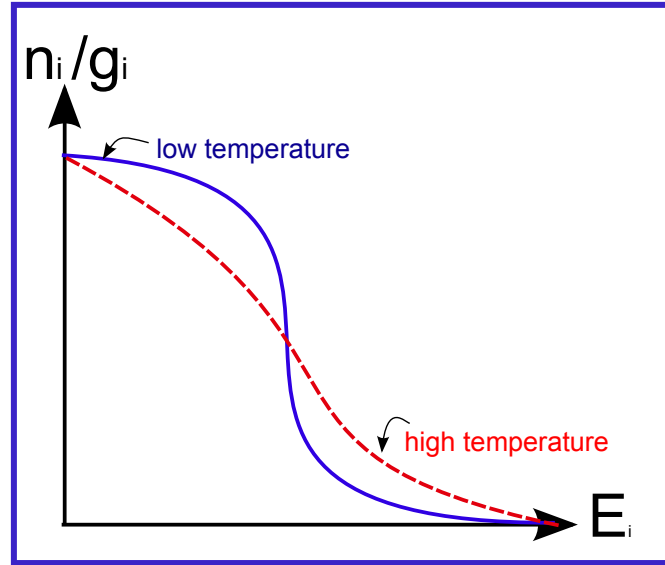


Figure 0-5: Fermi-Dirac distribution under different temperatures.

## Bose-Einstein Distribution

Bosons are another type of quantum particles that would be indistinguishable located on all the levels of energy. The Pauli principle is no longer applicable. We consider here a system composed of  $N$  particles identical and indistinguishable that are located on  $K$  level of energy  $\epsilon_i$ . Each level of energy is degenerated  $g_i \gg 1$  times.

Hence the total number of microstate is given by:

$$\Omega\{n_i\} = \prod_i C_{n_i+g_i-1}^{n_i} = \prod_i \frac{(n_i + g_i - 1)!}{n_i! (g_i - 1)!} \quad (47)$$

The Bose-Einstein distribution is given by

$$\bar{n}_i = \frac{g_i}{\exp(\alpha + \beta\epsilon_i) - 1} \quad (48)$$

This distribution is also the same as the Maxwell-Boltzmann distribution for high energies. Besides, it can diverge when  $\alpha + \beta\epsilon_i = 0$ . The coefficients  $\alpha$  and  $\beta$  can be determined by the conditions on  $U$  and  $N$ .

In the grand canonical ensemble, a non-degenerated level  $j$  of energy  $\epsilon_j$  can be occupied by an arbitrarily number of particles.

We find that:

$$\sum_{n=0}^{\infty} \exp\left(-n \frac{\epsilon_j - \mu}{k_B T}\right) = \frac{1}{1 - \exp\left(-\frac{\epsilon_j - \mu}{k_B T}\right)} \quad (49)$$

and the total partition function is given by

$$Q = \prod_i \left[1 - \exp\left(-\frac{\epsilon_j - \mu}{k_B T}\right)\right]^{-1} \quad (50)$$

where we have considered all the levels and under-levels. The average number of particles on the non-degenerated level  $j$  is given by:

$$\langle n_j \rangle = -k_B T \frac{\partial}{\partial \mu} \left\{ \ln \left[ 1 - \exp \left( -\frac{\epsilon_j - \mu}{k_B T} \right) \right] \right\} = \frac{1}{\exp \left( \frac{\epsilon_j - \mu}{k_B T} \right) - 1} \quad (51)$$

## Summarize

To summarize three conditions:

Statistics	Particles	Distributions
Maxwell-Boltzmann	Distinguishable	$\bar{n}_i = \frac{g_i}{\exp \left( \frac{\epsilon_i - \mu}{k_B T} \right)}$
Fermi-Dirac	Fermions	$\bar{n}_i = \frac{g_i}{\exp \left( \frac{\epsilon_i - \epsilon_F}{k_B T} \right) + 1}$
Bose-Einstein	Bosons	$\bar{n}_i = \frac{g_i}{\exp \left( \frac{\epsilon_i - \mu}{k_B T} \right) - 1}$