# **Classical Statistics of Maxwell-Boltzmann**

In this section, we review the basic assumptions on which Maxwell-Boltzmann built his statistical distribution. The statistical distribution is nothing but an equation by which the number of  $n_i$  particles occupying each of the  $\epsilon_i$  energy levels in the system is defined, with some limitations. We will find from this distribution all thermodynamic state functions.

The importance of the traditional Maxwell-Boltzmann statistics appears in many important theoretical applications such as calculating the physical properties of an ideal gas. The traditional statistic is only an approximation of advanced statistics such as the Bose-Einstein statistic or the Fermi-Dirac statistic at high temperatures.

#### 1. Hypotheses of classical Maxwell-Boltzmann statistics

We will assume a system with a large number of particles:

- 1. Identical
- 2. Distinguishable
- 3. To which the Pauli Exclusion Principle does not apply.

Identical particles mean that the particles are identical in composition and components (mass, charge...)

Distinctive particles mean that we can distinguish (or know the difference) between one particle and another even though

they match. An example is the coin model where we marked the coins by date or color.

We will assume here that the traditional system (as shown in the figure):



1. It consists of energy levels (E $_1$  , E $_2$  , E $_3$  ,.....) so that (E $_1 <$  E $_2 <$  E $_3$  ..... )

2. These levels are saturated with a number of particles  $(n_1, n_2, n_3, \ldots)$ 

#### Subject to the following two conditions:

1. The total number of N particles in the system is a fixed number, and it can be written mathematically as:

$$N = \sum_{i} n_i , \qquad (1)$$

2. The total internal energy U of the particles in the system is a constant quantity, and it is defined mathematically as:

$$U = \sum_{i} n_i \varepsilon_i \tag{2}$$

The number of ways needed to distribute N number of characteristic particles over j number of levels so that  $n_1$  is placed in the first level and  $n_2$  in the second level and so is:

$$\widetilde{\omega} = \omega \{n_i\} = \frac{N!}{\prod_{i=1}^{j} n_i!}$$
(3)

When a system consisting of an infinite number of particles and levels reaches the state of equilibrium, i.e. the highest possible distribution that contains a set of numbers  $n_i$ , the thermodynamic probability value  $\omega$  reaches a maximum value. Therefore, any change, even a slight, in the set of numbers {  $n_i$  } will not affects the value of  $\omega$ .

This means that the relationship:

$$\delta \widetilde{\omega} = 0$$

Realized under change:

$$\tilde{n}_i \rightarrow \tilde{n}_i + \delta n_i$$

Subject to the following two conditions:

$$\delta N = \sum_{i} \delta n_{i} = 0 \tag{4}$$

$$\delta U = \sum_{i} \varepsilon_{i} \delta n_{i} = 0 \tag{(\circ)}$$

The equivalent condition can be used:

$$\delta \ln \widetilde{\omega} = 0$$

Instead of using:

$$\delta \widetilde{\omega} = 0$$

This is because the logarithmic function is a monotonic function and is easy to work with.

And since the value of  $\omega$  reaches astronomical numbers, but the value of  $(\ln \omega)$  is considered finite and can be dealt with mathematically.

# Example 1:

From equation (3), using the Stirling approximation

$$\ln(z !) = z \ln(z) - z$$

Prove that:

$$\ln(\tilde{\omega}) = N \ln N - \sum_{i} n_{i} \ln n_{i}$$
(7)

And it was proved that:

$$\delta \ln(\tilde{\omega}) = -\sum_{i} \ln n_i \,\,\delta n_i \tag{8}$$

Using the logarithm of equation (3), we find that:

$$\begin{aligned} \ln(\widetilde{\omega}) &= \ln(\frac{N!}{\prod_{i=1}^{n} n_i!}) = \ln(N!) \left| -\ln(\prod_{i=1}^{n} n_i!) \right| \\ &= \ln(N!) - \ln[n_1! \times n_2! \dots \times n_n!] \\ &= \ln(N!) - [\ln(n_1!) + \ln(n_2!) + \dots] \\ &= \ln(N!) - \sum_i \ln(n_i!) \end{aligned}$$

Using Stirling's approximation to the previous equation, we find that:

$$\ln(\widetilde{\omega}) = N \ln N - N - \sum_{i} (n_{i} \ln n_{i} - n_{i})$$
$$= N \ln N - N - \sum_{i} n_{i} \ln n_{i} - \sum_{i} n_{i}$$
$$= N \ln N - \sum_{i} n_{i} \ln n_{i}$$
(7a)

It needs to be proven first.

Differentiating equation (7a) with respect to  $n_i$ , we find that:

$$\begin{split} \delta \ln(\widetilde{\omega}) &= \delta(N \ln N) - \sum_{i} \ln n_{i} \delta n_{i} - \sum_{i} n_{i} \underbrace{\delta(\ln n_{i})}_{\frac{1}{n_{i}} \delta n_{i}} \\ &= 0 - \sum_{i} \ln n_{i} \delta n_{i} - \underbrace{\sum_{i} \delta n_{i}}_{=0} \\ &= -\sum_{i} \ln n_{i} \delta n_{i} \end{split} \tag{8a}$$

This needs to be proven again.

Equation (8a) gives the change in the value of ln ( $\omega$ ) with the change in the number of particles  $\delta(n_i)$  for each level.

\*\* To calculate the statistical distribution with conditions 1 and 2 and the thermodynamic probability (Equation 3), we take the following two cases:

#### (وحيدة الانتماء) المستويات المنفردة I. Non-Degenerate levels

Due to the constraints applied to the system, the change of  $n_i$  will not become independent. Therefore, we will use Lagrange's method, by multiplying equation (1) by the coefficient ( $\alpha$ -) and equation (2) by the coefficient ( $\beta$ ) and adding them to equation (8), we find that:

$$\delta \left[ \ln(\widetilde{\omega}) + \alpha \sum_{i} n_{i} - \beta \sum_{i} \varepsilon_{i} n_{i} \right] = 0$$
(11)

 $\alpha$  and  $\beta$  are called "Lagrangian" coefficients, and they are related to the physical properties of the system.

And from the differential equation 11:

$$\sum_{i} \left[ -\ln n_{i} + \alpha - \beta \varepsilon_{i} \right] \delta n_{i} = 0$$

It represents an infinite number of equations.

Since the change  $\delta(ni)$  is optional and independent, so by equating the coefficients of  $\delta(ni)$  to zero, we arrive at the most famous relationship for the statistical distribution, which is:

$$n_i = e^{\alpha - \beta \varepsilon_i} \tag{12}$$

Classical Maxwell-Boltzmann Statistical Distribution وتسمي المعادلة ( ١٢ ) بالتوزيع الإحصائي التقليدي لماكسويل -بولتزمان And the quantity:

$$e^{-\beta \varepsilon_i}$$

It's called the Boltzmann coefficient, and it's a function that depends on temperature and volume.

# المستويات متعددة الانتماع 2. Degenerate States

If we assume that each energy level i is degenerate states, such that it consists of  $g_i$  number of energy levels, then each  $n_i$  particle can be stabilized in any level in a number of ways:

 $\cdot g_i^{n_i}$ 

For all energy levels, we find that the number of methods takes the final form:

$$\prod_{i=1}^{j} g_i^{n_i}$$

From it we find that the number of microscopic levels of the characteristic (distinguishes) particles is known by the equation:

$$\widetilde{\omega}\{n_i\} = N ! \prod_{i=1}^{J} \frac{g_i^{n_i}}{n_i!}$$
(13)

And if the particles are undistinguished, then we must divide by the value N to get:

$$\widetilde{\omega}\{n_i\} = \frac{N!}{N!} \prod_{i=1}^{j} \frac{g_i^{n_i}}{n_i!} = \prod_{i=1}^{j} \frac{g_i^{n_i}}{n_i!}$$
(13a)

#### Homework 1:

1. From equation 13 prove that:

$$\ln(\widetilde{\omega}) = \sum_{i} n_{i} \left( \ln \frac{g_{i}}{n_{i}} + 1 \right)$$

2. And it was proved that:

$$\delta \ln(\tilde{\omega}) = \sum_{i} \ln \frac{g_i}{n_i} \,\delta n_i \tag{14}$$

Using equations (1), (2) and (14) and Lacrangene coefficients  $\alpha$  and  $\beta$ , prove that the classical Maxwell-Boltzmann statistical distribution takes the form: a . •

$$n_i = g_i e^{\alpha - \beta \varepsilon_i} \tag{15}$$

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The applications of Maxwell-Boltzmann statistics, through equations (12) and (15), are many and varied.

One of the most important special applications of this distribution is the study of the process of light amplification by studying the interaction of materials with an external field of energy, such as electromagnetic radiation (Interaction of radiation with matter), the effect of which appears through photons on the electrons of materials.

# There are some important relationships:

# **1.** Calculate the coefficient ${}^{\alpha}\mathbf{e}$

And it is calculated using the prerequisite:

$$N = \sum_{i} n_{i} = \sum_{i} g_{i} e^{-\alpha - \beta \varepsilon_{i}} = e^{-\alpha} \sum_{i} g_{i} e^{-\beta \varepsilon_{i}}$$

From it we find that:

The new  $Z_{sp}$  function of a single particle, which is known as the Partition function, was originally derived from the German term "Zustandsumme" which means the summation of states (levels). So we'll use the German translation and call it a "level partition function", or for short a partition function.

# Using the partition function takes the Maxwell-Boltzmann distribution, equation (15)

$$n_i = N \, \frac{e^{-\beta \, \varepsilon_i}}{Z_{\rm sp}}; \tag{16}$$

or the general form:

$$n_i = Ng_i \frac{e^{-\beta s_i}}{Z_{\rm sp}}$$
(17)

$$\frac{\partial Z_{sp}}{\partial \beta} = \frac{\partial}{\partial \beta} \sum_{i} g_{i} e^{-\beta \varepsilon_{i}} = -\sum_{i} \varepsilon_{i} g_{i} e^{-\beta \varepsilon_{i}}$$

$$\Rightarrow \qquad \frac{\partial Z_{sp}}{\partial \beta} = -\sum_{i} \varepsilon_{i} g_{i} e^{-\beta \varepsilon_{i}} \qquad (18)$$

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$$\left(\frac{\partial Z_{sp}}{\partial V}\right)_{T,N} = \left(\frac{\partial}{\partial V}\sum_{i}g_{i}e^{-\beta\varepsilon_{i}}\right)_{T,N} = -\sum_{i}\beta g_{i}e^{-\beta\varepsilon_{i}}\left(\frac{\partial\varepsilon_{i}}{\partial V}\right)_{T,N}$$

$$\Rightarrow \left[\left(\frac{\partial Z_{sp}}{\partial V}\right)_{T,N} = -\beta\sum_{i}g_{i}e^{-\beta\varepsilon_{i}}\left(\frac{\partial\varepsilon_{i}}{\partial V}\right)_{T,N}\right]$$

$$(19)$$

# 4. Average Energy Calculation:

Calculate the mean energy from the relationship:

$$\overline{E} = \frac{1}{N} \sum_{i} n_{i} \varepsilon_{i} = \frac{1}{Z_{sp}} \sum_{i} \varepsilon_{i} g_{i} e^{-\beta \varepsilon_{i}} /$$

$$= -\frac{1}{Z_{sp}} \frac{\partial}{\partial \beta} \sum_{i} g_{i} e^{-\beta \varepsilon_{i}} = -\frac{1}{Z_{sp}} \frac{\partial Z_{sp}}{\partial \beta}$$

$$\Rightarrow \overline{E} = -\frac{\partial}{\partial \beta} [\ln(Z_{sp})] \qquad (20)$$

And the total internal energy becomes:

$$U = -N \frac{\partial}{\partial \beta} [\ln(Z_{sp})]$$
(21)

# Homework 2:

1. Prove that:

$$\overline{E^2} = \frac{1}{Z_{sp}} \frac{\partial^2 Z_{sp}}{\partial \beta^2}$$

2. Prove that the standard deviation is given by:

$$\sigma = \sqrt{\overline{E^2} - \left(\overline{E}\right)^2} = \sqrt{\frac{\partial^2}{\partial \beta^2} \ln Z_{sp}}$$

# **5.** Calculation of the average pressure:

The mean pressure is calculated in thermodynamics by:

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

$$= \frac{1}{Z_{sp}} \sum_{i} g_{i} e^{-\beta \varepsilon_{i}} \left(-\frac{\partial \varepsilon_{i}}{\partial V}\right)_{T,N}$$

$$= \frac{1}{\beta Z_{sp}} \left(\frac{\partial Z_{sp}}{\partial V}\right) = \frac{1}{\beta} \left(\frac{\partial \ln(Z_{sp})}{\partial V}\right)_{T,N}$$

$$\Rightarrow \overline{P} = \frac{1}{\beta} \left(\frac{\partial \ln(Z_{sp})}{\partial V}\right)_{T,N}$$
(22)

# 6. S entropy calculation

From equation (16) and using the Sterling approximation, we find that:

$$\ln(n_i) = \ln N - \ln Z_{\rm sp} - \beta \,\varepsilon_i$$

From equation (7), the entropy is calculated as follows:

$$S = k_B \ln(\widetilde{\omega}) = k_B \left( N \ln N - \sum_i n_i \ln n_i \right)$$

From there we get:

$$S = k_{B} \left( N \ln N - \sum_{i} n_{i} \lim_{\ln N \to \ln Z_{sp} \to \delta_{\varepsilon_{i}}} \right)$$
$$= k_{B} \left( N \ln N - \ln N \sum_{i} n_{i} + \ln Z_{sp} \sum_{i} n_{i} + \beta \sum_{i} n_{i} \varepsilon_{i}}{N} \right)$$
$$\Rightarrow S = k_{B} N \ln Z_{sp} + k_{B} \beta U$$
(23)

Where we used relations:

$$\sum_{i} n_{i} = N$$
, and  $\sum_{i} n_{i} \varepsilon_{i} = U^{\land}$ 

# 7. Calculation of the coefficient β

The coefficient  $\beta$  is calculated as: Using the law of thermodynamics:

$$TdS = dU + PdV$$

We find that:

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

From the entropy differential in equation (23) we get:

$$\left(\frac{\partial S}{\partial U}\right)_{V} = k_{B}N \underbrace{\frac{d \ln Z_{sp}}{d \beta}}_{-\frac{U}{N} \text{ from (21)}} \left(\frac{\partial \beta}{\partial U}\right)_{V} + k_{B}\beta + k_{B}U\left(\frac{\partial \beta}{\partial U}\right)_{V}$$

$$= k_{B}\beta$$
(b)

By equating equations a and b, we get:

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

$$\Rightarrow \qquad \beta = \frac{1}{k_B T} \qquad (23)$$

# Homework 3:

The system consists of three energy levels as follows:

$$E_3 = 200 \ k_B$$
 g  $E_2 = 100 \ k_B$  g  $E_1 = 0$ 

And their degenerates are:

 $g_3 = 5$  g  $g_2 = 3$  g  $g_1 = 1$ 

Calculate the relative population between levels at temperature

T= 100 K.

### <u>Note :</u>

From equation (15), we find that the relative population between levels is given by the relationship:

$$\frac{n_j}{n_i} = \frac{g_j e^{\alpha - \beta \varepsilon_j}}{g_i e^{\alpha - \beta \varepsilon_i}} = \frac{g_j e^{-\beta \varepsilon_j}}{g_i e^{-\beta \varepsilon_i}}$$

And from there we find that:

$$\frac{n_2}{n_1} = \frac{3e^{-100\,k_B/100k_B}}{1e^{-0}} = 3e^{-1}$$
$$\frac{n_3}{n_1} = \frac{5e^{-200\,k_B/100k_B}}{1e^{-0}} = 5e^{-2}$$
$$\frac{n_3}{n_2} = \frac{5e^{-200\,k_B/100k_B}}{3e^{-100\,k_B/100k_B}} \approx 1.7e^{-1}$$

# <u>Partition Function for Non-Degenerate States</u> دالة التجميع للمستويات المنفردة

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It is the most important function in statistical physics, which is the  $Z_{sp}$  levels partition function, which is considered the cornerstone in the calculations of thermodynamic properties and functions.

# The $Z_{sp}$ function is a partition of the Boltzmann coefficient $e^{-\beta \varepsilon}$ and has the following properties :

1. The partition of all the distinct microscopic levels of the system as a whole, i.e.

$$Z_{\rm sp} = \sum_{i} e^{-\beta \varepsilon_i} \tag{1}$$

2. Or it is a summation of all energy levels characteristic of the system as a whole, meaning that:

$$Z_{\rm sp} = \sum_{i} g_{i} e^{-\beta \varepsilon_{i}}$$
(2)

3. It depends on the properties of the system and its statistical microstructure.

4. Depends on the absolute temperature of the system by the coefficient  $\beta$ 

5. It is proportional to the volume of the gas through the density of the levels  $g(\mathcal{E})$  or  $g_i$ .

6. Its numerical value changes from value 1 to astronomical values.

# Example 1:

Consider a simple two-particle system. If the system exists in only two energy levels:

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$$g_1=g_2=1$$
 مع الشرط  $\mathcal{E}_1=0$ 

- 1. Calculate Z<sub>sp</sub>
- 2. Calculate  $Z_2$  if the two particles are distinct (Boltzmann particles).
- 3. Calculate  $Z_2$  if the two particles are indistinguishable.

1. For a single particle, we find that the number of microscopic states is two, as follows:



So we find that the partition function is:

$$Z_{\rm sp} = \sum_{i=1}^{2} e^{-\beta \varepsilon_i} = e^{-\beta \varepsilon_1} + e^{-\beta \varepsilon_2}$$
$$= e^0 + e^{-\beta \varepsilon} = 1 + e^{-\beta \varepsilon}$$

2. In the event that the two particles are distinct, we find that the number of microscopic states is four levels:



The partition function is calculated by the equation:

$$\begin{split} \boldsymbol{Z}_2 &= \sum_{i=1}^4 e^{-\beta \, \boldsymbol{\varepsilon}_i} = e^{-\beta \, \boldsymbol{\varepsilon}_1} + e^{-\beta \, \boldsymbol{\varepsilon}_2} + e^{-\beta \, \boldsymbol{\varepsilon}_3} + e^{-\beta \, \boldsymbol{\varepsilon}_4} \\ &= e^{-\beta(0+0)} + e^{-\beta(0+\varepsilon)} + e^{-\beta(\varepsilon+0)} + e^{\beta(-\varepsilon-\varepsilon)} \\ &= 1 + 2e^{-\beta \varepsilon} + e^{-2\beta \varepsilon} = (1 + e^{-\beta \varepsilon})^2 \\ &= \left(\boldsymbol{Z}_{\rm sp}\right)^2 \end{split}$$

3. In the case that the two particles are indistinguishable, we find that there are only three microscopic levels.



The partition function is calculated by the equation:

$$Z_{2}^{\vee} = \sum_{i=1}^{4} e^{-\beta \varepsilon_{i}} = e^{-\beta \varepsilon_{1}} + e^{-\beta \varepsilon_{2}} + e^{-\beta \varepsilon_{3}} + e^{-\beta \varepsilon_{4}}$$
$$= e^{-\beta(0+0)} + e^{-\beta(0+\varepsilon)} + e^{\beta(-\varepsilon-\varepsilon)}$$
$$= 1 + e^{-\beta\varepsilon} + e^{-2\beta\varepsilon}$$
$$\neq \left(Z_{sp}\right)^{2}$$

Note:

That in the general case of characteristic and identical classical particles, the partition function of each single particle is equal. Thus, the relationship between the total partition function  $Z_N$  and the partition function for single particle  $Z_{sp}$  is given by:

$$Z_N = \left(Z_{\rm sp}\right)^N \tag{3}$$

This does not apply to undistinguishable particles. و هذا لا ينطبق على الجسيمات الغير المميزة. We also note that the numerical values of the partition function in the case of distinguishable particles are more than the numerical values of the partition function in the case of undistinguished particles.

In general, for uncharacterized particles (undistinguishable particles), we find that the partition function is calculated from the following equation:

$$Z_N = \frac{Z_{\rm sp}^N}{N!} \tag{4}$$

ويصبح توزيع ماكسويل - بولتزمان بالشكل:

$$n_i = Ng_i \frac{e^{-\beta \varepsilon_i}}{Z_{\rm sp}} \tag{5}$$

# **The Maxwell-Boltzmann distribution function in the form:**

$$f(\varepsilon_i) = \frac{n_i}{g_i} = N \frac{e^{-\beta \varepsilon_i}}{Z_{sp}}$$
(6)

It specifies the average number of particles for each quantum level. We can also know the ratio:

$$P_i = \frac{n_i}{N} = g_i \frac{e^{-\beta \varepsilon_i}}{Z_{sp}}, \text{ with } N \to \infty$$
(7)

It is the random probability of having a particle in plane i with the two conditions:

$$\sum_{i} P_i = 1$$
 and  $\sum_{i} \varepsilon_i P_i = \overline{E}$ 

And the mean value of any physical quantity takes the form:

$$\overline{f} = \frac{1}{N} \sum_{i} n_{i} f(\varepsilon_{i}) = \frac{1}{Z_{sp}} \sum_{i} g_{i} f(\varepsilon_{i}) e^{-\beta \varepsilon_{i}}$$
(8)

# Homework 4:

Using the definition:

$$P_i = \frac{n_i}{N}$$

Were  $N \rightarrow \infty$ , prove that

$$s = \frac{S}{N} = -k_B \sum_i P_i \ln P_i \tag{9}$$

# Example 2:

The system consists of three energy levels as follows:

$$E_3 = 200 k_B$$
 و  $E_2 = 100 k_B$  و  $E_1 = 0$ 

And their degenerates are:

$$g_3 = 5$$
  $g_2 = 3$   $g_1 = 1$ 

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Calculate:

1. Partition function Z<sub>sp</sub>

2. Relative population for each level and average energy at temperature T=100 K.

The partition function is calculated from the equation:

$$Z_{sp} = \sum_{i} g_{i} e^{-\beta \varepsilon_{i}}$$
  
= 1 + 3e^{-100 k\_{B}/100k\_{B}} + 5e^{-200 k\_{B}/100k\_{B}}  
= 1 + 3e^{-1} + 5e^{-2} = 2.78

The relative housing for each level is given by the relationship:

$$P_i = \frac{n_i}{N} = g_i \frac{e^{-\beta \varepsilon_i}}{Z}$$

Thus, the probability of the presence of the particle at each level is given by the values:

$$P_o = \frac{1}{Z} = 0.360, \quad P_1 = \frac{3e^{-1}}{Z} = 0.397, \quad P_2 = \frac{5e^{-2}}{Z} = 0.243$$

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i	g <sub>i</sub>	$\varepsilon_i$	$g_i e^{-\beta \varepsilon_i}$	$P_i = g_i \frac{e^{-\beta \varepsilon_i}}{Z_{\text{sp}}}$	$\varepsilon_i P_i$
0	1	0	1	0.360	•
1	3	100 k <sub>B</sub>	$3e^{-1}$	0.397	39.7 k <sub>B</sub>
2	5	200 k <sub>B</sub>	5e <sup>-2</sup>	0.243	48.6 k <sub>B</sub>
			$Z_{sp} = 2.78$	Total = 1	$\overline{E} = 88.3 k_B$

والطاقة المتوسطة:

$$\overline{E} = \sum_{i} \varepsilon_{i} P_{i} = \left( 0 \times P_{0} + 100 \times P_{1} + 200 \times P_{2} \right) k_{B} = 88.3 k_{B}$$

# **Partition Function for Degenerate States:**

When the levels are close to each other (connected), we can dispense with the partition function:

$$Z_{\rm sp} = \sum_i g_i e^{-\beta \varepsilon_i}$$

$$Z_{\rm sp} = \int g(\varepsilon) e^{-\beta \varepsilon} d\varepsilon \tag{1}$$

Where  $g(\epsilon)$  density levels

The general form of the partition function becomes:

$$Z_{\rm sp} = \frac{1}{h^3} \int g(\varepsilon) e^{-\beta \varepsilon} d\varepsilon d\mathbf{r}$$
(2)

N is the number of particles in the system,  $\epsilon$  is the total energy of the particle, and r is the space coordinates of the particle.

For connected levels, the Maxwell-Boltzmann distribution function takes the form:

$$f(\varepsilon) = \frac{N(\varepsilon)}{g(\varepsilon)} = N \frac{e^{-\beta \varepsilon_i}}{\int g(\varepsilon) e^{-\beta \varepsilon_i} d\varepsilon}$$
(3)

#### Example 3:

Use equation (2) to calculate the partition function for monatomic gases (ideal gas).

\*\*An ideal gas has only transition kinetic energy (we neglect the interaction energy between atoms).

Since the gas occupies a large space and the energy levels converge in it, it can be considered that the  $g_i$  levels density function is a continuous function. So we can replace it with the quantity :

# And to calculate the partition function for a single particle $Z_{sp}$ :

From equation (2) where the density of levels is known by the equation:

$$g(\varepsilon) = \frac{V}{2\pi^2} \left(\frac{m}{\hbar^2}\right)^{3/2} \sqrt{\varepsilon}$$

$$Z_{sp} = \int_{0}^{\infty} g(\varepsilon)e^{-\beta\varepsilon}d\varepsilon = \frac{V}{2\pi^{2}} \left(\frac{m}{\hbar^{2}}\right)^{3/2} \int_{0}^{\infty} \sqrt{\varepsilon}e^{-\varepsilon/k_{B}T}d\varepsilon$$
$$= \frac{V}{2\pi^{2}} \left(\frac{m}{\hbar^{2}}\right)^{3/2} \left(k_{B}T\right)^{3/2} \int_{0}^{\infty} \sqrt{y}e^{-y}dy = \frac{V}{2\pi^{2}} \left(\frac{m}{\hbar^{2}}\right)^{3/2} \left(k_{B}T\right)^{3/2} \frac{\sqrt{\pi}}{2}$$
$$= V \left(\frac{2\pi m k_{B}T}{\hbar^{2}}\right)^{3/2} = V \left(\frac{2\pi m}{\beta h^{2}}\right)^{3/2}$$

For the N number of characteristic Maxwell particles, we find that the total partition function is:

$$Z_N = \left(Z_{\rm sp}\right)^N = V^N \left(\frac{2\pi \ m}{\beta h^2}\right)^{3N/2}$$
(4)

We often use the logarithm of the partition function and it takes the form:

$$\ln\left(Z_{\rm sp}\right)^N = N \,\ln V + N \,\ln\left(\frac{2\pi \,m}{\beta h^2}\right)^{3/2} \quad , \qquad \beta = 1/k_B \,\mathrm{T} \tag{4a}$$

$$= N \ln V + \frac{3}{2} N \ln \left( \frac{2\pi \ m \ k_{B}}{h^{2}} \right) + \frac{3}{2} N \ln \left( T \right)$$
(4b)

# <u>Some of the applications of the Partition Function of an ideal gas are:</u> بعض تطبيقات دالة التجميع للغاز المثالي هي:

The properties of an ideal gas are defined by physical quantities such as pressure and internal energy and specific heat. These quantities have been calculated by thermodynamics and kinetic theory.

Here we will use the partition function, equation (4), to calculate these quantities.

# **<u>1. Pressure calculation</u>**

Calculate the ideal gas pressure

Starting from equation (4), we find that the free energy of Helmholtz gives:

$$F = -k_{B}T \ln \left(Z_{sp}\right)^{N} = -Nk_{B}T \ln \left(Z_{sp}\right)$$

The pressure is calculated from the relationship:

$$p = -\left(\frac{\partial F}{\partial V}\right)_{T,\beta} = Nk_{B}T \left(\frac{\partial \ln Z_{sp}}{\partial V}\right)_{T,N} = Nk_{B}T \frac{\partial \left\{(4.a)\right\}}{\partial V}$$
$$= Nk_{B}T \frac{1}{V}$$
$$\Rightarrow \quad pV = Nk_{B}T, \qquad (5)$$
$$e = 0$$

# **<u>2. Calculation of internal energy</u>**

The internal energy of an ideal gas is calculated from the relationship:

$$U = -\frac{\partial}{\partial\beta} \ln Z_{N} = -\frac{\partial}{\partial\beta} \{(13.b)\}$$
$$= -\left(\frac{3}{2}\beta\left(-\frac{1}{\beta^{2}}\right)\right) = \frac{3}{2}\frac{N}{\beta} = \frac{3}{2}Nk_{B}T$$
$$\implies U = \frac{3}{2}Nk_{B}T$$
(6)

From here, we find that the average kinetic energy of a particle is:

$$\overline{\varepsilon} = \frac{U}{N} = \frac{3}{2}k_B T \tag{7}$$

This corresponds to the law of equal distribution of energy over degrees of freedom

# 3. Calculation of specific heat:

The specific heat of an ideal gas is calculated from the relationship:

$$C_{V} = \left(\frac{\partial U}{\partial T}\right)_{V,N} = \frac{3}{2}Nk_{B}$$
(8)

And from them we find that it is a fixed quantity and does not depend on temperature.

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**<u>4. Entropy calculation</u>** The entropy is calculated as:

$$S = -\left(\frac{\partial F}{\partial T}\right)_{V,N} = Nk_{B}\left[\ln V + \frac{3}{2}\ln T + S_{0}\right], \qquad (9)$$
$$S_{0} = \frac{3}{2}\left[\ln\left(\frac{2\pi mk}{h^{2}}\right) + 1\right]$$
$$N = N = V = 1 \quad \text{N} \quad V = 1 \quad \text{N}$$