Chapter 13 Section 1,2,3
Maxwell-Boltzmann distribution

- It is our goal to determine the equilibrium configuration (the Maxwell-Boltzmann (MB) distribution) for an ensemble of N identical systems (which may be labelled as 1, 2, … ,N), sharing a total energy E; let ε_n ($n=1,2,\dots$) denote the energy eigenvalues of the systems. If N_n denotes the number of systems which, at any time t, have the energy value ε_n , then the set of numbers $\{N_n\}$ must satisfy the Two restrictive conditions

$$N = \sum_i N_i = \text{ constant}, \qquad \text{(Conservation of particles)} \qquad \text{(i)}$$

$$U = \sum_i N_i \varepsilon_i = \text{ constant} \qquad \text{(Conservation of energy)} \qquad \text{(ii)}$$

where N_i is the number of particles on the energy level i with the energy ε_i.

The MB distribution function makes three assumptions:

[1] The particles in the system are distinguishable (identifiable) and non-interacting.
[2] The number of systems is constant $\rightarrow N$.
[3] The total energy is constant $\rightarrow E$.

Energy levels	ε_1	ε_2	$\cdots$	ε_n	
# of systems	N_1	N_2	$\cdots$	N_n	$N = \sum_i N_i$
energy	$N_1\varepsilon_1$	$N_2\varepsilon_2$	$\cdots$	$N_n\varepsilon_n$	$U = \sum_i N_i \varepsilon_i$
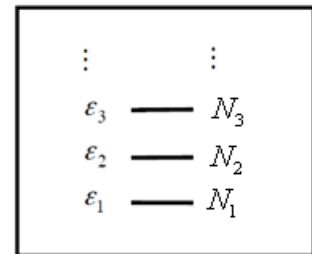
$(\varepsilon_1 < \varepsilon_2 < \varepsilon_3, \cdots)$

where $U\left(= E/N\right)$ denotes the average energy per system in the ensemble. Any set $\{N_n\}$ that satisfies the restrictive conditions (i, ii) represents a possible mode of distribution of the total energy E among the N members of the ensemble. Furthermore, any such mode can be realized in a number of ways, for we may effect a reshuffle among those members of the ensemble for which the energy values are different and thereby obtain a state of the ensemble that is distinct from the original one. Denoting the number of different ways of doing so by the symbol Ω, we have

$$\Omega\{N_n\} = \frac{N!}{\prod_{i=1}^{r} N_i!} \qquad \text{(iii)}$$

In view of the fact that all possible states of the ensemble, which are compatible with conditions (i, ii), are *equally likely* to occur, the frequency with which the distribution set f*nr*g may appear will be directly proportional to the number $\Omega\{N_n\}$. Accordingly, the "most probable" mode of distribution will be the one for which the number Ω is a maximum. We denote the corresponding distribution set by $\{N_i^*\}$; clearly, the set $\{N_i^*\}$ must also satisfy conditions (i, ii). As will be seen in the sequel, the probability of appearance of other modes of distribution, however little they may differ from the most probable mode, is extremely low! Therefore, for all practical purposes, the *most probable distribution set* $\{N_i^*\}$ is the only one we have to contend with.

Example: Use $w = \dfrac{N!}{\prod\limits_{i=1}^{r} N_i!}$ where $N = \sum\limits_{i} N_i$ to prove that

$$\ln(w) = N \ln N - \sum_i N_i \ln N_i$$

Answer:

$$\ln(w) = \ln\left(\dfrac{N!}{\prod\limits_{i=1}^{r} N_i!}\right) = \ln(N!) - \ln\left(\prod_{i=1}^{r} N_i!\right) = \ln(N!) - \ln\left[(N_1!)(N_2!)()\ldots\ldots\right]$$

$$= \ln(N!) - \left[\ln(N_1!) + \ln(N_2!) + \ldots\ldots\right] = \ln(N!) - \sum_i \ln(N_i!)$$

Apply Stirling's approximation in the form $\ln(N!) = N \ln(N) - N$, we can then approximate the expression for the number of microstates as

$$\ln(w) = N \ln N - N - \sum_i (N_i \ln N_i - N_i)$$

$$= N \ln N - N - \sum_i N_i \ln N_i - \underbrace{\sum_i N_i}_{N} = N \ln N - \sum_i N_i \ln N_i \cdot$$

➢ By differentiation with respect to N_i, we can get

$$\delta \ln(w) = \delta(N \ln N) - \sum_i \ln N_i \delta N_i - \sum_i N_i \underbrace{\delta(\ln N_i)}_{=\delta N_i / N_i}$$

$$= 0 - \sum_i \ln N_i \delta N_i - \underbrace{\sum_i \delta N_i}_{=0} = -\sum_i \ln N_i \delta N_i \cdot$$

The last equation gives the change in $\ln(w)$ as the number of particles in each level is varied.

Non-Degenerate Case:
Example: Use the two constrains

$$N = \sum_i N_i = \text{ constant } \Rightarrow \alpha \sum_i \delta N_i = 0, \tag{i}$$

$$\sum_i N_i \varepsilon_i = E = NU = \text{ constant } \Rightarrow \beta \sum_i \varepsilon_i \delta N_i = 0 \tag{ii}$$

And the the expression for the total number of miscrostsates:

$$\Omega = \dfrac{N!}{\prod\limits_{i=1}^{r} N_i!} \quad \Rightarrow \quad \delta \ln(\Omega) = -\sum_i \ln N_i \delta N_i = 0. \tag{iii}$$

To derive the MB-distribution
$$N_i^* = e^{-\alpha - \beta \varepsilon_i}$$

Answer: Start with the constrains

$$N = \sum_i N_i = \text{ constant } \Rightarrow \alpha \sum_i \delta N_i = 0, \tag{i}$$

$$\sum_i N_i \varepsilon_i = E = NU = \text{ constant } \Rightarrow \beta \sum_i \varepsilon_i \delta N_i = 0 \tag{ii}$$

where α and β are the Lagrangian undetermined multipliers and are related to the physical prosperities of the assembly. Also, the expression for the total number of microstates:

$$\Omega = \frac{N!}{\prod\limits_{i=1}^{r} N_i!} \qquad \Rightarrow \quad \delta \ln(\Omega) = -\sum_i \ln N_i \delta N_i = 0. \qquad \text{(iii)}$$

Adding (i), (ii) and (iii) implies:

$$\sum_i \left[\ln N_i^* + \alpha + \beta \varepsilon_i \right] dN_i = 0.$$

It is possible to select values of α and β such that one of the terms in the sum (i.e. i) is zero, the value of dN_i being immaterial. The remaining dN_i terms are then independent of one another (since dN_i may be obtained from equation (i). It is now possible to set each of the coefficients of dN_i to zero in the last equation and this gives:

$$N_i^* = e^{-\alpha - \beta \varepsilon_i}.$$

which gives the distribution for the most probable distribution. the * is used for most probable distribution, and it be suppressed in the following discussion.

 Degenerate Case : The only difference will be in equation (iii), which will be replaced by:

$$\Omega = N! \prod_{i=1}^{r} \frac{g_i^{N_i}}{N_i!} \qquad \Rightarrow \delta \ln(\Omega) = \sum_i \ln g_i \delta N_i - \sum_i \ln N_i \delta N_i. \qquad \text{(iv)}$$

The new distribution will be

$$N_i^* = g_i e^{-\alpha - \beta \varepsilon_i}.$$

We must now identify the two constants α and β in this distribution equation. In the following we will not use the *.

Identification of α : Now we have $\sum_i N_i = N \Rightarrow \sum_i g_i e^{-\alpha - \beta \varepsilon_i} = N$

$$\Rightarrow \boxed{e^{-\alpha} = \frac{N}{\sum\limits_i g_i e^{-\beta \varepsilon_i}} = \frac{N}{z}},$$

Where $z = \sum\limits_{\text{States}} g_i e^{-\beta \varepsilon_i} = \sum\limits_{\text{All levels}} e^{-\beta \varepsilon_i}$ is known as the **partition function for single particle** and is of the utmost importance in statistical thermodynamics.

The Maxwell-Boltzmann distribution is therefore ($N_i = N \dfrac{g_i e^{-\beta \varepsilon_i}}{Z_{\text{sp}}}$):

$$\Rightarrow \boxed{f(\varepsilon_i) = \frac{N_i}{g_i} = N \frac{e^{-\beta \varepsilon_i}}{z}}$$
<div align="center">average number of
particles per quantum state</div>

where $f(\varepsilon_i)$ is the probability of occupation of a single state belonging to the ith energy level.
    We can also define

$$P_i = \frac{N_i}{N} = g_i \frac{e^{-\beta \varepsilon_i}}{z}, \quad \text{with } N \to \infty$$

as the probability that a particle is chosen at random is in the level i (or the probability that a particular energy state is occupied), with the normalization condition:

<div align="center">3</div>

$$\sum_i P_i = 1$$

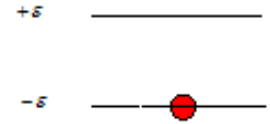The average value of a physical quantity will be expressed as:

$$\overline{R} = \sum_i P_i R_i = \frac{1}{N} \sum_i N_i R_i = \frac{1}{z} \sum_i g_i e^{-\beta \varepsilon_i} R_i \ .$$

For example, the average energy as:

$$U = \langle E \rangle = \frac{E}{N} = \sum_i \varepsilon_i P_i = \frac{1}{z} \sum_i \varepsilon_i g_i e^{-\beta \varepsilon_i},$$

Example: If a particle in a system can be in only two non-degenerate states of $+\varepsilon$ _____
energy $\varepsilon_1 = +\varepsilon$ and $\varepsilon_2 = -\varepsilon$, then

$$z = \sum_{\text{States}} g_i e^{-\beta \varepsilon_i} = (1)e^{-\beta \varepsilon_1} + (1)e^{-\beta \varepsilon_2} = e^{-\beta \varepsilon} + e^{\beta \varepsilon} = 2\cosh(\beta \varepsilon),$$ $-\varepsilon$ ⎯⎯●⎯⎯

$$U = \frac{E}{N} = \frac{1}{z}\left(\varepsilon_1 e^{-\beta \varepsilon_1} + \varepsilon_2 e^{-\beta \varepsilon_2}\right) = \frac{(\varepsilon)e^{-\beta \varepsilon} + (-\varepsilon)e^{\beta \varepsilon}}{2\cosh(\beta \varepsilon)} = -\varepsilon \tanh(\beta \varepsilon)$$

 and the total energy

$$E = NU = -N\varepsilon \tanh(\beta \varepsilon)$$

which allows us to find β in terms of U .

Example: A system has three energy levels of energy 0, $100\,k_B$, and $200\,k_B$, with degeneracy of 1, 3, and 5 respectively. Calculate the partition function, the relative population of each level, and the average energy at a temperature of 100 K. [Hint: take $\beta = 1/100k_B$]

$$z = \sum_i g_i e^{-\beta E_i} = (1)e^0 + 3e^{-100\,k_B/100k_B} + 5e^{-200\,k_B/100k_B} = 1 + 3e^{-1} + 5e^{-2} = 2.78$$

The probability is given by

$$P_i = \frac{N_i}{N} = g_i \frac{e^{-\beta \varepsilon_i}}{z}$$

So, the probability of the particles being in the lowest, first and second states are:

$$P_0 = \frac{1}{z} = 0.360, \quad P_1 = \frac{3e^{-1}}{z} = 0.397, \quad P_2 = \frac{5e^{-2}}{z} = 0.243$$

i	g_i	ε_i	$g_i e^{-\beta \varepsilon_i}$	$P_i = g_i \dfrac{e^{-\beta \varepsilon_i}}{z}$	$\varepsilon_i P_i$
0	1	0	1	0.360	0
1	3	$100\,k_B$	$3e^{-1}$	0.397	$39.7\,k_B$
2	5	$200\,k_B$	$5e^{-2}$	0.243	$48.6\,k_B$
			$Z_{\text{sp}} = 2.78$	Total $= 1$	$\langle E \rangle = 88.3\,k_B$

Note that: $P_0 + P_1 + P_2 = 1$.
The average energy is

$$U = \left(0 \times P_0 + 100 \times P_1 + 200 \times P_2\right) k_B = 88.3\,k_B$$

--

Example: Consider a system of *two* non-interacting, identical and non-interacting particles in a volume *V*. Each particle has three accessible energy levels $\varepsilon_1 = 0$, $\varepsilon_2 = 1\varepsilon$, and $\varepsilon_3 = 2\varepsilon$. The lowest energy level is doubly degenerate. Determine the partition function and the mean energy of the system if the particles are distinguishable and obey the classical Maxwell-Boltzmann statistics. Determine the high temperature limit of the mean energy.

Solution: For Maxwell-Boltzmann Statistics, we have the following distributions:

Energy	Microstates #			
	1	2	3	4
2ε	0	0	0	0
ε	0	0	0	0
0	ab | 0	0 | ab	a | b	b | a
Total Energy =	0	0	0	0

Energy	Microstates #			
	5	6	7	8
2ε	0	0	0	0
ε	b	a	b	a
0	a | 0	b | 0	0 | a	0 | b
Total Energy =	ε	ε	ε	ε

Energy	Microstates #				
	9	10	11	12	13
2ε	b	a	b	a	0
ε	0	0	0	0	ab
0	a | 0	b | 0	0 | a	0 | b	0 | 0
Total Energy =	2ε	2ε	2ε	2ε	2ε

Energy	Microstates #		
	14	15	16
2ε	b	a	ab
ε	a	b	0
0	0 | 0	0 | 0	0 | 0
Total Energy =	3ε	3ε	4ε

Number of macrostates = 4

The total number of microstates = $g^N = (2+1+1)^2 = 4^2 = 16$.

The partition function is:

$$Z_{MB} = \sum_i g_i e^{-\beta \varepsilon_i} = 4e^{-\beta \varepsilon_o} + 4e^{-\beta \varepsilon_1} + 5e^{-\beta \varepsilon_2} + 2e^{-\beta \varepsilon_3} + e^{-\beta \varepsilon_4}$$

$$= 4 + 4e^{-\beta \varepsilon} + 5e^{-2\beta \varepsilon} + 2e^{-3\beta \varepsilon} + e^{-4\beta \varepsilon}$$

$$U_{MB} = -\frac{1}{Z}\frac{\partial Z}{\partial \beta} = \frac{4\varepsilon e^{-\beta \varepsilon} + 10\varepsilon e^{-2\beta \varepsilon} + 6\varepsilon e^{-3\beta \varepsilon} + 4\varepsilon e^{-4\beta \varepsilon}}{4 + 4e^{-\beta \varepsilon} + 5e^{-2\beta \varepsilon} + 2e^{-3\beta \varepsilon} + e^{-4\beta \varepsilon}}$$
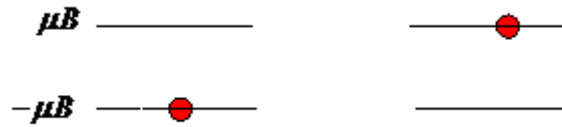
$$\rightarrow \frac{3}{2}\varepsilon \ (as \ T \rightarrow \infty)$$

Partition function

a- The N-particle partition function for distinguishable particles

Let's start with one spin particle in external magnetic field, we will have two states $\uparrow$ with energy $-\mu B$ and $\downarrow$ with energy μB, then

$$z_1 = e^{-\mu B \beta} + e^{\mu B \beta}$$

For two spins, there are four states of the whole system, $\uparrow\uparrow$ with energy $-2\mu B$, $\uparrow\downarrow$ and $\downarrow\uparrow$, both with energy zero, and $\downarrow\downarrow$ with energy $2\mu B$. Thus the two-particle partition function is

Distinguishable particles
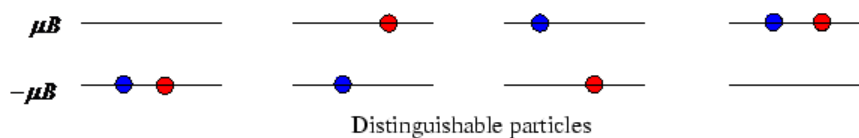
$$z_2 = e^{2\mu B \beta} + e^0 + e^0 + e^{-2\mu B \beta} = e^{2\mu B \beta} + 2e^0 + e^{-2\mu B \beta}$$

$$= \left(e^{2\mu B \beta} + e^{-\mu B \beta} \right)^2 = \left(z_1 \right)^2$$

In general, for N particles, the energies range through $-N\mu B, -(N-2)\mu B, \cdots, -(N-2n_\downarrow)\mu B, \cdots, N\mu B$ with there being $N!/\left[n_\downarrow !(N-n_\downarrow) \right]$ separate states with $n_\downarrow$ down-spins. So

$$Z_N = e^{-N\mu B\beta} + \ldots + \frac{N!}{n_\downarrow!(N-n_\downarrow)!} e^{-(N-2n_\downarrow)\mu B\beta} + \ldots + e^{N\mu B\beta}$$

$$= (e^{-\mu B\beta} + e^{\mu B\beta})^N = (Z_1)^N$$

There is a caution, which can be ignored on first reading. The argument says that there are a number of different states with the same number of down spins. Since the spins are arranged on a lattice, this is correct; every spin can be distinguished from every other spin by its position. When we go on to consider a gas, however, this is no longer so, and the relation between z_1 and z_N changes.

b- The N particle's partition function for indistinguishable particles, (No Pauli's' exclusion principle).

As we know for the N-distinguish particles (as held for the paramagnet by their position in the lattice) we have $z_N = \left(z_1 \right)^N$. Consider again the simplest case, of two particles and two energy levels. If the particles are distinguishable, as in the upper picture below, there are four states, two of which have energy ε, and the two-particle partition function is

$$z_2 = e^0 + 2e^{-\varepsilon\beta} + e^{-2\varepsilon\beta} = \left(z_1 \right)^2$$

Distinguishable particles

Indistinguishable particles
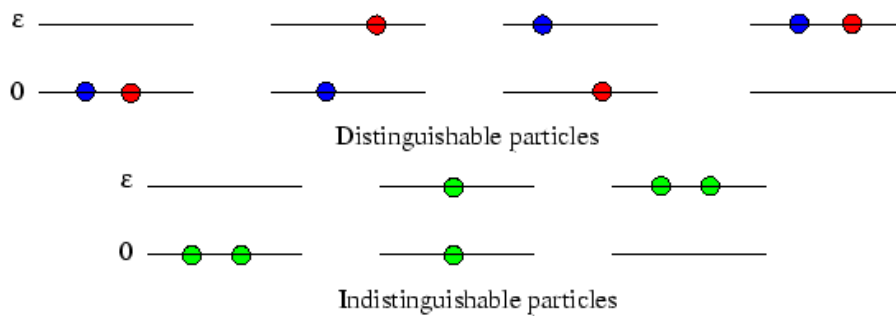
If the particles are *indistinguishable*, however, there are only three states, as in the lower picture, and the partition function is

$$z_2 = e^0 + e^{-\varepsilon\beta} + e^{-2\varepsilon\beta} \neq \left(z_1\right)^2$$

If we use $\left(z_1\right)^2$, we over-count the state in which the particles are in different energy levels. In general there is no simple expression for the N-particle partition function for indistinguishable particles.

However we note that $\left(Z_1\right)^N$ over-counts the states in which all N particles are in different energy levels by exactly $N!$. So if we are in a position where there are many more accessible energy levels (that is, levels with energy less than a few k_BT) than there are particles, the probability of any two particles being in the same energy level is small, and almost all states will have all the particles in different levels. Hence a good approximation is

$$z_N = \frac{\left(z_1\right)^N}{N!}$$

c- The N particle's partition function for indistinguishable particles, (with Pauli's' exclusion principle).

Do it.

We can prove the following (Sec. 14.1)

1- Average energy (the ensemble average of the energy of the system).

$$U = \sum_r \varepsilon_r P_r = \frac{1}{Z}\sum_r \varepsilon_r\, \mathrm{e}^{-\beta\varepsilon_r} = \frac{1}{Z}\frac{\partial}{\partial\beta}\sum_r \mathrm{e}^{-\beta\varepsilon_r} = -\frac{1}{Z}\frac{\partial Z}{\partial\beta} = \underline{\underline{-\frac{\partial \ln Z}{\partial\beta}}}$$

2- Equivalent expressions "average entropy" (**Shannon information entropy**)

$$\boxed{s = k_B \ln(\Omega_N) = -k_B \sum_i P_i \ln(P_i), \quad \text{where } P_i = \frac{N_i}{N}}$$

Proof: Start with the definition

$$S = k_B \ln(\Omega_N) = k_B \ln\left(N! / \prod_{i=1}^{r} N_i! \right) \approx k_B \left(N \ln N - \sum_i N_i \ln(N_i) \right)$$

The average entropy of one of the elements in the ensemble is $s = S/N,$ and

$$\frac{1}{N}\ln(\Omega_N) = \frac{1}{N}\left\{ N\ln N - \sum_i N_i \ln(N_i) \right\} = \frac{1}{N}\left\{ \sum_i N_i \ln N - \sum_i N_i \ln(N_i) \right\} = -\sum_i \frac{N_i}{N}\ln\left(\frac{N_i}{N}\right)$$

$$= -\sum_i P_i \ln(P_i)$$

3- Entropy

$$s = -k_B \sum_i P_i \ln(P_i) = -k_B \sum_i P_i \ln\left(\frac{e^{-\beta\varepsilon_i}}{Z_{sp}}\right) = -k_B \sum_i P_i\left(-\beta\varepsilon_i - \ln Z_{sp}\right)$$

$$= \beta k_B \sum_i \frac{\varepsilon_i e^{-\beta\varepsilon_i}}{Z_{sp}} + \frac{k_B}{Z_{sp}}\ln Z_{sp}\sum_i e^{-\beta\varepsilon_i} = \beta k_B \langle E \rangle + \frac{k_B}{Z_{sp}}\left(\ln Z_{sp}\right)Z_{sp} = \underline{\underline{\beta k_B \langle E \rangle + k_B \ln Z_{sp}}}$$

4- Identification of β:

Then the entropy will be:

$$\boxed{S = k_B \ln(\Omega) = k_B N \ln Z_{sp} + k_B \beta U}$$

Then Maxwell's law gives

$$\frac{1}{T} = \left(\frac{\partial S}{\partial U}\right)_V = k_B N \underbrace{\frac{d\ln Z_{sp}}{d\beta}}_{-\frac{U}{N}}\left(\frac{\partial\beta}{\partial U}\right)_V + k_B\beta + k_B U\left(\frac{\partial\beta}{\partial U}\right)_V = k_B\beta$$

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

5- Helmholtz Free Energy

The above equation for S can be rewritten as

$$F = U - TS = -k_B T \log Z_{sp} = \underline{\underline{-k_B T \ln Z_{sp}}}.$$

Comments:

i-   It is easy to find Z_{sp} as a function of F as: $Z_{sp} = e^{-\beta F}$

ii- Since $F = -k_B T \ln Z$ we can alternatively derive the internal energy from F.

$$U = -\frac{\partial}{\partial \beta} \ln Z = -\frac{\partial}{\partial \beta}\left(\frac{-F}{k_B T}\right) = \underline{\underline{\frac{\partial}{\partial \beta}(\beta F)}}$$

6- Average pressure

$$\overline{p} = \langle p \rangle = \sum_r P_r\, p_r = \frac{1}{Z}\sum_r e^{-\beta \varepsilon_r}\left(-\frac{\partial \varepsilon_r}{\partial V}\right)_{T,N}$$

With

$$Z_{sp} = e^{-\beta \varepsilon_1} + e^{-\beta \varepsilon_2} + \cdots$$

$$\Rightarrow \left(\frac{\partial Z_{sp}}{\partial V}\right)_{T,N} = -\beta e^{-\beta \varepsilon_1}\left(\frac{\partial \varepsilon_1}{\partial V}\right)_{T,N} - \beta e^{-\beta \varepsilon_2}\left(\frac{\partial \varepsilon_2}{\partial V}\right)_{T,N} + \cdots$$

So that

$$\frac{1}{\beta}\left(\frac{\partial Z_{sp}}{\partial V}\right)_{T,N} = -\sum_i e^{-\beta \varepsilon_1}\left(\frac{\partial \varepsilon_i}{\partial V}\right)_{T,N}$$

Substituting this result in the expression for mean pressure, we get

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

Density of States (Sec. 12.5 and 6)

The density of states refers to the number of quantum states per unit energy. In other words, the density of states, denoted by $g(E)$, indicates how densely packed quantum states in a particular system. So, what is the importance of the density of states?

Ultimately, we are going to be interested in calculating the available states of a particle in quantum system. The number of quantum states is important in the determination of optical properties of a material such as a semiconductor (i.e. carbon nanotubes as well as quantum dots). It will be used extensively in the transport phenomena, such as how a device conducts electric current.

One dimension

Let's once again look at the infinite potential well in one dimension
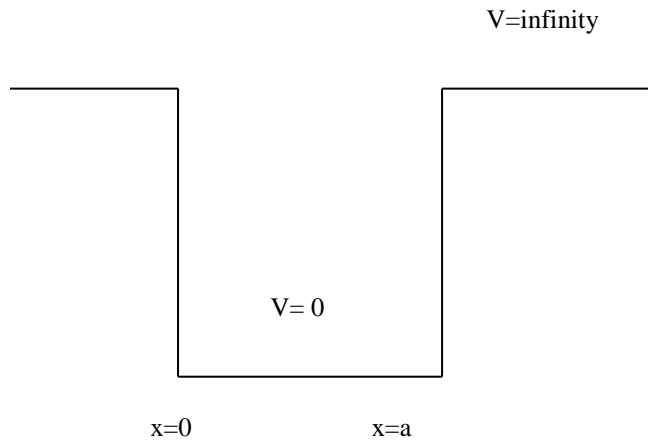
V=infinity

Figure 1. The infinite potential well

We decided that this had solutions of the form:

$$\psi(x) = \sqrt{\frac{2}{a}} \sin(k x) \qquad (1.1)$$

where k is the wave vector and has the only allowed values are:

$$k = \frac{n\pi}{a} \quad n = 1,2,3,... \qquad (1.2)$$

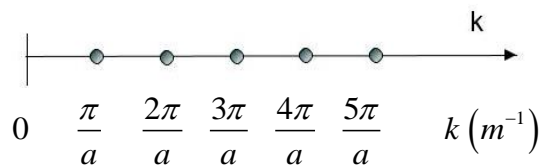So we could plot the allowed states on a simple one-dimensional graph, as in Fig. 2:

Figure 2. Plot of the allowed states in the 1D infinite well.

We could think in terms of how many states we had in a given length in the k-space. (Here you have to be a little careful, because k has units of inverse length.) Notice that the well has a finite dimension a, but k extends from zero to plus infinity. We could talk about the density of states. Since there are two states, due to the multiplicity of the spin $(2s+1)$, for each π/a length in the k-space

$$g_{1D}(k) = \frac{2a}{\pi} \qquad (1.3)$$

So if we wanted to total number of states between $k = 0$ and $k = 10\pi/a$, for instance

10

$$N = \int_0^{10\pi/a} 2\frac{a}{\pi} \, dk = \frac{2a}{\pi}\frac{10\pi}{a} = 20 \tag{1.4}$$

In actuality, we will be more interested in relating allowed states to energy. So we use

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

or

$$k = \frac{\sqrt{2mE}}{\hbar}.$$

Taking the differential gives

$$dk = \frac{1}{2}\frac{\sqrt{2m}}{\hbar}\frac{dE}{\sqrt{E}} \tag{1.5}$$

If we look for the available states up to a certain energy,

$$N = \int_0^{k_{max}} \frac{2a}{\pi} \, dk = \int_0^{E_{max}} \frac{2a}{\pi}\frac{1}{2}\frac{\sqrt{2m}}{\hbar}\frac{dE}{\sqrt{E}} = \int_0^{E_{max}} \frac{\sqrt{2}\sqrt{m}a}{\pi\hbar\sqrt{E}} \, dE.$$

The term in the integrand is the quantity we are looking for. We will divide out the *a* because we want a more general term for any confined region in one dimension. This is the *density of states*, i.e., the number of available states per energy per distance.

$$g_{1D}(E) = \frac{\sqrt{2m}}{\pi\hbar\sqrt{E}} \tag{1.6}$$

It has the units:

$$[g_{1D}] = \frac{[\text{kg}]^{1/2}}{[\text{J s}][\text{J}]^{1/2}} = \frac{[\text{kg}]^{1/2}}{[\text{J s}]\left[\dfrac{\text{kg}^{1/2}\ \text{m}}{\text{s}}\right]} = \frac{1}{[\text{J m}]}$$

Remember that energy of a state in the infinite potential well is given by E_n

$$E_n = \frac{\hbar^2}{2m}\left(\frac{n\pi}{a}\right)^2 = \frac{\hbar^2\pi^2}{2ma^2}n^2 \quad n = 1,2,3,..$$

So it makes sense that as we go higher up in energy, the density of the available states is reduced.

Two Dimensions

Suppose now that we have a two-dimensional infinite well, as shown in Fig. 3. For simplicity, we will assume both dimensions are *a*.

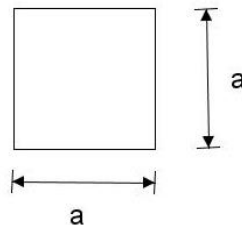

Figure 3. Diagram of a two-dimensional infinite well. Inside the rectangle, V= 0 and inside the rectangle $V = \infty$.

The separable solution will be of the form

$$\psi_{n,m}(x,y) = \frac{2}{a}\sin\left(\frac{n\pi}{a}x\right)\sin\left(\frac{m\pi}{a}y\right). \quad n = 1,2,3...,m = 1,2,3 \tag{1.7}$$

And the corresponding energies:

11

$$E_{n,m} = \frac{\hbar^2 \pi^2}{2ma^2}\left(n^2 + m^2\right).$$

This gives us the possibilities of *degenerate states*: states that have the same energy, but different functions.   Obviously, $E_{1,2} = E_{2,1}$, but they correspond to different states that are orthogonal to each other, i.e.,

$$\int_0^a \int_0^a \psi^*_{1,2}(x,y)\psi_{2,1}(x,y)\,dxdy = 0.$$

As *n* and *m* become large numbers, there will be more degeneracies.

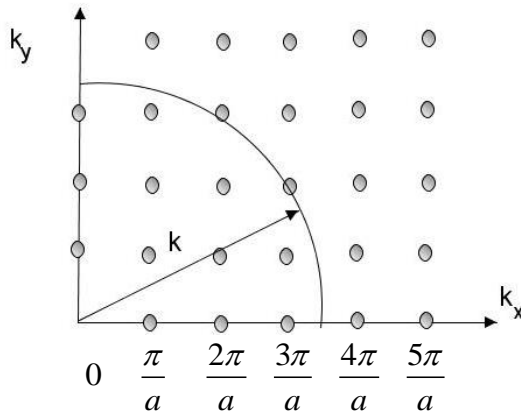We could now make a two-dimensional plot of the available states, as shown in Fig. 4.

Figure 4. Diagram of the two-dimensional k space

For a given absolute value of k, in the 2D k-space we will encompass an area of

$$Area = \frac{1}{4}\pi k^2$$

The factor ¼ indicates that I'm only using positive values of k. The differential is

$$dA = \frac{2}{4}\pi k\, dk.$$

So if we want to get the number of states up to k_{max}

$$N = 2\int_0^{k_{max}} \frac{1}{(\pi/a)^2}\frac{1}{2}\pi k\, dk = \frac{a^2 k_{max}^2}{2\pi} \tag{1.8}$$

The two in front of the integral is because we have two spins per state. Once again, I'm more interested with the distribution with respect to energy, so

$$E = \frac{\hbar^2 k^2}{2m}, \quad k = \frac{\sqrt{2mE}}{\hbar},$$

and,

$$dE = \frac{\hbar^2 k}{m}dk, \quad k\, dk = \frac{m}{\hbar^2}dE.$$

Substituting this into the integral above gives

$$N = \int_0^{E_{max}} \frac{a^2}{\pi}\frac{m}{\hbar^2}dE.$$

So my two-dimensional density of states, after dividing out the physical dimension a^2 is

$$g_{2D}(E) = \frac{m}{\pi\hbar^2}. \tag{1.9}$$

What are the units?

$$\left[g_{2D}\right] = \frac{[\text{kg}]}{[\text{J s}]^2} = \frac{[\text{kg}]}{J\left[\dfrac{\text{kg m}^2}{\text{s}^2}\,\text{s}^2\right]} = \frac{1}{[\text{J m}^2]}.$$

i.e, states per energy, per area.

Three Dimensions

In three dimensions, each state occupies a volume $(\pi/a)^3$. A volume in the 3D k space enclosed by a distance k space is given by

$$V = \frac{4}{3}\pi k^3$$

And the differential is

$$dV = 4\pi k^2 dk.$$

Now we think of k as the radius in a sphere. So the total available states up to k_{max} is

$$N = 2\frac{1}{8}\int_0^{k_{\text{max}}}\left(\frac{a}{\pi}\right)^3 dV = 2\frac{1}{8}\int_0^{k_{\text{max}}}\left(\frac{a}{\pi}\right)^3 4\pi k^2\,dk. \qquad (1.10)$$

The 1/8 indicates that we consider only positive values of k, and, as always, the 2 accounts for the two values of spin. Once again, we would prefer to work with energy so

$$k = \frac{\sqrt{2mE}}{\hbar},$$

and

$$dk = \frac{\sqrt{2m}}{\hbar}\frac{1}{2}\frac{dE}{\sqrt{E}} = \frac{\sqrt{m}}{\hbar}\frac{dE}{\sqrt{2E}},$$

so Eq. 1.10 becomes

$$N = \frac{2}{8}\int_0^{k_{\text{max}}}\left(\frac{a}{\pi}\right)^3 4\pi\left(\frac{\sqrt{2mE}}{\hbar}\right)^2\frac{\sqrt{m}}{\hbar}\frac{dE}{\sqrt{2E}}$$

$$= \frac{8\pi a^3 (2m)^{3/2}}{8\pi^3\hbar^3 2}\int_0^{E_{\text{max}}}\sqrt{E}dE$$

If we want to talk about the number "per volume," we can divide out the a^3. Also, we can replace $8\pi^3\hbar^3$ with just h^3. Then we have an expression for the 3D density of states in the form:

$$g_{3D}(E) = \frac{4\pi(2m)^{3/2}}{h^3}\sqrt{E} \qquad (1.11)$$

What are the units?

$$\left[g_{3D}\right] = \frac{[\text{kg}]^{3/2}}{[\text{J}-\text{s}]^3}[\text{J}]^{1/2} = \frac{[\text{kg}]^{3/2}}{J[J^2 s^3]}\left[\frac{\text{kg}-\text{m}^2}{\text{s}^2}\right]^{1/2}$$

$$= \frac{[\text{kg}]^{3/2}}{J\left[\dfrac{\text{kg}^2\text{m}^4}{\text{s}}\right]}\left[\frac{\text{kg}-\text{m}^2}{\text{s}^2}\right]^{1/2} = \frac{[\text{kg}^2\text{m}]}{[J\cdot\text{m}^4\cdot\text{kg}^2]} = \frac{1}{[J\cdot\text{m}^3]}$$

Density of states in different spaces (for your information)

In momentum space, particles within a small volume $\sigma_b \approx \dfrac{h^3}{V}$ are indistinguishable; therefore it represents an eigenstate. At any instant, all particles having the momenta between p and $p + dp$, will lie within a, shell of volume $4\pi p^2 dp$. Therefore, the total number of eigenstates is given by

$$g(p)dp = \frac{a}{\sigma_b} 4\pi p^2 dp$$

where that a is a constant related to the "polarization" of interested system, that is

$$a \approx \begin{cases} 2 & \text{in case of electrons and photons} \\ 3 & \text{in case of phonon in solids} \end{cases}$$

In a vibrating solid, there are three types of waves: one longitudinal with velocity c_l and two transverse with velocity c_t. All are propagated in the same direction. The *phonons* are related to the vibrations of the lattice in a crystal in the same fashion as *photons* are related to the vibrations of the electromagnetic field.

For photon (phonon) $\vec{p} = \hbar \vec{k} = \dfrac{h}{2\pi} \vec{k}$ so

$$g(k)dk = \frac{aV}{(2\pi)^3} 4\pi k^2 dk *$$

Since $\left| \vec{k} \right| = \dfrac{\omega}{c}$, then

$$g(\omega)d\omega = \frac{aV}{(2\pi)^3 c^3} 4\pi \omega^2 d\omega$$

In case $\omega = 2\pi \nu$, we can have

$$g(\nu)d\nu = \frac{aV}{c^3} 4\pi \nu^2 d\nu$$

In case $\nu = \dfrac{c}{\lambda} \;\Rightarrow\; \left| d\nu \right| = \dfrac{c}{\lambda^2}\left| d\lambda \right|$, we can get

$$g(\lambda)d\lambda = \frac{aVc}{\lambda^5} 4\pi d\lambda$$

*In 2-dimensios on can find

$$g(k)dk = \frac{aA}{(2\pi)^2} 2\pi k dk \qquad\qquad , A = \text{surface area} = L_x L_y$$

Example: Find the area in k-space

$$\int_0^{2\pi} \left(\int k\, dk \right) d\phi = 2\pi \left(\frac{k^2}{2} \right) = \pi k^2$$

What about 1-dimension?

More on Density of states (Note that $\int d\Omega = 4\pi$)

$$dn = \frac{1}{(2\pi\hbar)^3} d\tau\, d\vec{p} = \frac{V}{(2\pi\hbar)^3} p^2 dp\, d\Omega, \qquad d\Omega = \sin\theta\, d\theta\, d\varphi$$

So that

$$\rho = \frac{dn}{dE} = \frac{V}{(2\pi\hbar)^3} p^2 \frac{dp}{dE} d\Omega = \frac{V}{(2\pi\hbar)^3} \frac{p^2}{v} d\Omega$$

$$= \frac{mV}{(2\pi\hbar)^3} k\,d\Omega$$

Note that:

$$p = mv = \hbar k, \quad E = \frac{p^2}{2m} = \frac{\hbar^2 k^2}{2m} \quad \Rightarrow \quad \frac{dE}{dp} = \frac{p}{m} = v$$

$$dn = \frac{V}{(2\pi\hbar)^3} p^2 dp\, d\Omega = \frac{V}{(2\pi)^3} k^2 dk\, d\Omega = \frac{V}{(2\pi c)^3} \omega^2 d\omega\, d\Omega \quad , \quad \omega = kc$$

PARTITION FUNCTION AND ITS APPLICATIONS

The single particle partition function expressed as: $z = \sum_i e^{-\beta \varepsilon_i}$ involves the sum over the distinguishable microstates of the whole system. It may also be expressed as a sum over the energy levels of the systems and the degeneracies of the levels, g_i, $z = \sum_i g_i e^{-\beta \varepsilon_i}$. When the energy levels are closely spaced relative to the thermal energy of the system it is possible to transform the sum into an integral as:

$$z = \int g(\varepsilon) e^{-\beta \varepsilon} d\varepsilon,$$

where $g(\varepsilon)$ is the density of states.

A more general form of the partition function may be written as:

$$Z = \frac{1}{h^{3N}} \int g(\mathbf{p}) e^{-\beta \varepsilon} d^{3N}\mathbf{p} \ d^{3N}\mathbf{r}, \qquad \varepsilon = \frac{p^2}{2m}$$

where N is the number of particles, $\mathbf{p}$ the momentum and $\mathbf{r}$ the position. For classical particles (localized and distinguishable) the partition function for each of the N particles is identical. $Z = z^N$, is the relationship between the single-particle partition function and the partition function for the whole system for localized weakly interacting systems. For indistinguishable (non-localized) particles, $Z = z^N/N!$.

The meaning and the properties of the partition functions are:
1- Partition function is the sum-over-states.
2- It is of the utmost importance in statistical thermodynamics.
3- It depends on the temperature and on the parameters that determine the energy levels and quantum states.
4- It is proportional to the volume of the gas.
5- Finally $Z \equiv f(T, N, V)$

The Maxwell-Boltzmann distribution is therefore:

$$N_i = \frac{N g_i e^{-\beta \varepsilon_i}}{z} \quad \Rightarrow \quad f(\varepsilon_i) = \frac{N_i}{g_i} = N \frac{e^{-\beta \varepsilon_i}}{z} = N P_i,$$

where $f(\varepsilon_i)$ is the probability of occupation of a single state belonging to the ith energy level.

➢ The average value of a physical quantity will be expressed as:

$$\overline{f} = \frac{1}{N} \sum_i N_i f(\varepsilon_i) = \frac{1}{z} \sum_i g_i f(\varepsilon_i) e^{-\beta \varepsilon_i}$$

➢ For continuous distribution one can has:

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

In Brief:

$$N_i = \frac{N g_i e^{-\beta \varepsilon_i}}{z} \quad , \quad z = \sum_i g_i e^{-\beta \varepsilon_i} \Rightarrow \frac{\partial Z}{\partial \beta} = -\frac{Uz}{N} \ ,$$

$$E = \sum_i N_i \varepsilon_i = \frac{1}{z} \sum_i \varepsilon_i g_i e^{-\beta \varepsilon_i} = -\frac{1}{z} \frac{\partial z}{\partial \beta} = -\frac{\partial}{\partial \beta}[\ln(z)] = k_B T^2 \frac{\partial}{\partial T}[\ln(Z)]$$

$$S = k_B \ln W = k_B N \ln z + k_B \beta U, \qquad \left(\frac{\partial S}{\partial U}\right)_V = \beta k_B.$$

Helmholtz free energy :

$$F = U - TS \Rightarrow U = F + TS = F - T\left(\frac{\partial F}{\partial T}\right)_V = -T^2\frac{\partial}{\partial T}\left(\frac{F}{T}\right)$$

Use

$$\beta = \frac{1}{kT} \Rightarrow \frac{\partial \beta}{\partial T} = -\frac{1}{k_B T^2}, \quad \frac{\partial}{\partial \beta} = \frac{\partial T}{\partial \beta}\frac{\partial}{\partial T} = -k_B T^2\frac{\partial}{\partial T}$$

Then

$$U = -T^2\frac{\partial}{\partial T}\left(\frac{F}{T}\right) \Rightarrow - -\frac{\partial \ln(z)}{\partial \beta} = -T^2[-\frac{1}{kT^2}]\frac{\partial}{\partial \beta}\left(\frac{F}{T}\right)$$

$$F = -kT\ln Z_{sp} \Rightarrow z = e^{-\beta F}$$

Thermodynamic Variables

The following relations could be easily deduce using the PF: (use $z = Z_{sp} = \sum\limits_{States} g_i e^{-\beta \varepsilon_i} = \sum\limits_{All\ levels} e^{-\beta \varepsilon_i}$)

Quantity	Symbol	Formula
Partition function	z	$z = Z_{sp} = \sum\limits_{States} g_i e^{-\beta \varepsilon_i} = \sum\limits_{All\ levels} e^{-\beta \varepsilon_i}$
Helmholtz free energy	F	$F = -k_B T\ln z$
Entropy	$S = -\left(\frac{\partial F}{\partial T}\right)_{V,N}$	$S = k_B\left[\left(\frac{\partial\{T\ln z\}}{\partial T}\right)_{V,N}\right] = k_B\left[T\left(\frac{\partial\ln z}{\partial T}\right)_V + \ln z\right]$
Equation of state	$P = -\left(\frac{\partial F}{\partial V}\right)_{T,N}$	$P = k_B T\left(\frac{\partial\ln z}{\partial V}\right)_{T,N}$
Chemical potential	$\mu = -\left(\frac{\partial F}{\partial N}\right)_{T,V}$	$\mu = -k_B T\left(\frac{\partial\ln z}{\partial N}\right)_{V,T}$
Internal energy	$U = F + TS$	$U = -\left(\frac{\partial\ln z}{\partial\beta}\right)_{V,N} = kT^2\left(\frac{\partial\ln z}{\partial T}\right)_{V,N}$
Gibbs' function	$G = F + PV = F - V\left(\frac{\partial F}{\partial V}\right)_{T,N}$	$G = \mu N = k_B T\left[\left(\frac{\partial\ln z}{\partial\ln U}\right)_{T,N} - \ln z\right]$
Enthalpy	$H = U + PV$	$H = k_B T\left[\left(\frac{\partial\ln z}{\partial\ln T}\right)_{V,N} + \left(\frac{\partial\ln z}{\partial\ln V}\right)_{T,N}\right]$
Heat capacity	$C_V = T\left(\frac{\partial S}{\partial T}\right)_{V,N} = -T\left(\frac{\partial^2 F}{\partial T^2}\right)_{V,N}$	$C_V = k_B T\left[2\left(\frac{\partial\ln z}{\partial T}\right)_V + T\left(\frac{\partial^2\ln z}{\partial T^2}\right)_V\right]$

IDEAL GAS

For the ideal gas, the Partition function could be calculated with different methods and give you the same answer. For an ideal (Boltzmann) gas consisting of *N*-distinguishable molecules of mass m, the single particle partition function has the following form:

$$z = \int_0^\infty g(\varepsilon) e^{-\beta \varepsilon} d\varepsilon,$$

where $g(\varepsilon) = \dfrac{4\pi V \sqrt{2}}{h^3} m^{3/2} \varepsilon^{1/2}$, is the density of states. Using the standard integrals, one can find

$$z = \int_0^\infty g(\varepsilon) e^{-\beta \varepsilon} d\varepsilon = V \left(\frac{2\pi m k_B T}{h^2} \right)^{3/2} = V \left(\frac{2\pi m}{\beta h^2} \right)^{3/2}.$$

This is the partition function for a gas under the assumption that the energy levels are so closely spaced that they form a continuum. For *N* distinguishable particles, we have $Z = z^N$.

Quantity	Formula
Partition function	$Z = z^N = V^N \left(\dfrac{2\pi m k_B T}{h^2} \right)^{3N/2}$
Helmholtz free energy	$F = -kT \ln Z = -Nk_B T \left[\ln V + \dfrac{3}{2} \ln \left(\dfrac{2\pi m}{\beta h^2} \right) \right]$
Entropy	$S = -\left(\dfrac{\partial F}{\partial T} \right)_{V,N} = Nk_B \left[\ln V + \dfrac{3}{2} \ln T + S_0 \right]^*$
Equation of state	$P = \dfrac{1}{\beta} \left(\dfrac{\partial \ln Z}{\partial V} \right)_{T,N} = \dfrac{1}{\beta} \dfrac{N}{V} \Rightarrow PV = NRT$
Internal energy	$U = -\left(\dfrac{\partial \ln Z}{\partial \beta} \right)_{V,N} = \dfrac{3}{2} \dfrac{N}{\beta} \Rightarrow \bar{\varepsilon} = \dfrac{3}{2} k_B T$
Heat capacity	$C_V = \left(\dfrac{\partial U}{\partial T} \right)_{V,N} = \dfrac{3}{2} Nk_B$

*Comment for the Entropy of the Ideal gas:

The equation,

$$S = Nk_B \left[\ln V + \frac{3}{2} \ln T + S_o \right], \tag{**}$$

is known as the *Sackur-Tetrode* equation for the entropy of a monatomic gas. Here $S_0 = \dfrac{3}{2} \left[\ln \left(\dfrac{2\pi m k_B}{h^2} \right) + 1 \right]$ is a constant independent of *T*, *V*, or *N*. Recalling that $s = S/n$, $Nk/n = R$, we have

$$s = c_v \ln T + R \ln v + s_o, \tag{***}$$

which has obtained earlier in thermodynamics.

Comments on Sackur-Tetrode equation: It is not correct and turns into the following difficulties:

1- S is not additive because the volume *V* (and not *V/N*) occurs in the argument of the logarithm. This prevents us from dividing the system in two parts and writing $S=S_1+S_2$. This difficulty is not so easily to handle classically. In fact, it leads to the famous Gibbs paradox.

2- It is not valid down to absolute zero since S does not approach zero as $T \to 0$. Such contradiction would not have occurred if we had used the original summation of Z. The replacement of sum by integral in Z is not justified near the absolute zero. At $T = 0$ the lowest state ($\varepsilon = 0$) becomes important, while its contribution has been excluded altogether in the integration. In classical statistical, since p is a continuous variable and the size of the cell in the phase space is not fixed, we cannot estimate the third law. For this we have to go to quantum mechanics.

Equipartition theorem: *For every degree of freedom for which the energy is a quadratic function* $\left(\varepsilon(z) = az^2 \right)$, *the mean energy per particle of a system in equilibrium at temperature T is kT/2.*

H.W.   Prove that

$$\bar{\varepsilon}(z) = \frac{\int \varepsilon(z)N(z)dz}{\int N(z)dz} = \frac{\int az^2 e^{-az^2/kT}dz}{\int N(z)dz} = \frac{1}{2}kT$$

Standard integrals

$$\int_{-\infty}^{\infty} e^{-ax^2} dx = \sqrt{\frac{\pi}{a}}, \quad \int_{-\infty}^{\infty} x^{2n+1} e^{-ax^2} dx = \frac{n!}{2a^{n+1}}, \ n = 0,1,2,\dots \quad \Gamma(\frac{1}{2}) = \sqrt{\pi}, \Gamma(\frac{3}{2}) = \frac{\sqrt{\pi}}{2},$$