

The Canonical Ensemble

(Parthria Chapter 3)

In the preceding chapter we established the basis of ensemble theory and made a somewhat detailed study of the microcanonical ensemble. In that ensemble the macrostate of the systems was defined through a fixed number of particles N , a fixed volume V , and a fixed energy E [or, preferably, a fixed energy range $(E - \Delta/2, E + \Delta/2)$]. The basic problem then consisted in determining the number $\Omega(N, V, E)$ or $\Gamma(N, V, E; \Delta)$, of *distinct* microstates accessible to the system. From the asymptotic expressions of these numbers, complete thermodynamics of the system could be derived in a straightforward manner. However, for most physical systems, the mathematical problem of determining these numbers is quite formidable. For this reason alone, a search for an alternative approach within the framework of the ensemble theory seems necessary.

Practically, too, the concept of a fixed energy (or even an energy range) for a system belonging to the real world does not appear satisfactory. For one thing, the total energy E of a system is hardly ever measured; for another, it is hardly possible to keep its value under strict physical control. A far better alternative appears to be to speak of a fixed temperature T of the system — a parameter that is not only directly observable (by placing a “thermometer” in contact with the system) but also controllable (by keeping the system in contact with an appropriate “heat reservoir”). For most purposes, the precise nature of the reservoir is not very relevant; all one needs is that it should have an infinitely large heat capacity, so that, irrespective of energy exchange between the system and the reservoir, an overall constant temperature can be maintained. Now, if the reservoir consists of an infinitely large number of mental copies of the given system we have once again an ensemble of systems — this time, however, it is an ensemble in which the macrostate of the systems is defined through the parameters N, V , and T . Such an ensemble is referred to as a *canonical* ensemble.

In the canonical ensemble, the energy E of a system is variable; in principle, it can take values anywhere between zero and infinity. The question then arises: what is the probability that, at any time t , a system in the ensemble is found to be in one of the states characterized by the energy value E_r ? We denote this probability by the symbol P_r . Clearly, there are two ways in which the dependence of P_r on E_r can be determined. One consists of regarding the system as in equilibrium with a heat reservoir at a *common* temperature T and studying the statistics of the energy exchange between the two. The other consists of regarding the system as a member of a canonical ensemble (N, V, T) , in which an energy \mathcal{E} is being shared by \mathcal{N} identical systems constituting the ensemble, and studying the statistics of this sharing process. We expect that in the thermodynamic limit the final result in either case would be the same. Once P_r is determined, the rest follows without difficulty.

3.1 Equilibrium between a system and a heat reservoir

We consider the given system A , immersed in a very large heat reservoir A' ; see [Figure 3.1](#). On attaining a state of mutual equilibrium, the system and the reservoir would have a *common* temperature, *say* T . Their energies, however, would be variable and, in principle, could have, at any time t , values lying anywhere between 0 and $E^{(0)}$, where $E^{(0)}$ denotes the energy of the composite system $A^{(0)}$ ($\equiv A + A'$). If, at any particular instant of time, the system A happens to be in a state characterized by the energy value E_r , then the reservoir would have an energy E_r' such that

$$E_r + E_r' = E^{(0)} = \text{const.} \quad (1)$$

Of course, since the reservoir is supposed to be much larger than the given system, any *practical* value of E_r would be a very small fraction of $E^{(0)}$; therefore, for all practical purposes,

$$\frac{E_r}{E^{(0)}} = \left(1 - \frac{E_r'}{E^{(0)}}\right) \ll 1. \quad (2)$$

With the state of the system A having been specified, the reservoir A' can still be in *any one* of a large number of states compatible with the energy value E'_r . Let the number of these states be denoted by $\Omega'(E'_r)$. The prime on the symbol Ω emphasizes the fact that its functional form will depend on the nature of the reservoir; of course, the details of this dependence are not going to be of any particular relevance to our final results. Now, the larger the number of states available to the reservoir, the larger the probability of the reservoir assuming that particular energy value E'_r (and, hence, of the system A assuming the corresponding energy value E_r). Moreover, since the various possible states (with a given energy value) are *equally likely* to occur, the relevant probability would be directly proportional to this number; thus,

$$P_r \propto \Omega'(E'_r) \equiv \Omega'(E^{(0)} - E_r). \quad (3)$$

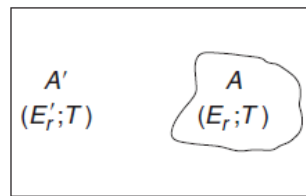


FIGURE 3.1 A given system A immersed in a heat reservoir A' ; in equilibrium, the two have a common temperature T .

In view of (2), we may carry out an expansion of (3) around the value $E'_r = E^{(0)}$, that is, around $E_r = 0$. However, for reasons of convergence, it is essential to effect the expansion of its logarithm instead:

$$\begin{aligned} \ln \Omega'(E'_r) &= \ln \Omega'(E^{(0)}) + \left(\frac{\partial \ln \Omega'}{\partial E'} \right)_{E'=E^{(0)}} (E'_r - E^{(0)}) + \dots \\ &\simeq \text{const} - \beta' E_r, \end{aligned} \quad (4)$$

where use has been made of formula (1.2.3), whereby

$$\left(\frac{\partial \ln \Omega}{\partial E} \right)_{N,V} \equiv \beta; \quad (5)$$

note that, in equilibrium, $\beta' = \beta = 1/kT$. From (3) and (4), we obtain the desired result:

$$P_r \propto \exp(-\beta E_r). \quad (6)$$

Normalizing (6), we get

$$P_r = \frac{\exp(-\beta E_r)}{\sum_r \exp(-\beta E_r)}, \quad (7)$$

where the summation in the denominator goes over *all* states accessible to the system A . We note that our final result (7) bears no relation whatsoever to the physical nature of the reservoir A' .

We now examine the same problem from the ensemble point of view.

Maxwell-Boltzmann distribution

A System in the canonical ensemble

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 obvious conditions

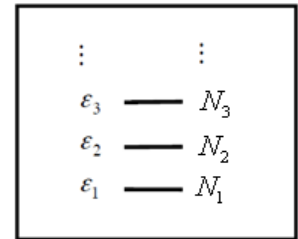
$$N = \sum_i N_i = \text{constant} \Rightarrow \alpha \sum_i \delta N_i = 0, \tag{i}$$

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

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	\dots	ϵ_n	
# of systems	N_1	N_2	\dots	N_n	$N = \sum_i N_i$
energy	$N_1 \epsilon_1$	$N_2 \epsilon_2$	\dots	$N_n \epsilon_n$	$U = \sum_i N_i \epsilon_i$



$(\epsilon_1 < \epsilon_2 < \epsilon_3, \dots)$

where $U (= E / N)$ 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

$$\Omega \{N_n\} = \frac{N!}{\prod_{i=1}^r N_i!} \Rightarrow \delta \ln(\Omega) = -\sum_i \ln N_i \delta N_i = 0. \tag{iii}$$

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 $\{N_n\}$ 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.

Non-Degenerate Case:

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

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

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

where α and β are the Lagrangian undetermined multipliers and are related to the physical properties of the assembly. Adding (i), (ii) and (iii) implies:

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

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.

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

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

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 $\sum_i N_i = N \Rightarrow \sum_i g_i e^{-\alpha - \beta \varepsilon_i} = N$

$$\Rightarrow e^\alpha = \frac{N}{\sum_i g_i e^{-\beta \varepsilon_i}} = \frac{N}{Z_{\text{sp}}},$$

Where $Z_{\text{sp}} = \sum_{\text{States}} g_i e^{-\beta \varepsilon_i} = \sum_{\text{All levels}} e^{-\beta \varepsilon_i}$ is known as the **partition function** and is of the utmost importance in statistical thermodynamics.

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

$$\Rightarrow f(\varepsilon_i) = \frac{N_i}{g_i} = N \frac{e^{-\beta \varepsilon_i}}{Z_{\text{sp}}}$$

average number of particles per quantum state

where $f(\varepsilon_i)$ is the probability of occupation of a single state belonging to the i^{th} energy level.

We can also define

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

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:

$$\sum_i P_i = 1$$

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

$$\bar{R} = \sum_i P_i R_i = \frac{1}{N} \sum_i N_i R_i = \frac{1}{Z_{\text{sp}}} \sum_i g_i e^{-\beta \varepsilon_i} R_i .$$

For example, the average energy as:

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

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

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

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

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.

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

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:

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

i	g_i	ε_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	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

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

With the Definition

$$P_i = \frac{N_i}{N} = g_i \frac{e^{-\beta \epsilon_i}}{Z_{sp}}, \quad \text{with } N \rightarrow \infty$$

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:

$$\sum_i P_i = 1$$

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

$$\bar{R} = \sum_i P_i R_i = \frac{1}{N} \sum_i N_i R_i = \frac{1}{Z_{sp}} \sum_i g_i e^{-\beta \epsilon_i} R_i .$$

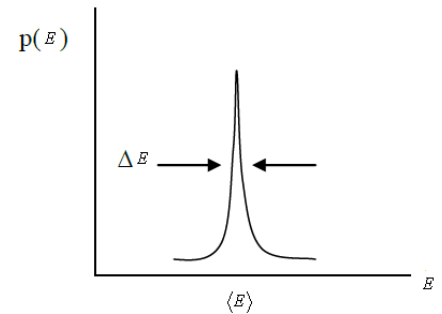
We can prove the following:

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

$$\langle E \rangle = \sum_r P_r \epsilon_r = \frac{1}{Z} \sum_r e^{-\beta \epsilon_r} \epsilon_r \equiv \frac{1}{Z} \sum_r \epsilon_r e^{-\beta \epsilon_r} = \frac{1}{Z} \frac{\partial}{\partial \beta} \sum_r e^{-\beta \epsilon_r} = \frac{1}{Z} \frac{\partial Z}{\partial \beta} = - \frac{\partial \ln Z}{\partial \beta}$$

The partial derivative here implies that we must keep the single particle energy levels fixed, eg. we have a fixed volume for a mechanical system, or a fixed external field for a magnetic system.

It is important to recognize that we have found an average value in $\langle E \rangle$ – averaged over time or over an ensemble. If we are dealing with a system in thermal equilibrium with its surroundings, heat can be lost or gained and the exact value of the internal energy may in principle differ from the mean value. However when we are dealing a system containing a large number of particles, this difference is very small. The figure below gives some suggestion of what the distribution of system energies may look like, if we measure it at different times or for different members of the ensemble.



The rms variation is very small and in fact for a system of N particles we have

$$\frac{\Delta E}{\langle E \rangle} \approx \frac{1}{\sqrt{N}} \approx \frac{1}{10^{10}}$$

for $N = 10^{20}$ particles or about 1 mole. In practice therefore we may write U in place of its mean without any significant error.

Another conclusion we may draw from this is that it does not matter whether we consider a thermally isolated (macroscopic) system or an isolated (macroscopic) system. The energies we calculate will be essentially the same.

2- Equivalent expressions $S = k_B \ln(\Omega_N) = -k_B \sum_i P_i \ln(P_i)$

Proof: Start with the definition

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

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

$$\begin{aligned} \frac{1}{N} \ln(\Omega_N) &= \frac{1}{N} \left\{ N \ln N - \sum_i n_i \ln(n_i) \right\} = \frac{1}{N} \left\{ \sum_i n_i \ln N - \sum_i n_i \ln(n_i) \right\} = - \sum_i \frac{n_i}{N} \ln \left(\frac{n_i}{N} \right) \\ &= - \sum_i P_i \ln(P_i) \end{aligned}$$

3- Entropy

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

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

4- Helmholtz Free Energy

The above equation for S can be rewritten as

$$F = \langle E \rangle - TS = -k_B T \log Z_{sp} = \underline{\underline{-k_B T \ln Z_{sp}}}$$

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 .

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

5- Average pressure

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

With

$$Z_{sp} = e^{-\beta \epsilon_1} + e^{-\beta \epsilon_2} + \dots$$

$$\Rightarrow \left(\frac{\partial Z_{sp}}{\partial V} \right)_{T,N} = -\beta e^{-\beta \epsilon_1} \left(\frac{\partial \epsilon_1}{\partial V} \right)_{T,N} - \beta e^{-\beta \epsilon_2} \left(\frac{\partial \epsilon_2}{\partial V} \right)_{T,N} + \dots$$

So that

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

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

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

6- 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

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

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

Example: Consider a system of *two* non-interacting, identical and non-interacting particles in a volume V . Each particle has three accessible energy levels $\epsilon_1 = 0$, $\epsilon_2 = 1\epsilon$, and $\epsilon_3 = 2\epsilon$. 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	Macrostates #			
	1	2	3	4
2ϵ	0	0	0	0
ϵ	0	0	0	0
0	ab	0	0	0
Total Energy =	0	0	0	0

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

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

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

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

The partition function is:

$$\begin{aligned}
 Z_{MB} &= \sum_i g_i e^{-\beta \epsilon_i} = 4e^{-\beta \epsilon_0} + 4e^{-\beta \epsilon_1} + 5e^{-\beta \epsilon_2} + 2e^{-\beta \epsilon_3} + e^{-\beta \epsilon_4} \\
 &= 4 + 4e^{-\beta \epsilon} + 5e^{-2\beta \epsilon} + 2e^{-3\beta \epsilon} + e^{-4\beta \epsilon} \\
 U_{MB} &= -\frac{1}{Z} \frac{\partial Z}{\partial \beta} = \frac{4\epsilon e^{-\beta \epsilon} + 10\epsilon e^{-2\beta \epsilon} + 6\epsilon e^{-3\beta \epsilon} + 4\epsilon e^{-4\beta \epsilon}}{4 + 4e^{-\beta \epsilon} + 5e^{-2\beta \epsilon} + 2e^{-3\beta \epsilon} + e^{-4\beta \epsilon}} \\
 &\rightarrow \frac{3}{2} \epsilon \quad (\text{as } T \rightarrow \infty)
 \end{aligned}$$

H.W. Do the problem for indistinguishable particles.

PARTITION FUNCTION AND ITS APPLICATIONS

The single particle partition function expressed as: $z = \sum_i e^{-\beta \epsilon_i}$ 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 , $z = \sum_i g_i e^{-\beta \epsilon_i}$. 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:

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

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

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

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

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.

The Maxwell-Boltzmann distribution is therefore:

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

where $f(\epsilon_i)$ is the probability of occupation of a single state belonging to the i^{th} energy level.

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

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

➤ For continuous distribution one can have:

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

In Brief:

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

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

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

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

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

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

Thermodynamic Variables

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

Quantity	Symbol	Formula
Partition function	z	$z = Z_{sp} = \sum_{\text{States}} g_i e^{-\beta \epsilon_i} = \sum_{\text{All levels}} e^{-\beta \epsilon_i}$
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 $g(\varepsilon) = \frac{4\pi V \sqrt{2}}{h^3} m^{3/2} \varepsilon^{1/2}$, 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	$Z = z^N = V^N \left(\frac{2\pi m k_B T}{h^2} \right)^{3N/2}$
Helmholtz free energy	$F = -kT \ln Z = -Nk_B T \left[\ln V + \frac{3}{2} \ln \left(\frac{2\pi m}{\beta h^2} \right) \right]$
Entropy	$S = - \left(\frac{\partial F}{\partial T} \right)_{V,N} = Nk_B \left[\ln V + \frac{3}{2} \ln T + S_0 \right]^*$
Equation of state	$P = \frac{1}{\beta} \left(\frac{\partial \ln Z}{\partial V} \right)_{T,N} = \frac{1}{\beta} \frac{N}{V} \Rightarrow PV = NRT$
Internal energy	$U = - \left(\frac{\partial \ln Z}{\partial \beta} \right)_{V,N} = \frac{3}{2} \frac{N}{\beta} \Rightarrow \bar{\varepsilon} = \frac{3}{2} k_B T$
Heat capacity	$C_V = \left(\frac{\partial U}{\partial T} \right)_{V,N} = \frac{3}{2} Nk_B$

***Comment for the Entropy of the Ideal gas:**

The equation,

$$S = Nk_B \left[\ln V + \frac{3}{2} \ln T + S_0 \right], \tag{**}$$

is known as the *Sackur-Tetrode* equation for the entropy of a monatomic gas. Here

$S_0 = \frac{3}{2} \left[\ln \left(\frac{2\pi m k_B}{h^2} \right) + 1 \right]$ is a constant independent of T , V , or N . Recalling that $s = S/n$, $Nk/n=R$, we have

$$s = c_v \ln T + R \ln v + s_0, \tag{***}$$

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 $T \rightarrow 0$. 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 ($\epsilon = 0$) 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 ($\epsilon(z) = az^2$), the mean energy per particle of a system in equilibrium at temperature T is $kT/2$.

H.W. Prove that
$$\bar{\epsilon}(z) = \frac{\int \epsilon(z)N(z)dz}{\int N(z)dz} = \frac{\int az^2 e^{-az^2/kT} dz}{\int N(z)dz} = \frac{1}{2}kT$$

Standard integrals

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

Appendices

Partition function for Non-interacting system

Ideal Gas

Derivation 1:

We will now discuss about the derivation of the translational partition function of the ideal monatomic gas. The translational energy states of an ideal monatomic gas can be obtained from the solution of a particle of mass m in a 3-dimensional box of side a .

$$\epsilon_{n_x, n_y, n_z} = \frac{h^2}{8ma^2} (n_x^2 + n_y^2 + n_z^2)$$

where n_x, n_y, n_z are integer and can have values in the range 1 to ∞ .

Now, one particle partition function (z_{trans}) can be written as

$$\begin{aligned} z_{trans} &= \sum_{n_x, n_y, n_z=1}^{\infty} e^{-\beta \epsilon_{n_x, n_y, n_z}} = \sum_{n_x=1}^{\infty} e^{-\frac{\beta h^2 n_x^2}{8ma^2}} \sum_{n_y=1}^{\infty} e^{-\frac{\beta h^2 n_y^2}{8ma^2}} \sum_{n_z=1}^{\infty} e^{-\frac{\beta h^2 n_z^2}{8ma^2}} \\ &= \left[\sum_{n=1}^{\infty} e^{-\frac{\beta h^2 n^2}{8ma^2}} \right]^3 \end{aligned}$$

This summation cannot be evaluated analytically. However, we can replace the summation by an integral because of the following reason

The energy difference between the state n_x and n_x+1 is

$$\Delta = \frac{\beta h^2 (n_x + 1)^2}{8ma^2} - \frac{\beta h^2 n_x^2}{8ma^2} = \frac{\beta h^2 (2n_x + 1)}{8ma^2}$$

At room temperature, for $m = 10^{-22}$ g and $a = 10$ cm, the difference is

$$\Delta \approx (2n_x + 1) \times 10^{-20}$$

A typical value of n_x at room temperature is of the order of 10^{10} , so Δ is very small for all but very large values of n_x . Again at the limit of very large value of n_x , $e^{-\frac{\beta h^2 n_x^2}{8ma^2}}$ will be negligible. Hence, the above summation can be replaced by an integral

$$z_{trans} = \left(\int_0^{\infty} e^{-\frac{\beta h^2 n^2}{8ma^2}} dn \right)^3 = \left(\frac{2\pi m k_B T}{h^2} \right)^{3/2} V$$

This is the desired expression for z_{trans} where V is written for a^3 .

Derivation 2:

We now derive the translational partition function of an ideal monatomic gas in another way. In the previous derivation, we have written z_{trans} as a sum over energy states. We now write the same as a sum over energy levels. Like energy states, energy levels are also very densely distributed (we will discuss it later) and hence the z_{trans} can be written as an integral.

$$z_{trans} = \int_0^{\infty} g(\epsilon) e^{-\beta \epsilon} d\epsilon$$

The function $g(\varepsilon)$ represents the density of states, and $g(\varepsilon)d\varepsilon$ is the **number of energy states between ε and $\varepsilon + d\varepsilon$** , or, in other words **effective degeneracy**.

Let us now try to get an expression of $g(\varepsilon)$. Consider a three dimensional space spanned by n_x , n_y , and n_z . One can easily understand that there is a one-to-one correspondence between energy (expression given in the previous section) and the points in the (n_x, n_y, n_z) space with coordinates given by the positive integers. Below is a two-dimensional version of such space (Figure 1).

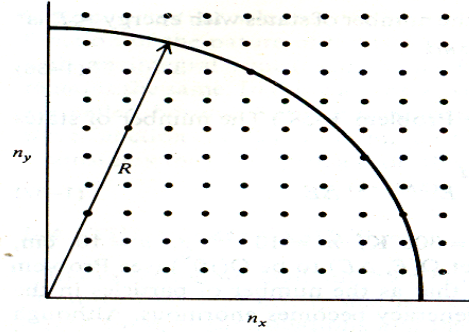


Figure 1: Two-dimensional version of the (n_x, n_y, n_z) space, the space with the quantum number n_x , n_y , and n_z as axes

In this space, equation of a sphere of radius R will be

$$n_x^2 + n_y^2 + n_z^2 = \frac{8ma^2\varepsilon}{h^2} = R^2$$

Now the number of microstates energy $(\Sigma(\varepsilon))$ having energy $\leq \varepsilon$ will be the volume of the one octant (1/8) of a sphere of the corresponding radius R in (n_x, n_y, n_z) space.

$$\Sigma(\varepsilon) = \frac{1}{8} \left(\frac{4\pi R^3}{3} \right) = \frac{\pi}{6} \left(\frac{8ma^2\varepsilon}{h^2} \right)^{3/2}$$

The factor 1/8 comes because the integer n_x, n_y, n_z can have only positive values and hence only the volume of the one octant has to be considered.

Now, the number of states between energy ε and $\varepsilon + d\varepsilon$ will be

$$g(\varepsilon)\Delta\varepsilon = \frac{d\Sigma(\varepsilon)}{d\varepsilon} \Delta\varepsilon = \frac{4}{\pi} \left(\frac{8ma^2}{h^2} \right)^{3/2} \varepsilon^{1/2} \Delta\varepsilon$$

[If we take $\varepsilon = 3k_B T/2$, $T = 300K$, $m = 10^{-22}$ g, $a = 10$ cm, and $\Delta\varepsilon$ to be 0.01ε , then number of states within this interval $\Delta\varepsilon$ will $\approx 10^{28}$.]

Now put the expression of $g(\varepsilon) = 4\pi V \left(\frac{2m}{h^2} \right)^{3/2} \sqrt{\varepsilon}$ in integral of z_{trans}

$$\begin{aligned} z_{trans} &= \int_0^{\infty} g(\varepsilon) e^{-\beta\varepsilon} d\varepsilon = 4\pi V \left(\frac{2m}{h^2} \right)^{3/2} \int_0^{\infty} \sqrt{\varepsilon} e^{-\frac{\varepsilon}{k_B T}} d\varepsilon \\ &= 4\pi V \left(\frac{2m}{h^2} \right)^{3/2} (k_B T)^{3/2} \underbrace{\int_0^{\infty} \sqrt{y} e^{-y} dy}_{\Gamma(3/2) = \frac{\sqrt{\pi}}{2}} = \frac{V}{2\pi^2} \left(\frac{m}{h^2} \right)^{3/2} (k_B T)^{3/2} \frac{\sqrt{\pi}}{2} \\ &= V \left(\frac{2\pi m k_B T}{h^2} \right)^{3/2} = V \left(\frac{2\pi m}{\beta h^2} \right)^{3/2} \end{aligned}$$

The expression the same as we got in the previous derivation.

The factor $\left(\frac{h^2}{2\pi mk_B T}\right)^{1/2}$ that occurs in the translational partition function has units of length and usually denoted by Λ (thermal de-broglie wavelength). In this notation q_{trans} becomes

$$z_{trans} = \frac{V}{\Lambda^3}$$

Partition function of a system of ideal gas of particle N

We have already evaluated the single particle translational partition function (z_{trans}) of ideal gas. Let us now consider a system of N ideal gas molecules confined in volume V and are at temperature T. As the particles are indistinguishable from each other, the N particle partition function will be

$$Z_N(V, T) = \frac{z_{trans}^N}{N!} = \frac{1}{N!} \left[\frac{2\pi mk_B T}{h^2} \right]^{3/2} V^N$$

Useful Relations

We will now use this expression of the partition function and derive some useful relation which we have already used for ideal gas at different context.

Ideal gas equation

From the properties of canonical ensemble, we know that free energy (F) is

$$F = -k_B T \ln Z_N(V, T) = -Nk_B T \ln \left[\left(\frac{2\pi mk_B T}{h^2} \right)^{3/2} \frac{Ve}{N} \right]$$

where we have used the relation $N! = N^N e^{-N}$

Now, from the thermodynamic relation pressure can be obtained as,

$$P = - \left(\frac{\partial F}{\partial V} \right)_T = \frac{Nk_B T}{V}$$

This is the ideal gas equation which we use

Energy and heat capacity

We can write the energy E of the system of canonical ensemble as,

$$E = k_B T^2 \left[\frac{\partial \ln Z_N(V, T)}{\partial T} \right]_{N, V} = Nk_B T^2 \frac{d \ln T^{3/2}}{dT} = \frac{3}{2} Nk_B T$$

Now the heat capacity (C_V) of the system can be obtain using thermodynamic relation as

$$C_V = \left(\frac{\partial E}{\partial V} \right)_V = \frac{3}{2} Nk_B$$

The results of energy and heat capacity are also known to us.

Entropy

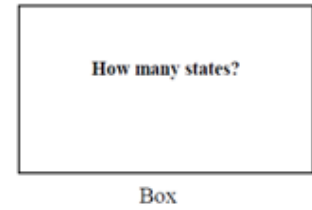
We will now derive the entropy of the system of N ideal gas particle. This we may not have seen earlier. We will use the thermodynamic relation to get the expression for entropy (S)

$$S = - \left(\frac{\partial F}{\partial T} \right)_V = Nk_B \ln \left[\left(\frac{2\pi mk_B T}{h^2} \right)^{3/2} \frac{Ve^{5/2}}{N} \right]$$

This equation is called **Sackur-Tetrode equation**.

A: Evaluation of Partition Function for Particles in an Isolated Box

Classical Particles in a Large Box: To specify the states of this system, we could divide the parameter space into 6 dimensional phase space (\mathbf{r}, \mathbf{p}) of arbitrarily small elementary volumes ($\Delta\mathbf{r}, \Delta\mathbf{p}$). Calculations are then carried out by integrating over properties defined with respect to these volumes. In the limit of small volumes, the size cancels out and is therefore not important. This approach has been adopted historically but the math's is obscure and has been supplanted by quantum models.



Quantum Particles in a Large Box

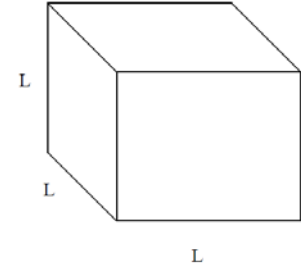
Consider a rectangular box (an infinite potential well in 3 dimensions) into which we will put otherwise free particles. We don't want the edges of the box to affect these particles in any way so we choose de-Broglie wavefunctions that have the periodicity of the edge lengths...

$$n_{xyz} \lambda = L, \quad n_{xyz} = 0, \pm 1, \pm 2, \pm 3 \dots$$

The particles' momentum in the three Cartesian directions is given by

$$p_{xyz} = h / \lambda = n_{xyz} h / L$$

From this we get the kinetic energy $E_{total} = \frac{h^2}{2mL^2} (n_x^2 + n_y^2 + n_z^2)$



In general each energy level of the particle will correspond to several different momentum vectors. Taking the energy of the particles to be governed by quantum constraints we have:

$$\varepsilon_j = \frac{h^2}{2mL^2} (n_x^2 + n_y^2 + n_z^2)$$

where L is the size of the box. We now evaluate the partition function sum.

$$Z = \sum_j e^{-\beta\varepsilon_j} \text{ where } j \text{ ranges from } -\infty \text{ to } +\infty$$

$$\equiv \sum_{n_x} e^{-\frac{\beta h^2}{2mL^2} n_x^2} \sum_{n_y} e^{-\frac{\beta h^2}{2mL^2} n_y^2} \sum_{n_z} e^{-\frac{\beta h^2}{2mL^2} n_z^2}$$

Most of the values of n_x, n_y, n_z are large so we replace these sums by integrals and get

$$Z = \int_{-\infty}^{+\infty} e^{-\frac{\beta h^2}{2mL^2} n_x^2} dn_x \int_{-\infty}^{+\infty} e^{-\frac{\beta h^2}{2mL^2} n_y^2} dn_y \int_{-\infty}^{+\infty} e^{-\frac{\beta h^2}{2mL^2} n_z^2} dn_z$$

Now $\int e^{-ax^2} dx = \sqrt{\frac{\pi}{a}}$

So

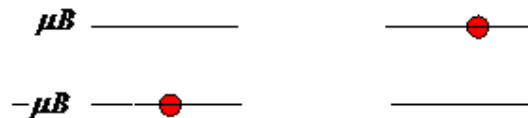
$$Z = \sqrt{\frac{\pi}{\beta h^2 / 2mL^2}} \times \sqrt{\frac{\pi}{\beta h^2 / 2mL^2}} \times \sqrt{\frac{\pi}{\beta h^2 / 2mL^2}} = V \left(\frac{2\pi m}{\beta h^2} \right)^{3/2}$$

B- The partition function for distinguishable and indistinguishable particles

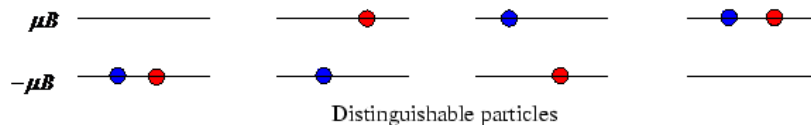
a- The N-particle partition function for distinguishable particles

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



$$Z_2 = e^{2\mu B \beta} + e^0 + e^0 + e^{-2\mu B \beta} = e^{2\mu B \beta} + 2 + e^{-2\mu B \beta} \\ = (e^{\mu B \beta} + e^{-\mu B \beta})^2 = (Z_1)^2$$

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

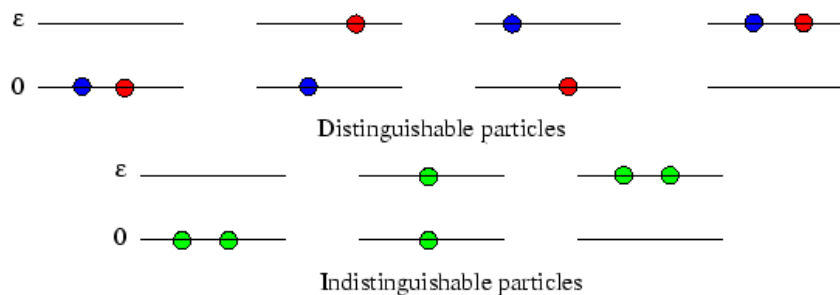
$$Z_N = e^{-N\mu B \beta} + \dots + \frac{N!}{n_\downarrow!(N-n_\downarrow)!} e^{-(N-2n_\downarrow)\mu B \beta} + \dots + e^{N\mu B \beta} \\ = (e^{-\mu B \beta} + e^{\mu B \beta})^N = (Z_1)^N$$

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.

As we know for the N -distinguish particles (as held for the paramagnet by their position in the lattice) we have $Z_N = (Z_1)^N$. 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

$$Z_2 = e^0 + 2e^{-\epsilon \beta} + e^{-2\epsilon \beta} = (Z_1)^2$$



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

$$Z_2 = e^0 + e^{-\epsilon\beta} + e^{-2\epsilon\beta} \neq (Z_1)^2$$

If we use $(Z_1)^2$, 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 $(Z_1)^N$ 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 $k_B T$) 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

$$Z_N = \frac{(Z_1)^N}{N!}$$

In the ideal gas, we can calculate the number of levels below, say, $2k_B T$, from $\int_0^{2k_B T} D(k) dk$ with $\hbar^2 k_{max}^2 / 2m = 2k_B T$, giving $2.1 n_Q V$. So we see that n_Q is a measure of the number of states available, and

we can use the approximation $Z_N = (Z_1)^N / N!$ provided $n_Q V \gg N$ (or $n_Q \gg n$). This is the **classical limit**. It is worth noting that, assuming a truly ideal gas which never condenses or solidifies, the **Sackur-Tetrode** equation is not valid for indefinitely low temperatures. It must be wrong, because as $T \rightarrow 0$, $n_Q \rightarrow 0$ and $S \rightarrow -\infty$. But we know that $S \rightarrow 0$ as $T \rightarrow 0$, because all the particles occupy the lowest energy level. But of course that is exactly the regime in which $Z_N = (Z_1)^N / N!$ is no longer valid.

C: APPLICABILITY OF MB DISTRIBUTION

Maxwell-Boltzmann statistics (classical regime) is valid under the dilute gas assumption $f(\epsilon_i) = \frac{N_i}{g_i} \ll 1$.

Use the definition $f(\epsilon_i) = \frac{N_i}{g_i} = N \frac{e^{-\beta \epsilon_i}}{Z}$, and for the ideal gas $z = V \left(\frac{2\pi mkT}{h^2} \right)^{3/2} = V n_Q$ where n_Q is the quantum concentration of the gas and has a dimension of m^{-3} .

$$f(\epsilon_i) = \frac{N_i}{g_i} = N \frac{e^{-\beta \epsilon_i}}{Z} = \left(\frac{N}{V} \right) \frac{1}{n_Q} e^{-\beta \epsilon_i}$$

For a gas with the density of air at STP, $n \approx 3 \times 10^{25} m^{-3}$. We have $n_Q \approx n$ for $T \approx 10^{-2} K$, so real gases are essentially always classical.

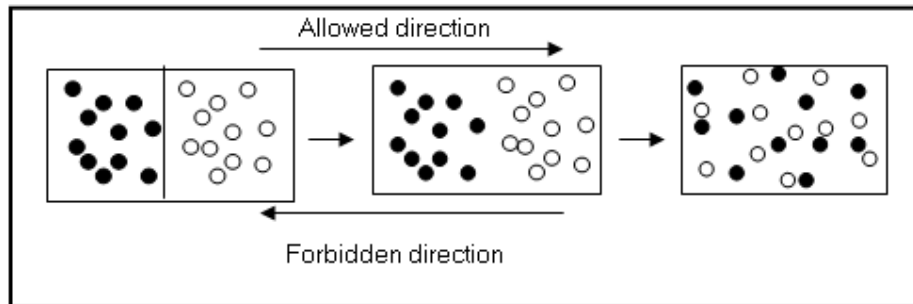
Note too that $n_Q \approx 1/\lambda^3$, where λ is the wavelength of a particle with energy $\frac{3}{2}k_B T$. This implies that the classical limit holds if the particle separation is large compared with their wavelength--a reasonable-sounding statement!

An example of **classical gas** is the Helium ($m = 6.65 \times 10^{-27}$ kg) under standard (STP) conditions, then $n_Q = 7 \times 10^{30} \text{ m}^{-3}$, $n = \frac{N}{V} = \frac{6.02 \times 10^{26}}{22.4} = 3 \times 10^{25} \text{ m}^{-3}$, $e^{-\beta \epsilon}$ in the order of unity and $f(\epsilon_i) = \frac{N_i}{g_i} = \frac{3 \times 10^{25}}{7 \times 10^{30}} \approx 4 \times 10^{-6}$.

An example of a **non-classical gas** is the conduction electrons in a metal; they are free to move within the metal and can be treated as a dense gas ($n \approx 10^{29} \text{ m}^{-3}$), but at room temperature ($n_Q \approx 10^{27} \text{ m}^{-3}$). So the quantum nature of the electron (specifically the fact that it is a fermion) becomes all important.

D: Gibbs' Paradox

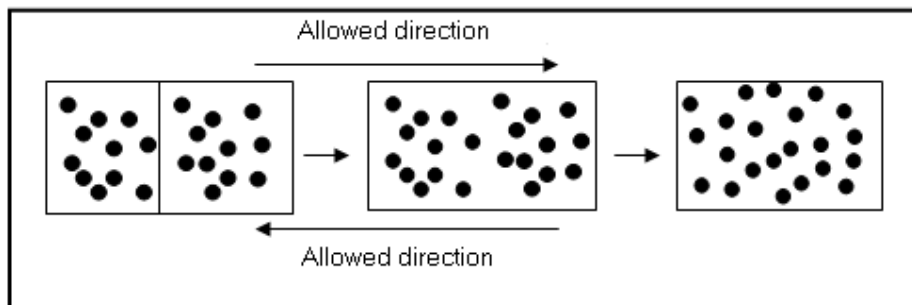
Gibbs paradox appears when we mix two similar ideal gases.



(A) *Mixing of two different ideal gases at constant temperature:* The mixing of two different gases is an irreversible process. If we consider mixing of two different gases (N_1, V_1, T) and (N_2, V_2, T) with $V = V_1 + V_2$ and $N = N_1 + N_2$ then the change in entropy of (**) is

$$\Delta S = S - (S_1 + S_2) = N_1 k \ln\left(\frac{V}{V_1}\right) + N_2 k \ln\left(\frac{V}{V_2}\right) > 0,$$

This gives the entropy of mixing for two different ideal gases and is in agreement with experiments. For $N_1 = N_2 = N$, $V_1 = V_2 = V/2$, we get $\Delta S = 2Nk \ln 2$.



(B) *Mixing of the same two ideal gases at constant temperature*: If the two gases are the same, the process is **reversal** one. The final entropy ought to be the same with, or without mixing, then the change in entropy is

$$\Delta S = S - (S_1 + S_2) = 0.$$

This result is in agreement with the thermodynamics of reversible processes and also with experiments, but contradict Eq. (**). The derivation of Eq. (**) does not depend on the identity of the molecules and would give the same increase in entropy as two different gases.

Comments:

1. In the case (A), mixing leads to diffusion of the molecules through the whole volume V (twice the initial volumes). There is a random mixing of the different molecules and so an increase in the disorder. This irreversible process and the increase of entropy make sense. The mixing is a process in which the positions of molecules one gas are interchanged with those of the other gas. Each such exchange creates new states, i.e. increasing the number of microstates or equivalently the entropy increases.
2. In case (B), any such interchange is always an interchange between two identical molecules. Therefore, no new state is created. In this case, the application of Eq. (**) overestimates the number of accessible states because classically we have taken all the molecules, even of the same gas, as distinguishable. To solve this paradox, we have to change Z by $z^N/N!$. The final results read

$$\ln Z = N \ln z - (N \ln N - N), \quad (+)$$

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

where $\sigma_o^* = S_o + 1 = \frac{3}{2} \ln \left(\frac{2\pi m k_B}{h^2} \right) + \frac{5}{2}$.

Eq. (+) has the properties of the entropy, and gives the correct answer for both cases, but it is not accurate at very low temperature.

Example: Using the corrected entropy formula (Sackur-Tetrode equation)

$$S = kN \ln \left(\frac{V}{N} \right) + \frac{3}{2} kN \left[\ln \left(\frac{2\pi m k_B}{h^2} \right) + \frac{5}{2} \right],$$

work out the entropy of mixing for the case of different gases and for identical gases, thus showing explicitly that there is no Gibbs paradox.

Answer:

(A) Mixing of two different ideal gases at the same temperature, the entropies of the gases before mixing are:

$$S_i = kN_i \ln \frac{V_i}{N_i} + \frac{3}{2} kN_i \left[\ln \left(\frac{2\pi m_i k_B T}{h^2} \right) + \frac{5}{2} \right], \quad i = 1, 2,$$

Mixing of the gases in the volume $V = V_1 + V_2$ implies the total entropy after mixing is

$$S_{total} = \sum_{i=1}^2 \left\{ k_B N_i \ln \frac{V}{N_i} + \frac{3}{2} k_B N_i \left[\ln \left(\frac{2\pi m_i k_B T}{h^2} \right) + \frac{5}{2} \right] \right\}$$

The entropy of mixing for the case of two different gases is:

$$\Delta S = S_{total} - (S_1 + S_2) = k_B N_1 \ln \frac{V}{V_1} + k_B N_2 \ln \frac{V}{V_2}$$

i.e. $\Delta S > 0$ for the mixing of two different gases.

(B) Mixing of two identical gases: $m_1 = m_2 = m$. Assume the densities are the same, i.e. $\frac{N}{V} = \frac{N_1}{V_1} = \frac{N_2}{V_2}$,

then (because they are identical, so will treat them as one with total volume V and total number N)

$$S_{total} = k_B N \ln \frac{V}{N} + \frac{3}{2} k_B N \left[\ln \left(\frac{2\pi m k_B T}{h^2} \right) + \frac{5}{2} \right]$$

The entropy of mixing is

$$\begin{aligned} \Delta S &= S_{total} - (S_1 + S_2) = N k_B \ln \left(\frac{V}{N} \right) - N_1 k_B \ln \left(\frac{V_1}{N_1} \right) - N_2 k_B \ln \left(\frac{V_2}{N_2} \right) \\ &= k(N - N_1 - N_2) \ln \frac{V}{N} = 0 \end{aligned}$$

$\Delta S = 0$ for the mixing of two identical gases with the same particle density, i.e. no Gibbs paradox.

$$\boxed{n_i = g_i e^{\alpha - \beta \varepsilon_i}} \quad (15)$$

Calculating e^α , from (15)

$$N = \sum_i n_i = \sum_i g_i e^{\alpha - \beta \varepsilon_i} = e^\alpha \sum_i g_i e^{-\beta \varepsilon_i}$$

$$e^\alpha = \frac{N}{\sum_i g_i e^{-\beta \varepsilon_i}} = \frac{N}{Z_{\text{sp}}}, \quad Z_{\text{sp}} = \sum_i g_i e^{-\beta \varepsilon_i}$$

$$n_i = N \frac{e^{-\beta \varepsilon_i}}{Z_{\text{sp}}}; \quad (16)$$

$$n_i = N g_i \frac{e^{-\beta \varepsilon_i}}{Z_{\text{sp}}} \quad (17)$$

Important differentiations

1-

$$\frac{\partial Z_{\text{sp}}}{\partial \beta} = \frac{\partial}{\partial \beta} \sum_i g_i e^{-\beta \varepsilon_i} = -\sum_i \varepsilon_i g_i e^{-\beta \varepsilon_i} \Rightarrow \boxed{\frac{\partial Z_{\text{sp}}}{\partial \beta} = -\sum_i \varepsilon_i g_i e^{-\beta \varepsilon_i}} \quad (18)$$

2-

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

$$\Rightarrow \boxed{\left(\frac{\partial Z_{\text{sp}}}{\partial V} \right)_{T,N} = -\beta \sum_i g_i e^{-\beta \varepsilon_i} \left(\frac{\partial \varepsilon_i}{\partial V} \right)_{T,N}} \quad (19)$$

Average energy

$$\bar{E} = \frac{1}{N} \sum_i n_i \varepsilon_i = \frac{1}{Z_{\text{sp}}} \sum_i \varepsilon_i g_i e^{-\beta \varepsilon_i} = -\frac{1}{Z_{\text{sp}}} \frac{\partial}{\partial \beta} \sum_i g_i e^{-\beta \varepsilon_i} = -\frac{1}{Z_{\text{sp}}} \frac{\partial Z_{\text{sp}}}{\partial \beta}$$

$$\Rightarrow \boxed{\bar{E} = -\frac{\partial}{\partial \beta} [\ln(Z_{\text{sp}})]} \quad (20)$$

Internal energy

$$\Rightarrow \boxed{U = N \langle E \rangle = N \bar{E} = -N \frac{\partial}{\partial \beta} [\ln(Z_{\text{sp}})]} \quad (21)$$

Average pressure

$$\bar{P} = -\left(\frac{\partial \bar{E}}{\partial V} \right)_{S,N} = \frac{1}{Z_{\text{sp}}} \sum_i g_i e^{-\beta \varepsilon_i} \left(-\frac{\partial \varepsilon_i}{\partial V} \right)_{T,N} = \frac{1}{\beta Z_{\text{sp}}} \left(\frac{\partial Z_{\text{sp}}}{\partial V} \right) = \frac{1}{\beta} \left(\frac{\partial \ln(Z_{\text{sp}})}{\partial V} \right)_{T,N}$$

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

Entropy

From (16)

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

$$\begin{aligned} S &= k_B \ln(\Omega) = k_B \ln\left(\frac{N!}{\prod_i n_i}\right) = k_B \left(N \ln N - \sum_i n_i \ln n_i \right) \\ S &= k_B \left(N \ln N - \sum_i n_i \frac{\ln n_i}{\ln N - \ln Z_{\text{sp}} - \beta \varepsilon_i} \right) = k_B \left(N \ln N - \underbrace{\ln N \sum_i n_i}_N + \underbrace{\ln Z_{\text{sp}} \sum_i n_i}_N + \underbrace{\beta \sum_i n_i \varepsilon_i}_U \right) \\ &\Rightarrow \boxed{S = k_B N \ln Z_{\text{sp}} + k_B \beta U} \end{aligned} \quad (23)$$

Diff (23)

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

Using:

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

$$(a)=(b) \Rightarrow \beta = \frac{1}{k_B T}$$

Helmholtz free energy

$$\begin{aligned} F &= U - TS = U - T(k_B N \ln Z_{\text{sp}} + k_B \beta U) = U - N k_B T \ln Z_{\text{sp}} - \underbrace{\beta k_B T U}_{1/\beta} \\ &\Rightarrow \boxed{F = -N k_B T \ln Z_{\text{sp}}} \end{aligned} \quad (24)$$

Entropy of an Isolated System from Z

We calculate here the entropy of an isolated system, starting from $S = k_B \ln(\Omega)$. If we write the statistical weight in terms of unique energy states rather than degenerate energy levels, becomes

$$\Omega = \prod_{\text{states}, i} \frac{1}{N_i!} \Rightarrow \ln \Omega = -\sum_i \ln N_i! = -\sum_i N_i \ln N_i + N$$

$$\text{Now } N_i = N \frac{e^{-\varepsilon_i/k_B T}}{Z_1}$$

$$\text{And } \ln N_i = \ln\left(\frac{N}{Z_1}\right) - \frac{\varepsilon_i}{k_B T}$$

So

$$S = -k_B \sum_i N_i \left(\ln \frac{N}{Z_1} - \frac{\varepsilon_i}{k_B T} \right) + k_B N = k_B \ln \frac{Z_1}{N} \left(\sum_i N_i \right) + N k_B + \frac{k_B}{k_B T} \sum_i N_i \varepsilon_i = N k_B \left(\ln \frac{Z_1}{N} + 1 \right) + \frac{U}{T}$$

$$\text{Now } Z_N = \frac{Z_1^N}{N!} \Rightarrow \ln Z_N = N \ln Z_1 - \ln N! = N \ln Z_1 - N \ln N + N = N \left(\ln \frac{Z_1}{N} + 1 \right)$$

Hence

$$S = k_B \ln Z_N + \frac{U}{T}$$

Another

Example: Calculate the most probable distribution for the probability, $P_i = \frac{N_i}{N}$, $N \rightarrow \infty$. Calculate S and F .

Answer: Use the conditions:

$$\sum_i P_i = 1 \quad \Rightarrow \quad \alpha \sum_i \delta P_i = 0, \text{ and}$$

$$\sum_i \varepsilon_i P_i = U \quad \Rightarrow \quad \beta \sum_i \varepsilon_i \delta P_i = 0,$$

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

At equilibrium $\delta S = \sum_i (1 + \ln P_i) \delta P_i = 0$, which gives $P_i = e^{-(\alpha + \beta \varepsilon_i)}$, $e^{-\alpha} = \frac{1}{Z}$

Substitute in S , we have

$$S = k\beta U + k \ln Z \quad \Rightarrow \quad F = U - TS = -kT \ln Z = -NkT \ln z.$$

Prove that:

$$S = -k_B \sum_{j=1}^{\Omega} p_j \ln p_j = k_B \ln \Omega$$

where the probabilities $p_j = 1/\Omega$ in the microcanonical ensemble, therefore:

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

where $\rho_i = p_i$ is the probability of the i 'th microstate, given by

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

Z is the canonical partition function given by $Z = \sum_i e^{-\beta E_i}$, and E_i is the energy of the system in i 'th microstate.

Q: use $\rho_i = \frac{e^{-\beta E_i}}{Z}$ in $S(E) = -k \sum_i \rho_i \log[\rho_i]$ to have $S = \beta k \langle E \rangle + k \log Z$. Compare the final expression with the thermodynamics expression $F = \langle E \rangle - TS$ to calculate the Helmholtz Free Energy in the form $F = -NkT \log Z$.

Answer:

$$\begin{aligned} S &= -k \sum_i \rho_i \log \rho_i = -k \sum_i \frac{e^{-\beta E_i}}{Z} \log \left(\frac{e^{-\beta E_i}}{Z} \right) = -k \sum_i \frac{e^{-\beta E_i}}{Z} (-\beta E_i - \log Z) \\ &= \beta k \sum_i \frac{e^{-\beta E_i} E_i}{Z} + \frac{k}{Z} \log Z \sum_i e^{-\beta E_i} \\ &= \beta k \langle E \rangle + \frac{k}{Z} \log(Z) Z \\ &= \beta k \langle E \rangle + k \log(Z) \end{aligned}$$

where $\langle E \rangle$ is the ensemble average of the energy of the system. The above equation can be rewritten as

$$F = \langle E \rangle - TS = -kT \log Z = -NkT \log Z.$$

$$S_N = k_B \ln \Omega_N = k_B \left[N \ln N - \sum_r N_r \ln N_r \right]$$

With $N_r = p_r N$, we have

$$S_N = k_B \left[N \ln N - \sum_r N p_r (\ln p_r + N) \right] = -Nk_B \sum_r p_r \ln p_r \Rightarrow S_1 = \underline{\underline{-k_B \sum_r p_r \ln p_r}},$$

$$S = -k_B \sum_r p_r [-\beta \epsilon_r - \ln Z] = k_B \sum_r p_r \epsilon_r + k_B \ln Z \sum_r p_r = \underline{\underline{\frac{U}{T} + k_B \ln Z}},$$

Or

Helmholtz Free Energy

$$-k_B T \ln Z = U - TS$$

If we define a new function, F , by the expression

$$F = -NkT \log Z.$$

then we have also

$$F = U - TS.$$

Thermodynamic Properties Derived from F

Eq(6.12) gives the 1st Law in entropy form for reversible processes

$$dU = T dS - p dV$$

Now

$$F = U - TS$$

and

$$dF = dU - T dS - S dT$$

$$\left. \begin{aligned} &= -S dT - p dV \\ &\equiv \left(\frac{\partial F}{\partial T} \right)_V dT + \left(\frac{\partial F}{\partial V} \right)_T dV \end{aligned} \right\}$$

so

$$S = - \left(\frac{\partial F}{\partial T} \right)_V \quad (8.4)$$

and

$$p = - \left(\frac{\partial F}{\partial V} \right)_T \quad (8.5)$$

from 1.TD we also have

$$T = - \left(\frac{\partial U}{\partial S} \right)_V \quad (8.6)$$

For a paramagnetic system, the analogous constraint to a constant volume (rigid system boundary) is a constant external magnetic field. If this field changes then work is done on reorienting the magnetic dipoles, changing the state of internal magnetisation. So for a magnetic system we write

$$dF = -S dT - \mu_0 M dH \quad (8.7)$$

This leads to the quantities derived for the magnetic system...

$$S = -\left(\frac{\partial F}{\partial T}\right)_V \quad (8.8)$$

and
$$M = -\frac{1}{\mu_0}\left(\frac{\partial F}{\partial H}\right)_T \quad (8.9)$$

and
$$T = -\left(\frac{\partial U}{\partial S}\right)_H \quad (8.10)$$

Pressure of Ideal Gas

By way of illustration we shall use eq(8.5) to derive the pressure of an ideal gas.

For a gas of N molecules we have $F = -k_B T \ln Z_N$ where, for indistinguishable particles, we have from,

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

and we have already calculated Z_1 as ...

$$Z_1 = V \left(\frac{2\pi m}{\beta h^2} \right)^{3/2}$$

So
$$F = -k_B T (\ln Z_1^N - \ln N!) \\ = -k_B T \left(N \ln V + N \ln \left(\frac{2\pi m}{\beta h^2} \right)^{3/2} - \ln N! \right)$$

using eq(8.5)
$$p = -\left(\frac{\partial F}{\partial V}\right)_{T,\beta} = Nk_B T \frac{1}{V}$$

or
$$pV = Nk_B T, \quad (8.11)$$

a very familiar result.

Entropy

We shall now show that eq(8.5) gives the same result as the derivations of entropy in sections 7.2 or 7.3. For the entropy of N particles, we have

$$S = k_B \ln Z_N + k_B T \frac{\partial}{\partial T} \ln Z_N$$

and

$$-\frac{1}{k_B T} \frac{d}{d\beta} = \frac{d}{dT}$$

so

$$S = k_B \ln Z_N - \frac{1}{T} \frac{\partial}{\partial \beta} \ln Z_N$$
$$= k_B \ln Z_N + \frac{U}{T}, \quad \text{using eq(7.1) for internal energy}$$