

Definitions:

Microstate: State of the system, as defined in terms of the behaviour of all constituent atoms;

Macrostate: State of the system, as defined in terms of macroscopic variables

Equal *a priori* probabilities: equal probability of happening

Ensemble: Collection of a large number of copies of the system, each in one of the allowed microstates

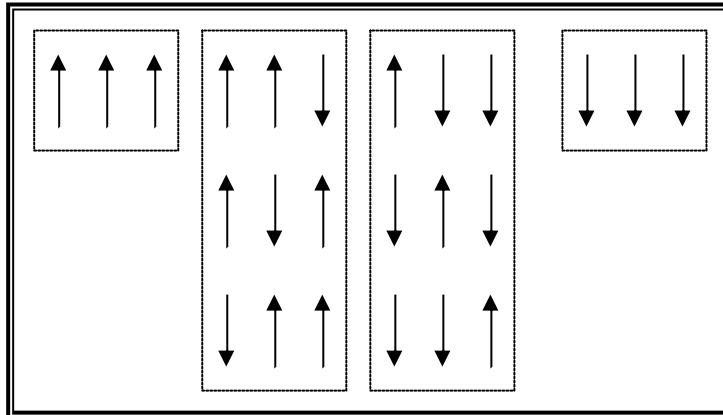


Figure 1. The whole system (in double lines) is an *ensemble*. Each dotted box is a *macrostate* (4 of these). Each group of 3 arrows is a *microstate* (8 of these).

Microcanonical ensemble: copies in the system are isolated from each other

Canonical ensemble: copies in the system are in thermal contact

Microcanonical Ensemble:

Suppose equal *a priori* probabilities:

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

Where: $\Omega \equiv$ statistical weight = # of microstates in a given macrostate

Notice that this must imply:

$$\sum_{i=0}^{\Omega} p_i = \Omega \cdot \frac{1}{\Omega} = 1$$

An example of this is the standard combinatorial system... number of ways to split N identical objects into 2 smaller groups: n and $(N - n)$. This is given by:

$$\# \text{ ways} = \frac{N!}{n!(N-n)!} = \binom{N}{n} = {}^N C_n$$

Thus, applying to some system, where we want how many ways (i.e. how many microstates exist) we can arrange a system to have the same energy (i.e. in one macrostate, as energy is a macroscopic variable):

$$\Omega = \frac{N!}{n!(N-n)!}$$

e.g. $\Omega(E, V, N)$ would be the number of ways to arrange a system so that all combinations would have the same macroscopic variables E, V, N . That is, the number of different microstates in a given macrostate.

We can relate this statistical weight to the entropy, via the Boltzmann Law:

$$S = k_B \ln \Omega$$

An example of such a system is that of the spin $\frac{1}{2}$ paramagnet.

Suppose we have N independent spin sites, each site can contain a dipole which is parallel, or anti-parallel to an external magnetic field; denoted by \uparrow or \downarrow . Notice that the spins are independent, and have an equal *a priori* probability of occurring. Thus, we can use the microcanonical ensemble.

If we want to count how many microstates will have the same energy, we may write:

$$\Omega(N, n_{\uparrow})$$

Which will find the number of microstates with a given number of parallel spins: up spins: n_{\uparrow} . Thus:

$$\Omega(N, n_{\uparrow}) = \frac{N!}{n_{\uparrow}!(N-n_{\uparrow})!}$$

Suppose we add up how many components (microstates) are in each macrostate, for all macrostates:

$$\sum_{n_{\uparrow}=0}^N \Omega(N, n_{\uparrow}) = 2^N \equiv \Omega(N)$$

Thus, counting the total number of microstates yields: 2^N

A useful mathematical approximation is that of *Stirling's Approximation*:

$$\lim_{n \rightarrow \infty} \ln(n!) = n \ln n - n$$

Now, looking at the entropy of the paramagnetic system:

$$S = k_B \ln(\Omega(N, n_{\uparrow}))$$

$$\begin{aligned}
 &= k_B \ln \left(\frac{N!}{n_\uparrow! (N - n_\uparrow)!} \right) \\
 &= k_B [\ln N! - \ln n_\uparrow! - \ln (N - n_\uparrow)!] \\
 &= k_B [N \ln N - N - (n_\uparrow \ln n_\uparrow - n_\uparrow) - ((N - n_\uparrow) \ln (N - n_\uparrow) - (N - n_\uparrow))]
 \end{aligned}$$

After using Stirling's approximation. Hence, an expression for the entropy of the system may be written:

$$S = k_B [n \ln N - n_\uparrow \ln n_\uparrow - (N - n_\uparrow) \ln (N - n_\uparrow)]$$

Now, from the fundamental thermodynamic relation for such a magnetic system:

$$dE = TdS - mdB \quad \Rightarrow \quad dS = \frac{1}{T}dE + \frac{m}{T}dB$$

Thus, we may note that $S(E, B)$; hence we may write:

$$dS = \left(\frac{\partial S}{\partial E} \right)_B dE + \left(\frac{\partial S}{\partial B} \right)_E dB$$

Thus, comparing the two, we get expressions for the temperature and magnetic moment, in terms of differentials of the entropy:

$$\frac{1}{T} = \left(\frac{\partial S}{\partial E} \right)_B \quad \quad \frac{m}{T} = \left(\frac{\partial S}{\partial B} \right)_E$$

Now, we notice that the energy of the system may be written in terms of the number of up- and down spins, multiplied by their magnetic dipole moment, and the magnetic field. Noting that $N = n_\uparrow + n_\downarrow$.

$$\begin{aligned}
 E &= n_\uparrow (-mB) + n_\downarrow (mB) \\
 &= (N - 2n_\uparrow)mB
 \end{aligned}$$

Hence, doing the differentiation & rearranging:

$$\begin{aligned}
 \frac{1}{T} &= \left(\frac{\partial S}{\partial E} \right)_B & \frac{m}{T} &= \left(\frac{\partial S}{\partial B} \right)_E \\
 &= \left(\frac{\partial S}{\partial n_\uparrow} \right) \left(\frac{\partial n_\uparrow}{\partial E} \right) & &= \left(\frac{\partial S}{\partial n_\uparrow} \right) \left(\frac{\partial n_\uparrow}{\partial B} \right) \\
 &= \frac{k_B}{2mB} \ln \left[\frac{n_\uparrow}{(N - n_\uparrow)} \right] = \frac{k_B}{2mB} \ln \left[\frac{n_\uparrow}{n_\downarrow} \right] & &= -\frac{k_B T}{2mB^2} \ln \left[\frac{n_\uparrow}{n_\downarrow} \right]
 \end{aligned}$$

This example illustrates how properties of the system can be found, once the statistical weight has been calculated; and the fundamental thermodynamic relation for the system written.

Canonical Ensemble:

Suppose we have a system in a heat bath, where the system has a constant energy E_0 . Now, if we want to find the probability that we will find the system in a state p_i , with energy e_i , where $e_i \ll E_0$. Now, there will be $\Omega(E_0 - e_i)$ microstates with this energy. Thus, we may write:

$$p_i \propto \Omega(E_0 - e_i)$$

Or, writing a properly normalised probability:

$$p_i = \frac{\Omega(E_0 - e_i)}{\sum_i \Omega(E_0 - e_i)}$$

Now, by the Boltzmann law $S = k_B \ln \Omega$:

$$\Omega(E_0 - e_i) = e^{\frac{S(E_0 - e_i)}{k_B}}$$

Now, when we expand the argument of the exponential by a Taylor series:

$$S(E_0 - e_i) = S(E_0) - e_i \left. \frac{\partial S}{\partial E} \right|_{E=E_0} + \dots$$

But, by the fundamental thermodynamic relation:

$$\frac{\partial S}{\partial E} = \frac{1}{T}$$

Thus:

$$p_i = \frac{e^{\frac{S(E_0) - e_i}{k_B T}}}{\sum_i e^{\frac{S(E_0) - e_i}{k_B T}}} = \frac{e^{-e_i b}}{\sum_i e^{-e_i b}} \quad \mathbf{b} \equiv \frac{1}{k_B T}$$

Hence, we may write the probability of finding the system (p_i) with a particular energy (e_i) in terms of its partition function, which comes about as a normalisation constant:

$$p_i = \frac{1}{Z} e^{-e_i b} \quad Z \equiv \sum_i e^{-e_i b}$$

Where the sum in the partition function is over all distinguishable states, which is what was implied in the derivation using the statistical weight. This is called the *Boltzmann Distribution*.

Notice that in the summation of states for the partition function, only distinguishable states were counted. This is condition was imposed during the derivation of the distribution. If there is a degeneracy of energy levels – that is, there is a number of different ways to make the a state with the same energy – given by a factor $g(\mathbf{e}_i)$, then the partition function may be written more completely as:

$$Z_1 = \sum_i g(\mathbf{e}_i) e^{-e_i b}$$

We may write the average energy of the system as:

$$\begin{aligned} \langle E \rangle &= \sum_i \mathbf{e}_i p_i \\ &= \sum_i \left\{ \frac{\mathbf{e}_i e^{-e_i b}}{e^{-e_i b}} \right\} \\ &= - \frac{\partial \ln Z}{\partial b} \end{aligned}$$

Similarly, the heat capacity:

$$\begin{aligned} \langle c_V \rangle &\equiv \left(\frac{\partial \langle E \rangle}{\partial T} \right)_V \\ &= k_B b^2 \left(\frac{\partial^2 \ln Z}{\partial b^2} \right)_V \end{aligned}$$

Now, the general form of the system entropy is given by:

$$\langle S \rangle = -k_B \sum_i p_i \ln p_i$$

So, for this case, with the above expressions for the probability:

$$\langle S \rangle = -k_B \sum_i p_i \ln \frac{e^{-e_i b}}{Z}$$

$$\begin{aligned}
 &= -k_B \sum_i p_i (-\mathbf{b} \cdot \mathbf{e}_i - \ln Z) \\
 &= k_B \mathbf{b} \underbrace{\sum_i p_i \mathbf{e}_i}_{=\langle E \rangle} + k_B \ln Z \underbrace{\sum_i p_i}_{=1} \\
 &= \frac{\langle E \rangle}{T} + k_B \ln Z
 \end{aligned}$$

Now, Helmholtz free energy is defined as $F = E - TS$, thus, we can rewrite this as, dropping the “expectation” symbols:

$$F = -k_B T \ln Z$$

Now for a hydrostatic system:

$$F = E - TS \quad \Rightarrow \quad dF = -pdV - SdT$$

Hence, we may write $F(V, T)$, and thus:

$$dF = \left(\frac{\partial F}{\partial V} \right)_T dV + \left(\frac{\partial F}{\partial T} \right)_V dT$$

Hence, comparing:

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

Or, analogously for a magnetic system:

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

Thus, once the partition function has been found, all other properties of the system may be calculated. This is the analogy to the statistical weight in the microcanonical ensemble.

Finding Partition Functions: simple systems:

Suppose we have a single magnetic dipole in a magnetic field. The possible energies of the system are given by:

$$\mathbf{e}_\uparrow = -\mathbf{m}\mathbf{B} \quad \mathbf{e}_\downarrow = \mathbf{m}\mathbf{B}$$

Hence, the partition function, for a single dipole:

$$Z_1 = \sum_i e^{-\mathbf{e}_i \cdot \mathbf{b}} = e^{\mathbf{m}\mathbf{B} \cdot \mathbf{b}} + e^{-\mathbf{m}\mathbf{B} \cdot \mathbf{b}} = 2 \cosh(\mathbf{m}\mathbf{B} \cdot \mathbf{b})$$

Another example is that of a quantum-mechanical energy level system:



Figure 2. The possible configurations of a system with one particle, and two energy levels.

Now, the partition function for a single particle, as described above can be written:

$$Z_1 = \sum_i e^{-e_i b} = e^{-e_1 b} + e^{-e_2 b}$$

Now, suppose we have a similar system, but with two *distinguishable* particles:

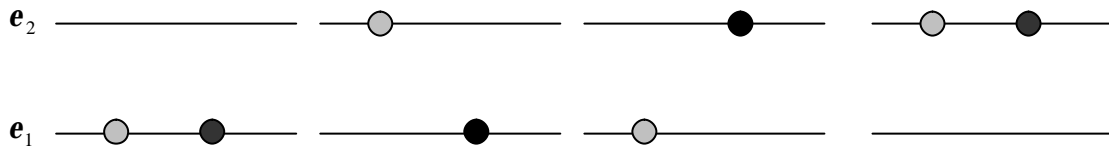


Figure 3. The possible configurations of a system with two distinguishable particles, with two energy levels.

The partition function for the 2-particle system in Figure 3. may be written:

$$Z_2^{dist} = \sum_i e^{-e_i b} = e^{-2e_1 b} + 2e^{-(e_1+e_2)b} + e^{-2e_2 b}$$

Now, notice that $Z_2^{dist} = Z_1^2$.

Infact, it is true in general, for *distinguishable particles* only, that the N -body partition function may be found by the N^{th} power of the one-body partition function:

$$Z_2^{dist} = Z_1^N$$

Suppose that the particles in Figure 3. were indistinguishable. Thus, drawing the configurations again, with the restriction that the particles are indistinguishable:

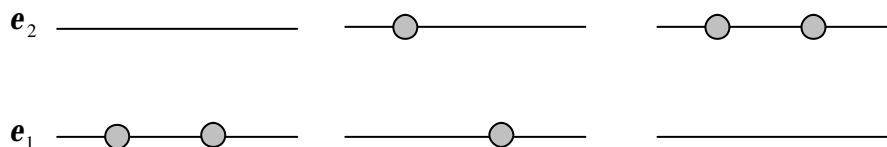


Figure 4. Possible configurations for a two particle system, where the particles are indistinguishable.

If the two-particle partition function is written for the system in Figure 4:

$$Z_2^{indist} = \sum_i e^{-\mathbf{e}_i \mathbf{b}} = e^{-2\mathbf{e}_1 \mathbf{b}} + e^{-(\mathbf{e}_1 + \mathbf{e}_2) \mathbf{b}} + e^{-2\mathbf{e}_2 \mathbf{b}}$$

Notice that we **cannot write** $Z_N^{indist} = Z_1^N$. The only way we can do this, is in the “classical limit”; where there are many more accessible energy states than particles. In this case:

$$Z_N^{indist} \approx \frac{Z_1^N}{N!}$$

Energy States of Diatomic Molecules:

Vibrational States:

From quantum mechanics, we know that the energy states of a 1D SHO can be written:

$$\mathbf{e}_n = \left(n + \frac{1}{2} \right) \hbar \omega \quad n = 1, 2, 3, \dots$$

The one body partition function will turn out to be:

$$Z_1 = \frac{1}{2 \sinh\left(\frac{1}{2} \hbar \omega \mathbf{b}\right)}$$

And the average energy may be calculated:

$$\begin{aligned} \langle E \rangle &= - \left(\frac{\partial \ln Z}{\partial \mathbf{b}} \right) \\ &= \frac{1}{2} \hbar \omega \coth\left(\frac{1}{2} \hbar \omega \mathbf{b}\right) \end{aligned}$$

Looking at high and low temperature limits, remembering that $T \propto \frac{1}{\mathbf{b}}$:

$$\begin{aligned} \lim_{T \rightarrow 0} \langle E \rangle &= \frac{1}{2} \hbar \omega & \hbar \omega \gg \mathbf{b} \\ \lim_{T \rightarrow \infty} \langle E \rangle &= k_B T & \hbar \omega \ll \mathbf{b} \end{aligned}$$

Rotational States:

Again, from QM, we know that the energy states of a rigid-rotor can be expressed as:

$$\mathbf{e}_\ell = \frac{\ell(\ell+1)\hbar^2}{2I} \quad \ell = 0, 1, 2, \dots$$

Also, need to remember that there is a degeneracy of $(2\ell+1)$ per state. Thus, the partition function is:

$$Z_1 = \sum_{\ell=0}^{\infty} (2\ell+1) e^{-\frac{\ell(\ell+1)\hbar^2}{2I} \mathbf{b}}$$

In the high temperature limit, that is there are many thermally accessible energy levels, and that $k_B T \gg \frac{\hbar^2}{2I}$, the discrete sum is very well approximated by an integral:

$$\lim_{T \rightarrow \infty} Z_1 = \int_0^{\infty} d\ell (2\ell+1) e^{-\frac{\ell(\ell+1)\hbar^2}{2I} \mathbf{b}}$$

Which may be evaluated with the substitution $x = \ell(\ell+1)$ to give:

$$\lim_{T \rightarrow \infty} Z_1 = \frac{2I}{\hbar^2 \mathbf{b}} = \frac{2Ik_B T}{\hbar^2}$$

And the corresponding high-temperature limit of the internal energy:

$$\lim_{T \rightarrow \infty} \langle E \rangle = k_B T$$

Translational States:

Suppose a single particle in a spherical system. We can define the Density of States to be the number of states in a spherical shell $k \rightarrow k + dk$ as:

$$D(k)dk = \frac{Vk^2}{2\mathbf{p}^2} dk$$

And then the partition function can be found to be:

$$Z_1 = \int_0^{\infty} D(k) e^{-\mathbf{b}e(k)} dk \quad e(k) = \frac{\hbar^2 k^2}{2m}$$

In the evaluation of the integral, we will end up being able to define the quantum concentration as:

$$n_Q \equiv \left(\frac{m}{2\mathbf{p}\hbar^3} \right)^{\frac{2}{3}}$$

Thus, the single-particle partition function can be found to be:

$$Z_1 = Vn_Q$$

And the average internal energy due to translational motion, with 3 degrees of freedom:

$$\langle E \rangle = \frac{3}{2} k_B T$$

This leads quite nicely onto the *Equipartition theorem*:

Equipartition Theorem:

For each degree of freedom of a system with an energy which is *quadratic* in either position or momentum, the average energy is $\frac{1}{2}k_B T$; in the corresponding high temperature limit.

So, as examples:

Vibrational:	$E = \frac{1}{2}m\dot{x}^2 + \frac{1}{2}kx^2$	2dofs	$\lim_{T \rightarrow \infty} \langle E \rangle = k_B T$
Rotational:	$E = \frac{1}{2}I_1\dot{\mathbf{q}}_1^2 + \frac{1}{2}I_2\dot{\mathbf{q}}_2^2$	2dofs	$\lim_{T \rightarrow \infty} \langle E \rangle = k_B T$
Translational:	$E = \frac{1}{2}m(\dot{x}^2 + \dot{y}^2 + \dot{z}^2)$	3dofs	$\lim_{T \rightarrow \infty} \langle E \rangle = \frac{3}{2}k_B T$