

**Department of Physics, Durham University**

**Foundations of Physics 2B/3C 2019-2020**

# **STATISTICAL MECHANICS**

*Entropy is introduced in thermodynamics as that rather shadowy function of the state of a system associated with the second law of thermodynamics. The essence of the idea concerns the direction (the 'arrow of time') of a spontaneous or natural process.....In a natural process, the second law tells us that the entropy,  $S$ , of the universe (or any isolated system) never decreases.....All this is a statement of probability rather than necessity – it is possible in principle to separate a mixture of sugar and sand, but it is almost infinitely improbable. And thermodynamics is the science of the probable! Statistical physics enables one to discuss entropy in terms of probability in a direct and simple way.*

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## 21. Statistical Mechanics Introduction

This subject is closely related to thermodynamics and provides a way to conveniently describe assemblies containing large numbers of particles, which may or may not be distinguishable. We first note that the microscopic view of system becomes incredibly detailed if we try to consider all the molecules in a system ( $10^{23}$  for one mole), so it makes sense to appeal statistical methods to help us. The subject uses probabilistic methods to provide predictions of the thermodynamic properties of materials. As we shall see, at thermal equilibrium substances will always end up occupying their most likely state, which in the terminology of statistical physics is the observable macrostate that contains the most microstates. We will also find that it is the concept of entropy that links the subjects of statistical mechanics and thermodynamics together.

### Macro and Microstates

The macrostate of a system provides a description of how the system is behaving on average. A microstate on the other hand, is the most detailed description of a system or assembly of particles that we could possibly imagine. In any system, the number of microstates is finite and is related to the ways we can arrange the individual particles within that system. We denote the number of microstates in a macrostate by  $\Omega$ . Any system will be in one of many equally likely microstates. When we observe a system, we measure its macrostate, the state of the system having most microstates associated with it, corresponding to equilibrium. In other words, a system appears to choose a macroscopic configuration that maximises the number of associated microstates.

In a thermal system, we would need to know the position and energy of every particle to determine its particular microstate, whereas a macrostate is simply determined by the macroscopic parameters (pressure, volume etc.). The macrostate that is measured will have a huge number of microstates associated with it. This means that the thermodynamic limit is defined by a system's macrostate, which is described by just enough information to allow the thermodynamic state to be well defined.

#### Example 21.1

#### Example 21.2

A box contains 100 coins. After shaking the lid is opened and the contents investigated. The 100 coins will be arranged in one of  $2^{100} \approx 10^{30}$  ways. Since each of which is equally likely to happen, it has a  $\sim 1/10^{30}$  chance of occurring. To identify a microstate each coin would need an individual label. It is thus much simpler to measure the macrostate –the total number of heads and total number of tails. Example macro and microstates are given below

Macrostate	Number of Microstates
50 H and 50 T	$100! / 50! 50! \sim 4 \times 10^{27}$
53 H and 47 T	$100! / 50! 47! \sim 3 \times 10^{27}$
90 H and 10 T	$100! / 90! 10! \sim 1 \times 10^{13}$

## Counting Particles

Statistical physics can be used to consider both distinguishable and indistinguishable particle types. In both cases, the particles must be weakly interacting since if no interactions are present, an equilibrium state cannot be attained. If we look at the behaviour of a large number of particles (too many for us to handle individually) each particle will have an assigned energy, with some condition being placed on the total system energy. The interaction energies between the particles, needed for equilibrium, will be much less than the particle energies, hence the term weakly interacting.

### Distinguishable particles

These can, in principle, be identified by some label. For example, the atoms in a solid can be distinguished by their type and position on the lattice. Each atom will each be in some energy state,  $\varepsilon_j$ , but we are not concerned with the detailed quantum mechanics of those levels. Instead, we distribute the total number of particles,  $N$ , by states (usually defined by the subscript  $j$ ) and this tells us the number of particles,  $n_j$ , having energy  $\varepsilon_j$ . There will then be a number of different energy levels possible. We can count the number of microstates of the system

$$\Omega = \frac{N!}{\prod_j n_j!}.$$

$N!$  is the number of ways of arranging the  $N$  particles in the system ( $N$  for the first particle,  $(N - 1)$  for the second etc.), but we are not bothered as to how the  $n_j$  particles of energy  $\varepsilon_j$  are arranged within each level, hence the division by the product  $\prod_j n_j! = n_1! \times n_2! \times n_3! \times \dots$

#### Example 21.3

Dealing with large numbers

As we have seen, when we are dealing with even quite small systems (100 coins) the number of microstates in a given macrostate becomes large very quickly. In a real system, the number of particles is much larger than this (one mole has  $6.01 \times 10^{23}$  molecules, for example) so the most probable macrostate will have an enormous number of microstates associated with it. The Stirling approximation is thus very useful in this situation

$$\ln X! \cong X \ln X - X$$

#### Example 21.4

$\ln 5! = \ln 120 = 4.79$ . The Stirling approximation gives  $5 \ln 5 - 5 = 3.04$ , a 40% underestimate.

$\ln 100! = 364$ , and using Stirling we obtain 361, a 1% underestimate

$\ln 1000! = 5912$ , Stirling gives 5908 which is just a 0.1% underestimate.

## 22. Statistical Definitions of Temperature and Entropy

If we consider two systems in thermal contact, which are thermally isolated from the rest of the world, they can only exchange energy with each other, so the total energy is  $E = E_1 + E_2$ , where  $E_i$  is the energy of each respective system. After some time an equilibrium situation is reached, which

will usually be at some temperature,  $T$ . The equilibrium situation is described by the macrostate having the most microstates associated with it, i.e.) the preferred macrostate, providing: each possible microstate has an equal chance of occurring; the system's internal dynamics allow the microstates to continually change; and given enough time, the system explores all microstates, spending an equal amount of time in each (the ergodic hypothesis).

Consequently, the system will most likely be found in the configuration represented by the most microstates. When the system is large enough system, the phrase 'most likely' can be replaced by absolutely, overwhelmingly likely! Maximising the total number of microstates of the system, gives us a statistical definition of temperature.

$$\beta = \frac{1}{k_B T} = \frac{d(\ln \Omega)}{dE}.$$

#### Proof 22.1

The entropy of a system in a particular macrostate is given in terms of the number of microstates of the system,

$$S = k_B \ln \Omega$$

#### Proof 22.2

##### Example 22.1

If we consider the entropy change of a Joule expansion, we can show the statistical and thermodynamic answers are identical. Consider a gas whose volume doubles in size by the removal of a partition in a container.

For one mole of ideal gas, doubling in size isothermally,  $U = U(T)$  for an ideal gas, so  $dU = 0$ , and the first law ( $dU = \delta Q + \delta W$  becomes  $TdS = pdV$

$$\Delta S = \int_V^{2V} \frac{p}{T} dV = \int_V^{2V} \frac{R}{V} dV = R \ln 2.$$

Statistically, on removing partition, any single molecule can exist on either the left or right hand side, i.e.) it can be placed in two ways. One mole thus has  $2^{N_A}$  ways of placing the molecules. The number of possible microstates becomes larger by a multiplicative factor of  $2^{N_A}$ , so

$$\begin{aligned}\Omega_{After} &= 2^{N_A} \Omega_{Before} \\ S_{After} &= k_B \ln \Omega_{After} = k_B \ln(2^{N_A} \Omega_{Before}) = k_B \ln(2^{N_A}) + \ln \Omega_{Before} \\ &= N_A k_B \ln 2 + k_B \ln \Omega_{Before}. \\ S_{Before} &= k_B \ln \Omega_{Before} \\ \Delta S &= N_A k_B \ln 2 = R \ln 2.\end{aligned}$$

This statement for entropy was postulated by Boltzmann after considering the canonical distribution of particles, which is more commonly referred to as the **Boltzmann distribution**. Furthermore, entropy is related to probability with a system's entropy depending upon the number of states in which it can exist. If a macrostate is made up from a large number of microstates that are hard to measure, it is possible to show that the entropy is given by,  $S = -k_B \sum_j P_j \ln P_j$  where  $P_j$  is probability that the particle is in the  $j$ th macrostate.

For a system of  $N$  microstates, each of which is equally likely, the chance of a particle being in a particular group of microstates, with  $n_j$  particles in the  $j$ th microstate is  $P(j) = n_j/N$ . The total entropy is  $S_{tot} = k_B \ln N$  but it can't be measured. The microstate entropy is

$$S_{micro} = \sum_j P_j S_j = \sum_j P_j k_B \ln n_j.$$

The total entropy is  $S_{tot} = k_B \ln N$ , which is our measured entropy,  $S$  plus the entropy from being able to be in different microstates within the macrostates,  $S_{tot} = S + S_{micro}$ . Hence,

$$S = k_B \ln N - k_B \sum_j P_j \ln n_j = -k_B \sum_j P_j \ln \left( \frac{n_j}{N} \right) = -k_B \sum_j P_j \ln P_j.$$

## 23. The Boltzmann Distribution

We wish to consider the distribution of a collection of distinguishable particles in thermal equilibrium, or how a collection of particles, at temperature,  $T$ , are distributed into states having energy  $\varepsilon_j$ . To do this we consider the most probable arrangement, which means finding the macrostate having the maximum number of microstates associated with it.

### Ensembles

This idea was introduced by Gibbs in which we mentally make lots of copies of a system to allow us to describe things probabilistically. Two concern us: the micro-canonical ensemble, an ensemble of systems each having the same fixed energy; and the canonical ensemble, an ensemble of systems, each of which can exchange energy with a heat reservoir that fixes and defines the system's temperature.

The canonical ensemble is described by a probability distribution,

$$P(\varepsilon) \propto \exp\left(-\varepsilon/k_B T\right) = \exp(-\beta T).$$

This is known as the Boltzmann distribution and it describes how a small system behaves when it is coupled to a heat reservoir. The distribution must be normalised giving the probability that a given particle will have energy,  $\varepsilon_j$  at temperature,  $T$  as

$$P(\text{state } j) = \frac{\exp\left(-\varepsilon_j/k_B T\right)}{\sum_i \exp\left(-\varepsilon_i/k_B T\right)}.$$

The sum on the bottom is known as the partition function.

Let's look at this for determining the number of particles  $n_j$  having energy  $\varepsilon_j$ . As we are dealing with large numbers, the Stirling approximation can be used and the most probable macrostate is found by maximising  $\ln \Omega$ . Various conditions exist on the particle number and energy,

$$\sum_j (\ln(n_j)) dn_j = 0 \quad ; \quad \sum_j dn_j = 0 \quad ; \quad \sum_j \varepsilon_j dn_j = 0.$$

The trick of Lagrange multipliers can then be used to solve this problem so that  $\sum_j (\ln n_j + \alpha + \beta \varepsilon_j) dn_j = 0$ . For this to be true, the term in brackets must be identically zero and this gives the

Boltzmann distribution  $n_j = \exp(-\alpha - \beta \varepsilon_j)$ . Here,  $\alpha$  is the normalisation factor, which is related to the partition function, whilst  $\beta = 1/k_B T$ , is related to the temperature. Both of these can be found using thermodynamics. This gives the final Boltzmann distribution, telling us the number of particles in state  $\varepsilon_j$  as

$$n_j = \frac{N}{Z} \exp\left(-\frac{\varepsilon_j}{k_B T}\right)$$

### Proof 23.1

Probabilistically, the distribution centres on the macrostate containing the most microstates.

## Boltzmann Distribution Derivation

*I don't expect you to remember the derivations of this, or any of the other distributions. However, you should understand how this arises and be able to use them to do some simple physics.*

To obtain the distribution, we maximise the number of macrostates. This is obtained from the way of arranging  $N$  particles into  $j$  states with  $n_j$  particles in the  $j$ th state. Because the system contains a finite number of particles, the minimisation takes place under the following conditions:

- The total particle number is fixed, so  $N = \sum_j n_j$ ;
- The total energy of the system, its internal energy, is also fixed,  $E = \sum_j \varepsilon_j n_j$ .

(Note in statistical physics,  $E$  is normally used for the system energy, but it can be thought of as corresponding to,  $U$ , the internal energy of classical thermodynamics.)

Since we are dealing with a large number of particles, we maximise  $\ln \Omega$  and use the Stirling approximation to make things easier.

The total differential of  $\ln \Omega$  is given by

$$d(\ln \Omega) = \left[ \frac{\partial(\ln \Omega)}{\partial n_1} \right] dn_1 + \left[ \frac{\partial(\ln \Omega)}{\partial n_2} \right] dn_2 + \dots + \left[ \frac{\partial(\ln \Omega)}{\partial n_i} \right] dn_i.$$

This tells us how we can vary the number of particles in each energy level by making small changes  $dn_j$  to the number in each level,  $n_j$  individually. When we are at a maximum this differential will equal zero and it gives a condition on the most probable state.

Taking the natural logarithm of  $\Omega = N! / \prod_j n_j!$ , and applying the Stirling Approximation gives

$$\ln \Omega = N \ln N - N - \sum_j (n_j \ln(n_j) - n_j) = N \ln N - \sum_j n_j \ln(n_j).$$

Here, we used the fact that  $\sum_j n_j = N$ . Differentiating this last expression gives

$$\begin{aligned} d(\ln \Omega) &= \left[ \frac{\partial}{\partial n_j} \left( N \ln N - \sum_j n_j \ln(n_j) \right) \right] dn_j \\ &= \left[ \frac{\partial N}{\partial n_j} \ln(N) + N \frac{1}{N} \frac{\partial N}{\partial n_j} - \sum_j \left\{ \ln(n_j) + \frac{1}{n_j} \times n_j \right\} \right] dn_j. \end{aligned}$$

$N$  is a constant, so  $\frac{\partial N}{\partial n_j} = 0$  and this simplifies to  $d(\ln \Omega) = -\sum_j \{ \ln n_j + 1 \} dn_j$ . Because we are dealing with large numbers,  $n_j \gg 1$ , so we can approximate this as

$$d(\ln \Omega) \approx -\sum_j \ln(n_j) dn_j.$$

When this is equal to zero, it will determine the most probable macrostate. We therefore have three conditions for the most probable macrostate:

- $\sum_j dn_j = 0$ , because the particle number is constant (C1);
- $\sum_j \varepsilon_j dn_j = 0$ , because the particle energy is constant (C2);
- $-\sum_j \ln(n_j) dn_j = 0$ , the condition on the most probable macrostate (C3).

We can appeal to Lagrangian multipliers to solve the above problem. Using this technique, we write

$$\sum_j (\ln(n_j) + \alpha + \beta \varepsilon_j) dn_j = 0. \quad (B1)$$

This has to hold for all states of the system, so each term in the bracket must be equal to zero. Therefore,  $\ln(n_j) + \alpha + \beta \varepsilon_j = 0$ , which solves as

$$n_j = A \exp(\beta \varepsilon_j).$$

where  $A = \exp(-\alpha)$ . This gives us the distribution of particles in state,  $j$ , having energy,  $\varepsilon_j$ . The number of particles with energy,  $\varepsilon_j$ , decreases as the energy increases. Thermodynamics can then be used to find the constants.

We know that

$$N = \sum_j n_j = \exp(\alpha) \sum_j \exp(\beta \varepsilon_j).$$

This gives  $A = \exp(\alpha)$  as our normalisation factor, such that  $A = N / \sum_j \exp(\beta \varepsilon_j) \equiv \frac{N}{Z}$ , where  $Z$  is the partition function.

The First Law of thermodynamics tells us  $dU = \delta Q + \delta W = TdS - pdV$ . Now, for our distribution of particles with total energy,  $E = U$ , the total differential is given by

$$dE = d\left(\sum_j \varepsilon_j n_j\right) = \sum_j \varepsilon_j dn_j + \sum_j n_j d\varepsilon_j (= dU).$$

Comparing with the First Law it can be stated that  $TdS = \sum_j \varepsilon_j dn_j$ . This is because the energy levels of the system can only depend on the volume, in other words  $-pdV$  can only be addressed by the second term, whilst from the Boltzmann formalism of entropy, we know that the occupation number is related to the state entropy. Using the Boltzmann formulation of entropy we can write

$$TdS = T d(k_B \ln(\Omega)) = Tk_B d(\ln \Omega).$$

Using the differential form for the number of microstates, this becomes

$$TdS \approx -Tk_B \sum_j \ln(n_j) dn_j = \sum_j \varepsilon_j dn_j.$$

Returning to relation (B1), our formalism for the Lagrange multipliers, and multiplying it by  $k_B T$ , we see

$$k_B T \sum_j \ln(n_j) dn_j + k_B T \alpha \sum_j dn_j + k_B T \beta \sum_j \varepsilon_j dn_j = 0$$

We can simplify this using the condition we had on the initial distribution (constant particle number means the second term is identically equal to zero) and substitute in for the  $TdS$  bit from above. This gives

$$-\sum_j \varepsilon_j dn_j + k_B T \beta \sum_j \varepsilon_j dn_j = 0,$$

that tells us that  $\beta = 1/k_B T$ . This gives is a statistical definition of temperature, which agrees with the absolute thermodynamic scale of temperature.



NOTE, that some books (e.g. Guénault) set the Lagrange multiplier up keeping the negative sign in front of the  $\ln n_j$ . This means that  $A = \exp(\alpha)$  and  $\beta = -1/k_B T$ , but the overall final distribution function remains the same.

## 24. The Partition function

This important function acts as a normalisation factor to ensure correct counting and, furthermore, contains the relevant information needed to find many thermodynamic properties. Thus it is the most useful function in statistical physics. If it can be found – which is not always the case since the Schrödinger equation can only be fully solved for a few systems - it becomes possible to calculate all other thermodynamic quantities. Its Germanic name means “sum over states” and it tells us that the  $N$  particles can be split into  $i$  different states with  $n_j$  particles contained in the state with energy  $\varepsilon_j$  in the same ratio as the Boltzmann factors. It is thus defined as

$$Z = \sum_j \exp\left(-\frac{\varepsilon_j}{k_B T}\right).$$

This function is a “zipped-up” version of all other properties of the system and is related to the entropy and internal energy via

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

$$U \equiv E = -\frac{d \ln Z}{d\beta} = -\frac{dT}{d\beta} \times \frac{d}{dT} (\ln Z) = -\frac{1}{(d\beta/dT)} \frac{d}{dT} (\ln Z) = k_B T^2 \frac{d}{dT} (\ln Z)$$

These two definitions can be used to determine the Helmholtz function, which can then be used to find all other thermodynamics properties,

$$F = -k_B T \ln Z \Leftrightarrow Z = \exp(-ZF).$$

We should note here, that the zero of energy can be taken arbitrarily, so it is only possible to define  $Z$  upto a multiplicative constant. Since many thermodynamic functions are proportional to  $\ln(Z)$  they can only be defined up to an additive constant. It should also be noted, that we'll many be concerned with single particle systems this year, but analogous results hold for many particle systems, with the equations being multiplied by  $N$  for the total particle number.

To solve problems in statistical mechanics, our basic procedure is thus to write the partition function and then evaluate the various functions of it to get the thermodynamic properties. Partition functions can be combined in a multiplicative way. If the energy of a system depends on independent contributions, such that  $\varepsilon_{i,j} = \varepsilon_i + \varepsilon_j$  it is easy to show that the combined partition function is given by  $Z_{tot} = \sum_i \exp(-\beta \varepsilon_i) \sum_j \exp(-\beta \varepsilon_j) = Z_A Z_B$ .

### Deriving Partition Function Expressions

You do not need to be able to derive the relationship between the Helmholtz function and the partition function. You should, however, be able to apply the principles of statistical mechanics to thermodynamics.

- For the total particle number,

$$N = \sum_j n_j = \sum_j A \exp\left(-\frac{\varepsilon_j}{k_B T}\right) = AZ.$$

- For the energy,

$$E = \sum_j n_j \varepsilon_j = A \sum_j \varepsilon_j \exp\left(-\frac{\varepsilon_j}{k_B T}\right) = \frac{N}{Z} \sum_j \varepsilon_j \exp\left(-\frac{\varepsilon_j}{k_B T}\right).$$

Furthermore,  $\ln Z = \ln \sum_j \exp\left(-\frac{\varepsilon_j}{k_B T}\right) = \sum_j \left(-\frac{\varepsilon_j}{k_B T}\right)$ , and taking its derivative with respect to temperature gives  $\frac{d}{dT} \ln Z = + \sum_j \left(\frac{\varepsilon_j}{k_B T^2}\right)$ . Multiplying either side by  $k_B T^2$ , gives

$$N k_B T^2 \frac{d}{dT} \ln Z = +N \sum_j \varepsilon_j = \sum_j n_j \sum_j \varepsilon_j = \sum_j n_j \varepsilon_j = E.$$

In a similar way, it can be shown that

$$E = -N \frac{d}{d\beta} (\ln Z),$$

where  $\beta = 1/k_B T$ .

- For the entropy, first, recall the Boltzmann formulation of entropy and consider distinguishable particles, i.e.)  $S = k_B \ln(\Omega)$  with  $\ln(\Omega) = N \ln N - \sum_j n_j \ln n_j$ . Using the Boltzmann distribution function, we can then write

$$\frac{S}{k_B} = \ln(\Omega) = N \ln N - \sum_j n_j \left( \ln A - \frac{\varepsilon_j}{k_B T} \right).$$

Using the constraints on particle number,  $N \sum_j n_j$ , and total energy,  $E = (U) = \sum_j \varepsilon_j n_j$ , we can write the above expression as

$$\frac{S}{k_B} = \ln(\Omega) = N \ln N - N \ln A + \frac{E}{k_B T}.$$

Using the Partition function,  $N = AZ$ , this simplifies to

$$\frac{S}{k_B} = N \ln Z + \frac{E}{k_B T},$$

which can be written as  $TS = TN k_B \ln Z + E$ .

Comparing with the Helmholtz equation,  $F = U - TS$ , we see

$$F = -NT k_B \ln Z.$$

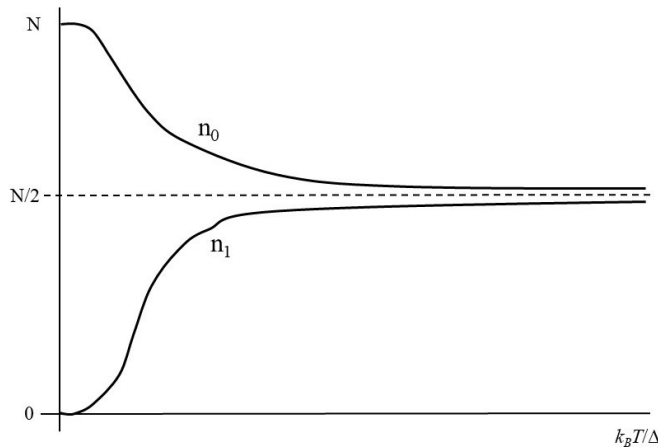


Figure 36: Populations of a system having two energy levels varying with temperature.

#### Example 24.1

A system has two energy levels. Spin-up has  $n_0$  particles of energy  $\varepsilon_0$ , and spin-down has  $n_1$  particles of energy  $\varepsilon_1$ . The energy difference is  $\Delta = \varepsilon_1 - \varepsilon_0$ .

The ground state is spin-up and is of lower energy.

**The Probability of state occupation is**

$$P(\epsilon_0) = \frac{n_0}{N} = \frac{\left( A \exp\left(\frac{-\epsilon_0}{k_B T}\right) \right)}{A \exp\left(\frac{-\epsilon_0}{k_B T}\right) + A \exp\left(\frac{-\epsilon_1}{k_B T}\right)} = \frac{1}{1 + \exp\left(\frac{-\Delta}{k_B T}\right)}$$

$$P(\epsilon_1) = \frac{n_1}{N} = \frac{\exp\left(\frac{-\Delta}{k_B T}\right)}{1 + \exp\left(\frac{-\Delta}{k_B T}\right)}.$$

$$\text{As } T \rightarrow 0, P(\epsilon_0) = \frac{1}{1 + e^{-\infty}} = 1 \quad ; \quad P(\epsilon_1) = \frac{e^{-\infty}}{1 + e^{-\infty}} = 0$$

$$\text{As } T \rightarrow \infty, P(\epsilon_0) = \frac{1}{1 + e^{-0}} = 1/2 \quad ; \quad P(\epsilon_1) = \frac{e^{-0}}{1 + e^{-0}} = \frac{1}{2}.$$

At low temperature, all the particles are in the ground state, whilst at high temperature we have an equal number of particles in each state as shown in figure 36.

#### Example 24.2

For a single particle with the above two energy levels

$$Z = \exp\left(-\frac{\epsilon_0}{k_B T}\right) + \exp\left(-\frac{\epsilon_1}{k_B T}\right) = 2 \cosh\left(\frac{\Delta}{2k_B T}\right)$$

It is easy to compute the internal energy using the statistical definition of the Helmholtz function

$$E = -\frac{d \ln Z}{d\beta} = -\frac{1}{2 \cosh(\beta\Delta/2)} \times 2 \times \frac{\Delta}{2} \sinh(\beta\Delta/2) = -\frac{\Delta}{2} \tanh(\beta\Delta/2).$$

The heat capacity, is as always the derivative of the energy with respect to temperature,

$$C_V = \left(\frac{\partial E}{\partial T}\right)_V = k_B \left(\frac{\Delta\beta}{2}\right)^2 \text{sech}^2\left(\frac{\beta\Delta}{2}\right).$$

As  $T \rightarrow 0, U \rightarrow 1$  and  $S \rightarrow 0$ , since  $\Omega = 1$ . At high temperature, the energy levels are degenerate so the energy approaches zero as expected and entropy tends to  $k_B \ln 2$ . Heat capacity is small at both low (only lower energy occupied) and high (both levels equally occupied) temperature. In between we have what is known as the Schottky anomaly.

## Chemical Potential

This concept arises in systems that can exchange energy with their surroundings. If the **chemical potential** is different between two places, particles can flow, rather like heat flows between temperature differences. If a particle is added to a system, the internal energy changes according to

$$dU = TdS - pdV + \mu dN,$$

where  $\mu$  is the chemical potential and  $N$  is the number of particles. Furthermore, the chemical potential can be related to both the Gibbs and Helmholtz functions as  $\mu = \left(\frac{\partial F}{\partial N}\right)_{V,T} = \left(\frac{\partial G}{\partial N}\right)_{p,T}$ .

## 25. Quantum Particles

Unlike distinguishable particles which are unlikely to swap places between the times we inspect them, and are localised, so return to their initial location after a perturbation, the particles of a gas

for example are intrinsically indistinguishable. **Indistinguishable particles** besides being identical, cannot be labelled either. These include the molecules of a gas and fermions and bosons. For a **classical gas** we use a distribution by levels, which tells us the number of particles contained in a certain energy level of given degeneracy, or the number of states within the level. **Fermions and bosons** have different properties due to the nature of their wave functions that must be solutions of the *Schrödinger equation*, satisfying the symmetry requirement of interchanging the particle labels.

Quantum mechanics gives two types of indistinguishable particle, bosons and fermions. We look at the wavefunction whereby swapping particles either leaves the wavefunction unchanged, or introduces an overall minus sign. In both cases, the probability of state occupation doesn't change.

Consider the two particle wavefunction  $\psi(1,2)$ , where 1,2 represent the coordinates of each particle. If the particles are indistinguishable, changing the particle labels will not result in a change to the physical observables. The solution of Schrödinger equation for the two particles can be written as product of the one-particle wavefunctions,  $\psi(1,2) = \psi_a(1) \psi_b(2)$ , where  $a$  and  $b$  are values of state label. This is combined with interchanged partner to get

**Example 25.1**

$$\psi_s(1,2) = \frac{1}{\sqrt{2}} [\psi_a(1)\psi_b(2) + \psi_a(2)\psi_b(1)]$$

**Bosons are described by a symmetric wavefunction, so swapping the particles does not change the wavefunction. Any number of bosons are allowed to occupy a given energy level, they have integer spin and include photons, phonons and liquid Helium 4.**

$$\psi_A(1,2) = \frac{1}{\sqrt{2}} [\psi_a(1)\psi_b(2) - \psi_a(2)\psi_b(1)]$$

**Fermions are described by an anti-symmetric wavefunction and include electrons. Swapping the particles introduces an overall negative sign into the wavefunction. Fermions satisfy the Pauli Exclusion Principle, which states that no two identical particles may occupy the same quantum state. They have half-integer spin, but due to the particles being able to have spin-up or spin-down, two are actually allowed in each energy level.**

## Distribution Functions

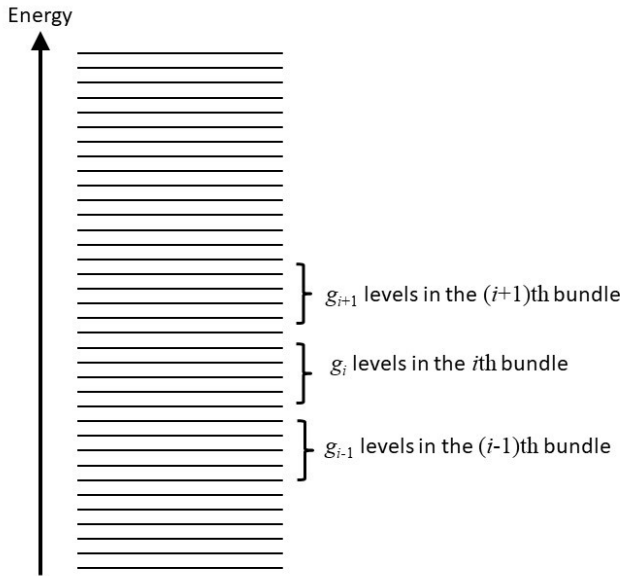


Figure 37: Grouping of indistinguishable particles into energy levels.

In some situations (gases etc.) where the particles are indistinguishable, it is better if we consider distribution functions. The distributions are considered in terms of energy levels, as opposed to states. In other words, lots of energy levels are collected together into bundles, with the  $i$ th bundle having  $g_i$  states, or energy levels, containing  $n_i$  particles associated with it. Some definitions are:

- A **distribution function**,  $f(\varepsilon)$ , tells us the occupancy (expressed as a fraction) of a given energy state. It is probabilistic, telling us the probability that the state of energy  $\varepsilon_j$  is occupied.
- The **density of states** on the other hand,

provides a measure of how many energy states exist in a given energy range,  $d\varepsilon$ , or equivalently momentum range, and is given by  $g(\varepsilon)d\varepsilon$ . Its form depends on the particle type and geometry.

The number of states in the system having energy  $\varepsilon$  is then given by

$$n(\varepsilon) = f(\varepsilon)g(\varepsilon) \quad ; \quad n(\varepsilon)d\varepsilon = f(\varepsilon)g(\varepsilon)d\varepsilon$$

The second expression considers the number of particles in an energy range  $d\varepsilon$ , i.e. between  $\varepsilon$  and  $\varepsilon + d\varepsilon$ . The second expression can be integrated to get the total number of particles between energies  $\varepsilon_i$  and  $\varepsilon_f$ . We should also note that  $f(\varepsilon)$  and  $g(\varepsilon)$  are unrelated.

### Maxwell Boltzmann Distribution

This gives the classical gas distribution, with the number of ways of arranging the particles being

$$\Omega_{MB} = \prod_i \frac{(n_i + g_i + 1)!}{n_i! (g_i + 1)!} \sim \prod_i \frac{(g_i)^{n_i}}{n_i!}.$$

Since we have a large number of particles, and many more energy levels than particles meaning that  $g_i \gg n_i$  the approximation follows.

Following similar mathematical methods to those used to derive the Boltzmann distribution, we find  $n_i/g_i = A \exp(-\beta\varepsilon_i)$ . This function contains no details about the states, except their energies, so can be thought of as a continuous function of the one particle energy,  $\varepsilon_i$ , or simply,  $\varepsilon$ , and written

$$f_{MB}(\varepsilon) = A \exp\left(\frac{-\varepsilon}{k_B T}\right)$$

## Bose-Einstein Distribution

To derive this distribution we count the number of microstates in which  $n_i$  bosons can be arranged in  $g_i$  states, with any number of particles allowed in each state. The total number of arrangements is

$$\Omega_{BE} = \prod_i \frac{(n_i + g_i - 1)!}{n_i! (g_i - 1)!} \sim \prod_i \frac{(n_i + g_i)!}{n_i! g_i!},$$

And the distribution is  $n_i/g_i = 1/(\exp(\alpha + \beta \varepsilon_i) - 1)$ . In a similar fashion as distinguishable particles, the constants  $\alpha$  and  $\beta$  can be found.  $\alpha$  is related to the chemical potential  $\alpha = -\mu/k_B T$  and  $\beta$  to the temperature,  $\beta = 1/k_B T$ . Writing the distribution in terms of a function, obtained by imagining that the energy levels become smeared out,

$$f_{BE}(\varepsilon) = \frac{1}{\exp\left(\frac{\varepsilon - \mu}{k_B T}\right) - 1}.$$

## Bose-Einstein Condensation

As the term in the exponent tends towards one, funny things happen and the distribution “blows – up”. All particles end up migrating to the lowest energy state and quantum effects become apparent on a macroscopic scale. **Bose-Einstein condensation** is a universal phenomenon underlying many of the more exotic areas of modern physics, e.g. superfluidity and superconductivity. This phenomenon was first observed by Cornell and Weimann in 1995, when 2000 Rubidium atoms were seen to behave as one for 10 s. It is also thought to exist in biological systems in what is known as the Fröhlich hypothesis.

### Example 25.2

**At low temperature the chemical potential approaches the energy of the lowest state, so  $\varepsilon_0 - \mu \rightarrow 0$  and the exponential term tends to 1. The denominator approaches 0 and probability of state occupation blows up – hence all particles migrate to lowest energy state in Bose-Einstein condensation!**

## Fermi-Dirac Distribution

This time, the number of ways of counting the available microstates is

$$\Omega_{FD} = \prod_i \frac{g_i!}{n_i! (g_i - n_i)!},$$

since we know how many levels will be filled. Again, maximising this using similar maths, the distribution function can be determined as  $n_i/g_i = 1/(\exp(\alpha + \beta \epsilon_i) + 1)$ , which for a continuous range of energies becomes

$$f_{FD}(\epsilon) = \frac{1}{\exp\left(\frac{\epsilon - \epsilon_F}{k_B T}\right) + 1}$$

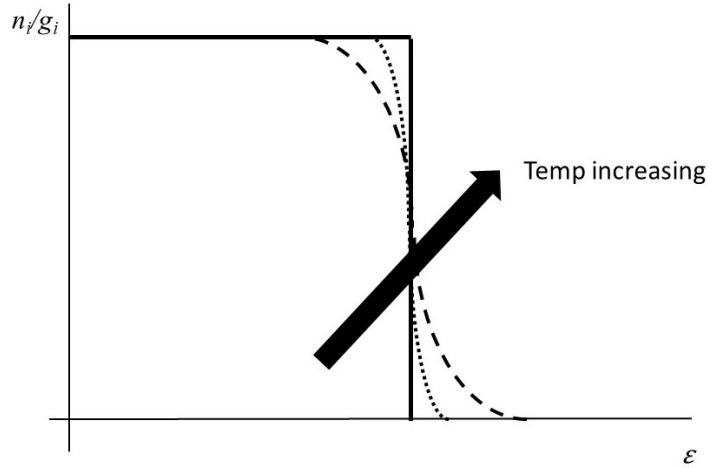


Figure 38: The behaviour of the Fermi-Dirac distribution with temperature.

The chemical potential is defined as the energy where the occupation probability of a state is half. It reaches its maximum value, the **Fermi energy**,  $\epsilon_F$ , as the temperature tends towards zero. At  $T = 0$  K, all the states up to and including the Fermi energy are occupied by particles, and all states above this energy are empty. Adding one more particle increases the overall energy by  $\mu = \epsilon_F$ . Figure 38 indicates how this distribution becomes more “smeared out” at higher temperatures.

### Example 25.3

## Distribution Classical Limits

When the probability of state occupation is low – many more accessible quantum states than particles – the two distributions tend towards the Boltzmann distribution as shown in figure 39. This is easily seen by examination of the number of microstates in the way we count the particles. When  $g_i \gg n_i$  (many more states than particles), both expressions tend to the limit of the Classical Gas. The quantum world reverts to semi-classical one if probability of state occupation is low.

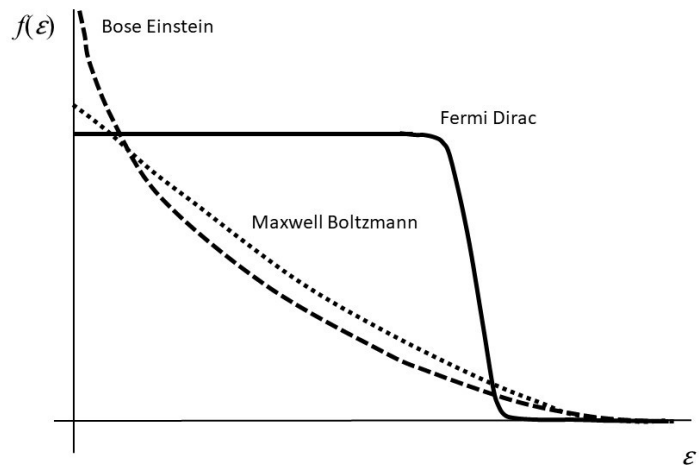


Figure 39: The classical limits of the distributions.