3. Entropy, equilibrium, and the second law

See Mandl chapter 2

3.1 Principle of equal a-priori probabilities and its consequences

We can now formulate the axiomatic foundation of statistical physics:

> 💡 Key Point 5: The principle of equal a priori probabilities:
>
> An *isolated* system is equally likely to be found in any one of its allowed microstates.

Although we state it here as a postulate, it can be justified through the degree of belief view of probabilities: our microscopic model prescribes the available microstates which is the most detailed description of the state we can (or are prepared) to offer. Since we have no further information we have to assume that each of these microstates is equally likely. Recalling that the weight of a macrostate is the number of corresponding microstates, a direct consequence of key point 5 is

> 💡 Key Point 6:
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> The probability that an isolated system, of energy E, will be found in a *macrostate* $N, E, \{\alpha\}$ is proportional to the weight $\Omega(N, E, \{\alpha\})$, ie the number of microstates associated with the macrostate $N, E, \{\alpha\}$

In other words we can think of the microstate as the outcome of a trial (measuring which microstate our system is in) and the number of outcomes corresponding to a macrostate is given by the weight. Thus the probability of being in a macrostate is proportional to the weight. Since different macrostates have different weights they will have different probabilities.

We saw that since weight functions are typically exponentially large in N, the maximum for the weight function is extremely sharp. This means with macrostates in which the (free) macroscopic variables maximise the weight function are overwhelming more probable than other possible values. This was illustrated in chapter 2 where we plotted the weight function of the model magnet link to image and link to image.

The probability that an isolated system will be found in macrostate $N, E, \{\alpha\}$ is proportional to the weight of macrostate $\Omega(N, E, \{\alpha\})$. From the sharpening of the weight functions we deduce another key point

> 💡 **Key Point 7:**
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> The equilibrium values $\{\alpha^\star\}$ of the macroscopic properties $\{\alpha\}$ of an isolated system are those that maximise the weight function $\Omega(N, E, \{\alpha\})$

Thus while, in principle, macroscopic properties $\Omega(N, E, \{\alpha\})$ are free to take up a wide range of values, in practice they are sharply defined so that equilibrium is characterised by macroscopic properties unique to the equilibrium state that is singled out by the constraints.

Saying that a thermodynamic system is 'in equilibrium' is saying (essentially) that enough time has elapsed since the last change in constraints for the system to find its way to the most probable macrostate consistent with those constraints.

A consequence of this, together with KP4, is that

> 💡 **Key Point 8:**
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> The equilibrium entropy of an isolated system of N constituents with energy E is $S(N, E) = k \ln \Omega(N, E, \{\alpha^\star\})$

3.2 The second law

To illustrate the second law we consider the model magnet of the previous chapter: N atoms (magnetic dipoles), energy E and n atoms in excited states. Let us consider starting from an initial condition where all the excited dipoles are in the left hand half of the system and none in the right. One can think of inserting a thermally insulating wall to ensure that no energy can be transferred between the two sub-systems.

Now when we remove the wall the system finds itself in a macrostate which is far from the most probable. The system will evolve, by more and more of the excited dipoles appearing in the right hand half, through macrostates which have greater and greater weights. Finally it reaches the macrostate where there are equal numbers of excited dipoles in the left and right hand sides and which is the macrostate with the maximal weight. Of course when we say equal we mean equal to within $O(N^{1/2})$.

In effect there has been a flow of energy from the left hand side to the right hand side of the system until equilibrium was reached. A related example is of a gas starting with all molecules in the left hand half of the system. Similar considerations apply to that system although now there is a flow of particles or mass from left to right.

We summarise with a statement not quite worthy of being a key point, as we will not pursue dynamics much further, but which is nevertheless worth a box

> An isolated system evolves through macrostates with greater and greater weight until it reaches the macrostate with the largest weight and stays there.

Now considering the entropy, which is by Planck's relation proportional to the logarithm of the weight we see that

The entropy of an isolated system can only increase

which is a statement of the second law of thermodynamics. Moreover we now understand why the law holds only in a statistical sense. In the example of the ideal gas there is nothing in Newton's laws to prevent all the molecules moving into the left hand side, which would mean a decrease in entropy. However we know statistically that this will basically never happen.

3.3 Entropy and disorder

Entropy is often referred to as a measure of disorder. For this statement to be meaningful we have to know what we mean by ordered and disordered.

Basically the idea is that when something is 'disordered' it may be so in many different ways, whereas 'order' places many restrictions on the ways things can exist.

Consider the example of a bedroom. For a bedroom to be tidy i.e. ordered, everything has to be in its correct place, and there are not many ways to place ones possessions and clothes correctly in the room. However in an untidy, i.e. disordered room, there are many, many different ways for things to be scattered about.

Another example is problem question 2.6 where a order/disorder transition is discussed. There copper and gold atoms are arranged in a crystal lattice. In the ordered phase the copper atoms occupy certain positions and the gold atoms occupy other positions. This is an orderly arrangement compared to the disordered phase where any atom can occupy any of the positions. In that question entropy differences are calculated.

Question 2.5 highlights that a liquid (water) is more disordered than a solid (ice).

3.4 Additivity of entropy

Consider dividing our system (whether it be the model magnet or ideal gas) in half i.e. into two subsystems 1 and 2, each with number N_i of constituents and containing energy E_i where $i = 1, 2$. For example, in we divide our array of N magnetic atoms into two sub-systems of fixed $N_1 = N_2 = N/2$ which are in thermal contact (they exchange energy). The fixed total energy corresponds to a total of say $n = N/2$ excited dipoles. The weight for the macrostate where n_1 of the dipoles in the left half are excited is a product of weight functions for the two halves

$$\Omega(N, E, n_1) = \Omega_1(N_1, E_1, n_1)\Omega_2(N_2, E_2, n - n_1)$$

This factorisation of the weight function into two terms from each subsystem is quite general. Thus using Planck's relation we see that for the two sub-systems

$$S(N, E, n_1) = S_1(N_1, E_1, n_1) + S_2(N_2, E_2, n_2).$$

This property of the entropy being the sum of the entropy of the subsystems is quite general and is referred to as additivity of the entropy i.e. the entropy of a composite system is the sum of entropies of macroscopic component subsystems. In particular in an equilibrium system, where the energies of the two sub systems are $E_1, E_2 = E_1^\star, E_2^\star$

$$S(N, E) = S(N_1, E_1^\star) + S(N_2, E_s^\star)$$

3.5 Entropy and temperature

We now analyse the condition for equilibrium more mathematically. For our two systems in thermal equilibrium we have

$$S(E) = S_1(E_1) + S_2(E_2) \qquad E = E_1 + E_2.$$

where we have been lazy and dropped the Ns since we take them to be fixed.

We wish to consider the effect of changing E_1 to $E_1 + dE_1$ which implies changing E_2 by $dE_2 = -dE_1$, since total E is fixed.

Now consider the effect on the entropy

$$
\begin{aligned}
dS &= dS_1 + dS_2 \\
&= \left(\frac{\partial S_1}{\partial E_1}\right) dE_1 + \left(\frac{\partial S_2}{\partial E_2}\right) dE_2 \\
&= \left(\frac{\partial S_1}{\partial E_1} - \frac{\partial S_2}{\partial E_2}\right) dE_1
\end{aligned}
$$

Now since the entropy is an extremum (i.e. it should be maximised) dS must be 0. Therefore we deduce

$$\frac{\partial S_1}{\partial E_1} = \frac{\partial S_2}{\partial E_2}$$

Recalling the zeroth law of thermodynamics, which states that two systems in thermal equilibrium must share the same temperature, and comparing with the condition for equilibrium that we have derived, we deduce that

$$\frac{\partial S_1}{\partial E_1} = \text{some function of } T$$

In fact the correct identification is

> 💡 Key Point 9:
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> $$\frac{1}{T} = \frac{\partial S}{\partial E}$$

(To understand why this particular function of T is the correct one will need the ideas of free energy minimisation that we shall meet later and in question 3.5)

We now ask what happens when we put two systems at different temperatures T_1 and T_2 in thermal contact. In this case we expect from the second law that $dS > 0$.

Using the identification of key point 9 we find

$$dS = \left(\frac{1}{T_1} - \frac{1}{T_2} \right) dE_1$$

So if $T_1 > T_2$ we must have dE_1 $-ve$ for dS to be $+ve$ and we see energy (or heat) flows from the hotter to the colder system.

One can generalises the arguments of this subsection to the consideration of systems free to exchange volume (e.g. a balloon) or particles (e.g. a liquid and gas in coexistence).