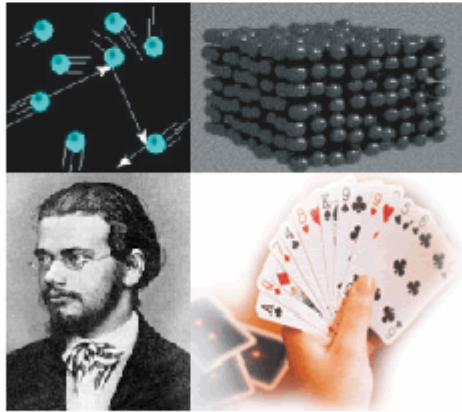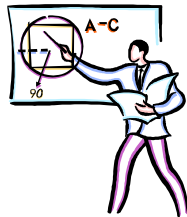# Introduction to Thermodynamics and Kinetics

F31STI

School of Physics & Astronomy

Lecture Notes
Set 3b: Entropy and the 2nd law

3.5 The Boltzmann Distribution revisited

Before moving on to consider the 2nd law of thermodynamics, I'd like to revisit the Boltzmann distribution in light of our discussions of permutations, combinations and arrangements of objects and quanta of energy. Let's consider 6 identical but distinguishable particles and a 10 level system as shown in Fig. 3.12. We ask the question: which of the three distributions shown is most probable? To answer this we need to consider the total number of arrangements of the particles. It turns out that this is a problem somewhat similar to that involving the arrangements of pool balls discussed in Section 3.2. In this case, however, as the particles are distinguishable, you should imagine labelling each particle with a number or letter to distinguish it from the others. To calculate the total number of arrangements of the 6 particles, we need to make sure that we account for the permutations of particles within a given level. That is, if we have three particles in a level, arrangement ABC = BAC = CAB etc… Note that each of the arrangements in Fig. 3.12 gives the same total energy.
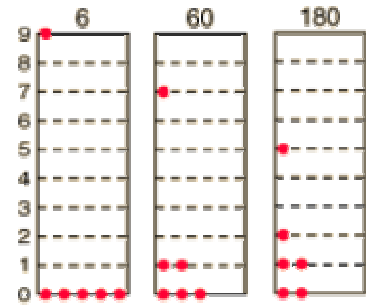

Fig. 3.12 (Taken from the Hyperphysics website). 6 particles arranged amongst 10 energy levels.

> ❓ *What is the total energy of the system in Fig. 3.12 assuming that the energy levels are spaced by ε?*

The number of distinct configurations (microstates), *W*, associated with *N* distinguishable particles being placed in a set of energy levels so that the occupations of the energy levels are n_0, n_1, n_2 etc… is:

$$\frac{N!}{n_0!n_1!n_2!.....}$$

Considering the first arrangement in Fig. 3.12, the total number of distinct configurations (microstates) is therefore $6!/(5!\ 1!) = 6$. This is because there are 5! permutations of the particles possible in the lowest level but only 1 permutation possible in the highest level. (Note also that as $0! = 1$ unoccupied levels do not make a contribution).

> ❓ *How many distinct configurations (microstates) are associated with the second and third arrangements shown in Fig. 3.12? Which configuration is therefore most likely?*

Boltzmann's distribution formula was derived by maximising the quantity $W = \dfrac{N!}{n_0! n_1! n_2! \ldots}$ (or, more correctly, $\ln (W)$) under the condition that the total number of particles and total energy of the system remained constant. We shall not attempt this (very difficult) derivation! I shall simply quote the result (which you've seen before in Section 2):

$$n_i = A \exp(-\frac{\varepsilon_i}{kT})$$

Or, in words: at thermal equilibrium, the total number of particles in level i (i.e. n_i) having energy ε_i is a constant, A, multiplied by $\exp(-\frac{\varepsilon_i}{kT})$ (where k is Boltzmann's constant and T is temperature).

If we want to know the *relative* populations of particles in two different energy levels then we have the simple result:

$$\frac{n_2}{n_1} = \frac{A \exp(-\frac{\varepsilon_2}{kT})}{A \exp(-\frac{\varepsilon_1}{kT})} = \exp(-\frac{\Delta E}{kT})$$

where ΔE is $\varepsilon_2 - \varepsilon_1$ (the energy level separation).

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3.6 Entropy and the 2nd law of thermodynamics

The 1st law of thermodynamics is simply a restatement of the conservation of energy principle and may be concisely written as:

$$\Delta U = Q + W$$

where ΔU, Q, and W are the change in internal energy of the system, the heat output or input, and the work done (or on) the system respectively. Remarkably, Carnot (who is pictured to the right) developed the 2nd law before the conservation of energy principle had been put forward. We'll encounter very many equivalent descriptions of the 2nd law in the coming sections (and we'll also not infrequently encounter the work and genius of Carnot). For now, we'll start with the following statements:

"The entropy of a thermally isolated system increases in any irreversible process and is unaltered in a reversible process" (p.79, *"Thermal Physics"*, CB Finn)

"If a closed system is not in equilibrium, the most probable consequence is that the entropy will increase" (p.354, *"Matter and Interactions Vol. I"*, Chabay and Sherwood).

A more succinct statement of the second law is as follows: "*a closed system will tend towards maximum entropy*".
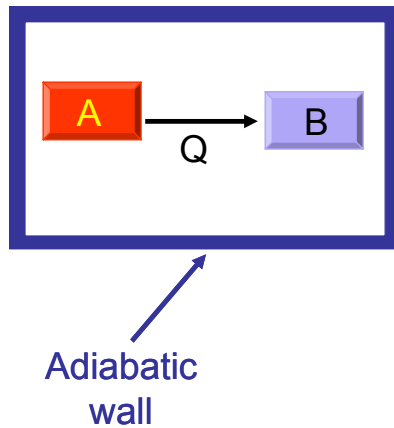
There are very many pitfalls associated with unclear language when considering entropy and the 2nd law. Sloppy thinking and poorly worded statements of the laws of thermodynamics (which I'll do my very best to avoid) have led to many 'abuses' of the concept of entropy – some of these are described briefly in the final section of this set of the lecture notes. Before proceeding, we'll define some of the terms in the statements above:

<u>*"thermally isolated system"*</u>: by this we mean a system surrounded by adiabatic walls – there is no heat flow into or out of the system;

<u>*"closed system"*</u>: this means that there is no energy (or matter) flow into or out of the system – the Universe as a whole is the archetypal example of a closed system but small portions of the Universe can also be considered closed systems under certain circumstances (e.g. when isolated using adiabatic barriers).

<u>*"…will tend towards maximum entropy…"*</u>: this is a very important phrase - the *tendency* is for entropy to increase, but echoing our discussion of Boltzmann factors in Set 2 of the notes, the system can be constrained from reaching the maximum entropy state – the microstates may be *inaccessible*. (Indeed, $S = k \ln W$ and the Boltzmann factor expression given in Section 2 are just different statements of the same law).

The concepts of 'reversibility' and 'irreversibility' will be encountered a considerable number of times in the remainder of the module. We return to an introductory discussion of reversibility in Section 3.6.

Fig. 3.13 A small amount of heat is transferred from Block A to Block B which are both contained within an adiabatic enclosure. The temperature of block A is lowered whereas that of Block B is increased. The number of accessible microstates in system B is increased whereas there are fewer accessible microstates in Block A following the energy transfer. Hence, although the entropy of Block B increases that of Block A is reduced.

One common misconception with regard to the 2nd law is that the entropy of an object always increases. That this is incorrect can be shown by considering the system shown in Fig. 3.13. As heat is transferred from Block A to Block B, the temperature of Block A is reduced and that of Block B is increased. Hence, the entropy of Block A is reduced in this case. *However, the <u>net</u> entropy of the closed system is increased.*

The net increase in entropy arises because the most probable energy distribution is that which maximizes the total number of microstates (sections 3.3 – 3.5).

It is worth noting at this point that although we're concerned with energy distributions, the concept of microstates is equally applicable to spatial distributions of particles. The analysis of diffusion processes in Set 2c of the notes illustrated that particles diffuse from regions of high to low concentration, so that at equilibrium no concentration gradients exist and the particles have spread out to fill the available space. The equilibrium spatial distribution is associated with a uniform, homogeneous 'spread' of particles.

This homogeneous spread is analogous to the uniform distribution of energy quanta observed for a system at thermal equilibrium. In both cases the uniform distribution of particles arises because the entropy for that macrostate far outweighs that of other less homogeneous arrangements. For the same reason that we don't observe cold objects becoming colder when placed in contact with a hot object, the odds against particles moving from a homogeneous distribution to an inhomogeneous, 'ordered' arrangement are such that on average we'd have to wait for a period very many times the age of our Universe to see such an arrangement appear for a mole of atoms. Particles spread out to fill the available space uniformly because the largest number of microstates (by far) is associated with this 'disordered' macrostate.

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3.6 Reversibility

One of the statements of the 2nd law given above notes that the entropy of a thermally isolated system is unaltered in a *reversible* process. What precisely is meant by reversible in the context of thermodynamics?

> ***In a reversible process the system must be capable of being returned to its original state with no other change in the surroundings.***

The 'classic' example of a reversible process involves the piston-gas system shown in Fig. 3.14. Here a gas undergoes an infinitesimally small compression due to an infinitesimally small weight, *dm*, which is placed on the <u>frictionless</u> piston. If the weight is then removed, the gas expands back to its original volume and the temperature returns to its original value. This is a **reversible** process.

It is important not to assume that a reversible process requires an adiabatic enclosure. If the adiabatic enclosure in Fig. 3.14 is replaced with a container with diathermal walls it is also possible to have a reversible change. For example, let the temperature of the surroundings increase by an amount dT – energy will flow in through the walls of the container. If the surroundings are then slowly cooled to the original temperature the gas will contract back to its initial volume. This is again a reversible process.

Note that a reversible process is an *idealization* – it is not possible to have a completely reversible change in a real system. Nevertheless, as will be shown below, the concept of a reversible process somewhat remarkably allows us to treat many processes that are not reversible of themselves.
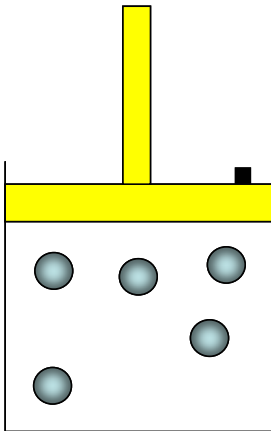
Fig. 3.14 A gas contained in an adiabatic enclosure with a completely frictionless piston. A small mass, dm, is placed on the piston to produce an infinitesimally small pressure change..

Quasistatic changes

You might ask yourself whether a reversible process must therefore always involve infinitesimally small changes – what if we want to reversibly change, for example, the pressure of a system by a large amount? Well, we can make a large change *as long as we break it down into a sequence of very small steps.* The key feature of this sequence is that the system must remain in equilibrium at all times. If this is the case then the process is referred to as a *quasistatic* process. If, for example, we decided to push the piston down very rapidly this would most certainly not be a quasistatic process – there would be finite temperature and pressure gradients, and turbulence would likely play a role.

Hence, a reversible process involving a large change in the properties of the system must proceed via a sequence of quasistatic steps. Reversing this process step-by-step would then produce the same initial state. Processes which don't involve quasistatic states are irreversible. However, are quasistatic processes *always* reversible?

? *When might a quasistatic process not be reversible?*

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The concept of reversibility will crop up a considerable number of times in the remainder of the module.

3.7 Reversible and irreversible processes: calculation of entropy

There now appears to be an inconsistency between a statement of the 2nd law given in Section 3.5 and Eqn. 3.7. The statement in question is: "the entropy of a thermally isolated system increases in any irreversible process and is unaltered in a reversible process". However, Eqn 3.7 holds only for a reversible process involving a very small amount of heat, dQ – how do we calculate the entropy change in an irreversible process?! (Remember that a reversible process is an idealization – every real process is irreversible). There are some rather subtle thought processes underlying the use of Eqn. 3.7 to calculate entropy changes in irreversible processes which are best illustrated with an example (taken from Finn, p. 75).

We want to calculate the entropy change of a beaker of water when it is heated from 293 K (i.e. about room temperature) to 373 K (Fig. 3.15). The beaker is placed on a heat reservoir (i.e. a 'heat bath' which is so large its temperature does not change) and its temperature raised to 373 K (steps 2 and 3 in Fig. 3.15). The beaker is then removed from the reservoir and placed in a jacket with adiabatic walls so there is no longer any heat flow into or out of the system.
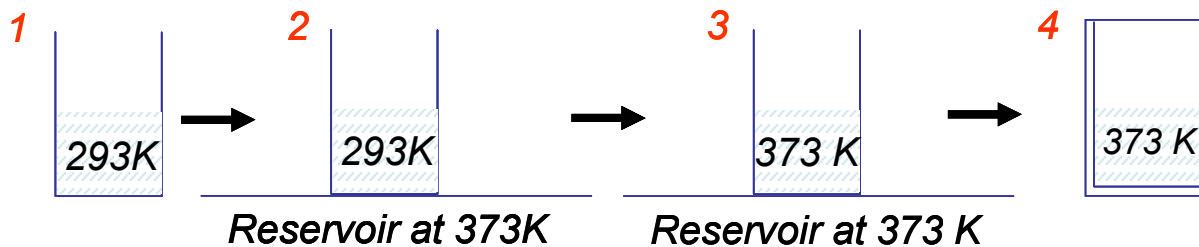

Fig. 3.15 *Raising the temperature of a beaker of water from 293 K to 373 K in one step is an irreversible process.*
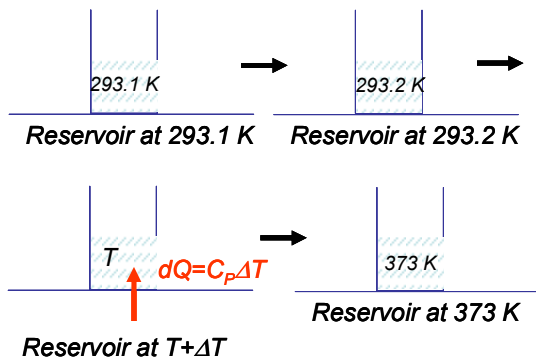

Fig. 3.16 *Increasing the temperature of a beaker of water via a series of reversible steps.*

As this is an irreversible process (due to the large temperature gradients set up as the water is heated) it is not possible to apply Eqn. 3.7 directly. However, the water is in well-defined *equilibrium* states at the start and end of the process. We *imagine* a reversible process that moves the state of the water between these two end points.

To apply Eqn. 3.7 the irreversible process shown in Fig. 3.15 can be broken down into a series of reversible steps. Starting with the water at T = 293K, the beaker is placed on a reservoir with a temperature of T + ΔT (= 293.1 K). The temperature difference is so small that the system remains in equilibrium as its temperature changes. A reservoir with T = 293.2 K is then placed next to the beaker and the temperature of the water again increases with the water remaining in equilibrium (see Fig. 3.16).

When the water is at a temperature T and it is heated to a temperature T + ΔT, the heat entering (*reversibly*) is $dQ = C_P \Delta T$ where C_P is the heat capacity at constant pressure. From Eqn. 3.7 (if we now consider infinitesimally small changes in temperature):

$$dS = \frac{C_P dT}{T} \qquad\qquad 3.8$$

Eqn. 3.8 is the entropy change of the water for each reversible step. To get the *total* entropy change it is necessary to integrate between the lower and upper limits of temperature (namely, 293 K and 373 K). Thus, the total change in entropy, ΔS is:

$$\Delta S = C_P \int_{293}^{373} \frac{dT}{T}$$

I'll leave you to do the integration as an exercise. The reason we can determine changes of entropy in this fashion is related to the concept of a *function of state* which is covered in Section 4 of the module.

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3.8 Some 'abuses' of the 2nd law and the concept of entropy

Finally, one of the most misunderstood concepts in popular science writing is that of entropy. Lazy use of terms such as 'order', 'disorder', and 'reversibility' has led to very many misconceptions regarding the 2nd law. For example, very many cranks (and some scientists who should have known better) have dreamt up perpetual motion machines which disobey the 2nd law – these machines have their own special category: ' perpetual motion machines of the second kind' to distinguish them from perpetual motion machines 'of the first kind' which disobey the 1st law of thermodynamics! In the next section of the module one of the topics with which we'll be concerned will be heat engines and refrigerators – hopefully after you study that section of the course you should be able to debunk many of the designs for perpetual motion machines that have been proposed and continue to be proposed on a daily basis by those who refuse to accept the 2nd and 1st laws of thermodynamics. (A brief introduction to the nonsense of perpetual motion machines can be found at: http://manor.york.ac.uk/htdocs/perpetual/perpetual.html. There are very many other sites on the web related to this concept!).


A key 'abuse' of the 2nd law is in its application to arrangements of macroscopic objects such as socks in a drawer, books on a desk, cards in a deck, and the contents of a room. An eloquent discussion (by Prof. Frank Lambert) of just how wrong it is to apply the concept of thermodynamic entropy to these situations may be found at: http://jchemed.chem.wisc.edu/Journal/Issues/1999/Oct/abs1385.html. (Note that links to these sites are provided on the module website). I will not repeat the arguments of Prof. Lambert in detail here. His 'take home' message is that simply rearranging macroscopic objects does not result in an increase in the number of microstates accessible to those objects – hence there is no increase in thermodynamic entropy. That your sock drawer 'evolves' from an ordered, tidy state (perhaps!) to a disordered mess has absolutely nothing to do with entropy.

A 'loose' and **completely incorrect** statement of the 2nd law is as follows: 'the entropy of a body always increases'. An easy way to address this misconception is to ask how a 'fridge works. Heat is extracted from a 'fridge, therefore there must be an entropy decrease somewhere. The problem with the statement as written is that it mixes up *net* entropy changes with the entropy change of an element of a system. It is the net entropy of a closed system that increases – the entropy of individual elements of that system may either increase or decrease. We'll return to a consideration of fridges in Section 4 of the module.
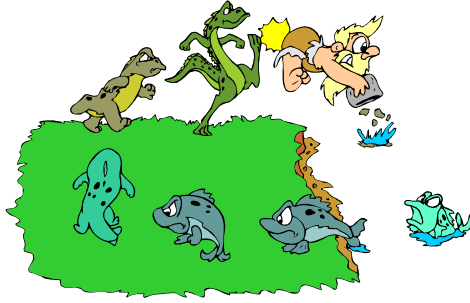
Finally, the most insidious abuse of the 2nd law is by creationists who use it to apparently debunk the theory of evolution. The argument runs as follows:

1. Humans and animals are complex, ordered beings
2. Entropy is a measure of disorder
3. The 2nd law states disorder always increases.
4. Therefore order can't 'evolve' from disorder – Darwin must have got things wrong

I'll leave you to work out the (gaping) holes in this argument. For more debate on this subject see http://www.talkorigins.org/faqs/thermo.html.

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