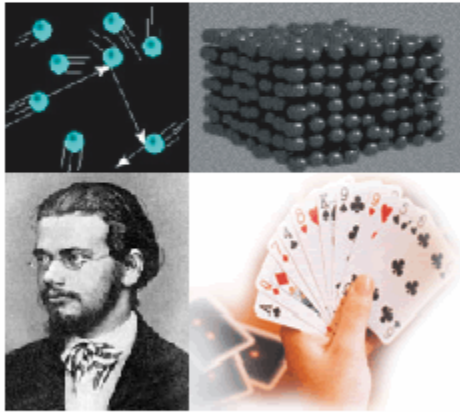


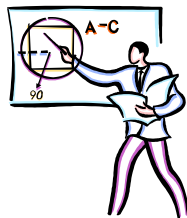
Introduction to Thermodynamics and Kinetics

F31ST1



School of Physics & Astronomy
Spring Semester 02-03

Lecture Notes *Set 3a: Probabilities,* *Microstates and Entropy*



Thus far.....

In Sections 1 and 2 of the module we've covered a broad variety of topics at the heart of the thermal and statistical behaviour of matter. These topics include: distributions and mean values, the ideal gas law, Boltzmann factors, the Maxwell-Boltzmann distribution, equipartition of energy, specific heats, blackbody radiation, and diffusion and thermal conductivity in a gas.

However, we still don't yet fully understand why heat flows from a hot to a cold object (and not vice versa) *nor* why molecules diffuse from regions of high to low concentration so that at equilibrium they are evenly distributed across the available space. Furthermore, although we (correctly) think of temperature as being related to the mean energy of a system, we've yet to quantifiably define the relationship between temperature and the direction of heat flow.

In this section of the module we'll explore distributions in even more depth. A key focus will be a consideration of the very many arrangements of quanta of energy that are possible even for very small numbers of atoms and quanta. This will lead to a discussion of entropy and the – related – second law of thermodynamics. These are conceptually challenging topics which have a history of being 'misrepresented' in popular science writing. The final part of this section of the module is therefore concerned with attempting to dispel some of the myths associated with the 2nd law.

3.1 Energy transfer

In Section 2 we found that there was a very close connection between temperature and the average kinetic energy of the molecules in a system, i.e., $\frac{1}{2} m \langle v^2 \rangle = 3kT/2$ – a fundamental result of equipartition of energy theory. Intuitively, we know that a hot block of material will lose energy to a colder block of material and we can explain this by reasoning that the average energy

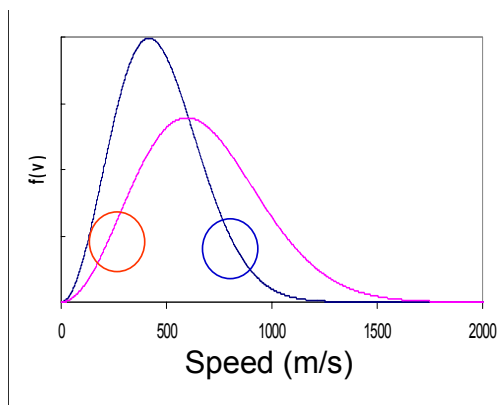


Fig. 3.1 Maxwell-Boltzmann distribution of speeds of molecules in two (separate) gases – the taller peak is the distribution associated with the cooler gas. Note that for both gases a substantial fraction of the molecules have speeds well below and well above the mean speed. The question then arises as to why energy doesn't transfer from the 'cold' to the 'hot' gas if the two gases are mixed (rather than from hot to cold, as is observed).

of the atoms in the hot block is greater than the average energy of the atoms in the cold block. Therefore, it is more likely that an atom in the hotter block will lose energy to an atom in the colder block.

However, how much more likely is a transfer of energy from the hot to the cold block? The atoms have a *distribution* of energies. If we consider the Maxwell-Boltzmann distribution for gas molecules shown in Fig. 3.1 it is clear that many molecules in the hot gas have energies well below the mean energy. Similarly, many molecules in the cold gas have energies well in excess of the mean energy of the gas.

Similarly, why don't the atoms in a cold block of material tend to transfer their energy to the hot block, rather than the other way around? What is it that defines the direction of energy transfer? (A closely related question is "what defines the 'arrow of time'?" – a topic we'll also discuss).

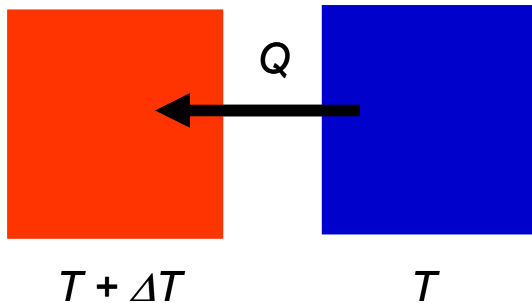


Fig. 3.2 The direction of heat transfer shown above doesn't violate the 1st law of thermodynamics but is prohibited by the 2nd law of thermodynamics. A primary aim of Section 3 of the module is to explain the physical principles underlying the 2nd law.

The direction of heat flow shown in Fig. 3.2 wouldn't violate the conservation of energy – the 1st law of thermodynamics – because the total energy remains the same. However, throughout Section 3 of the module we'll be concerned with determining just what physical principle would be violated if heat were to flow from a cold to a hot body so that, at equilibrium, the temperature of the hot body was increased. Later on, when we explore heat engines in Section 4 of the module, we'll see that this principle – which is, in fact, the 2nd law of thermodynamics – also makes it impossible to convert heat into work at a single temperature.

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3.2 An introduction to statistical mechanics

To answer the questions raised in Section 3.1, the *statistical* behaviour of large assemblies – or ensembles – of atoms will need to be explored in some detail. This area of physics is called *statistical mechanics*. We will touch on only the basic concepts underlying statistical mechanics – you will cover this topic in much more depth and with much more rigour in your 2nd year course. However, even the basic statistical mechanics concepts we'll cover in the *Thermal & Kinetic* module lead to powerful and extremely important insights into the behaviour of matter.

First, consider a model of a solid which comprises a collection of simple harmonic oscillators (see Fig. 3.3). (You might ask why, after we spent so much time discussing gases in Section 2 of the module, we've now switched to a discussion of solids. We'll return to gases soon enough! Solids are easier to consider at the moment because the atoms are fixed in place.) We can simplify the model shown in Fig. 3.3 even further (as first devised by Einstein in 1907).

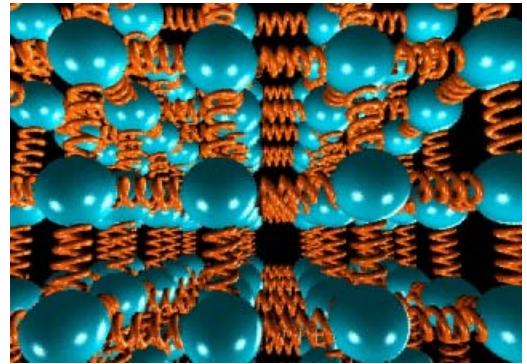


Fig. 3.3 A model of a solid comprising a collection of interacting simple harmonic oscillators (movie frame taken from Chabay and Sherwood's website at http://www4.ncsu.edu:8030/~rwchabay/mi/mi_voll_files.html)

Instead of considering coupled harmonic oscillators, we envisage each atom in the solid as moving independently of its neighbours. (This is obviously a big assumption but bear in mind that we're interested only in the distribution of energy amongst the atoms (the oscillators) – not the detailed dynamics of the atomic motion). A second assumption we make (as did Einstein) is that each 3D oscillator (i.e. each atom) may be replaced with three - also *independent* – 1D simple harmonic oscillators (i.e. one for each of the x , y , and z directions).

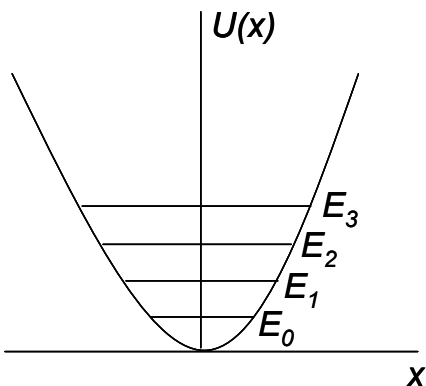


Fig. 3.4 Quantised energy levels of simple harmonic oscillator.

The energies of the simple harmonic oscillators comprising the solid are quantized (see Section 2 and Fig. 3.4):

$$E_n = \left(n + \frac{1}{2}\right)\hbar\omega_0 \quad 3.1$$

As discussed for the Planck model of blackbody radiation (Set 2b of the lecture notes), the energy difference between consecutive energy levels is $\hbar\omega_0$ and we'll ignore the zero point energy – that is, we'll set E_0 to zero.

Having set up this model (known, unsurprisingly, as the *Einstein model*), we can now address the key question:

*how is energy distributed amongst the available energy states?
Energy distributions*

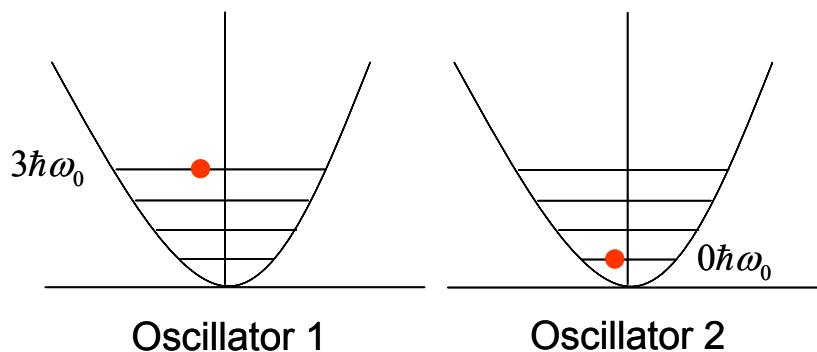
Consider bringing two identical blocks of material which are at different temperatures (say, T_1 and T_2) into contact.

? *What is the final temperature of the blocks (i.e. the temperature when they reach thermal equilibrium)?*

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The most probable distribution of energy is ‘intuitively’ that where the total thermal energy is shared equally between the two blocks. However, what is the *probability* that – at equilibrium – the first block has more energy than the second, or, indeed, that the first block ends up with *all* the thermal energy? To answer these questions, the possible arrangements of energy quanta must be considered.

We have $3N$ independent 1D oscillators (where N is the total number of atoms in the solid) – we now need to determine how many ways there are of distributing a certain number of quanta of energy amongst these oscillators. Mathematical principles related to counting combinations and permutations of objects will prove to be very useful. Let’s start with a straight-forward example:



? *The arrangement shown in Fig. 3.5 is one possible distribution of 3 quanta of energy amongst two oscillators. Sketch the remaining possibilities. How many possibilities in total are there?*

Fig. 3.5 One way of distributing 3 quanta of energy between two oscillators.

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Counting arrangements: permutations and combinations

Clearly we are not going to count by hand every arrangement of energy possible for $3N$ oscillators in, for example, a mole of material ($N \sim 6 \times 10^{23}$). We need to determine the appropriate formula to use and this involves spending a little time thinking about permutations and combinations.

A *permutation* is an arrangement of a collection of objects where the ordering of the arrangement is important.

The number of permutations of r objects selected from a set of n distinct objects is denoted by ${}^n P_r$, where ${}^n P_r = n!/(n-r)!$

Consider the following question:

? A CD reviewer is asked to choose her top 3 CDs from a list of 10 CDs and rank them in order of preference. How many different lists can be formed?

NOTES

Now consider the following case:

? *A CD club member is asked to pick 3 CDs from a list of 10 CDs. How many different choices are possible?*

NOTES

The number of combinations of r objects selected from a set of n distinct objects is denoted by ${}^n C_r$, where ${}^n C_r = \frac{n!}{r!(n-r)!}$

One final example:

? *Take a collection of 10 pool (billiard) balls, 6 of which are yellow and 4 of which are red. How many different arrangements of the coloured balls are possible (eg RRYYYYYYRR)?*

NOTES

Arranging quanta

Returning to distributing quanta of energy amongst a collection of oscillators, we can now establish a formula for the number of possible arrangements. (What follows is based heavily on Chabay and Sherwood, p.348). Take the two oscillator, three quanta problem considered in Fig 3.5 above. Another possible arrangement (one of the three you should have sketched earlier) is shown on the left hand side of Fig. 3.6.

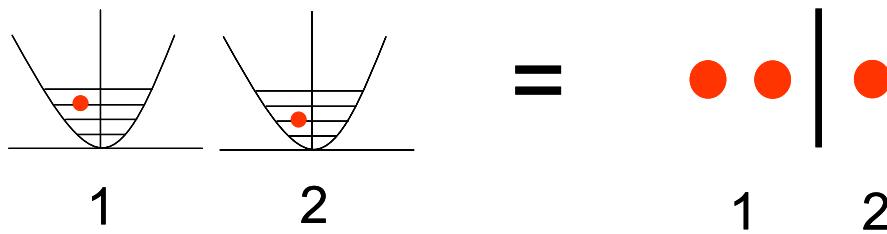


Fig. 3.6 We can consider the distribution of 3 quanta of energy between 2 oscillators as a problem involving the arrangement of 4 objects, namely 3 dots representing the energy quanta and a bar representing a ‘separator’ between the oscillators. If there are N oscillators there are $N-1$ bars.

On the right hand side of Fig. 3.6 the dots represent the three energy quanta and the vertical bar represents a ‘separator’ between the two oscillators. With N oscillators, there will be $N-1$ separators. Counting up the number of arrangements of dots and bars (i.e. the arrangements of quanta amongst the oscillators) thus reduces to the pool ball problem except instead of red and yellow pool balls we need to arrange \bullet and $|$ objects. The total number of arrangements of three quanta amongst two oscillators is thus: $\frac{4!}{3!!}$. More generally:

The number of ways to arrange q quanta of energy amongst N 1D oscillators is:

$$\frac{(q + N - 1)!}{q!(N - 1)!}$$



How many ways can 4 quanta of energy be arranged amongst four 1D oscillators?

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3.3 Microstates and Macrostates

Taking another example, five quanta of energy can be arranged in 21 different ways among 3 oscillators.

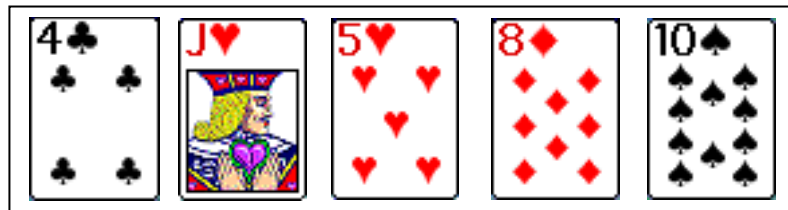
- Each of the 21 different distributions of energy is a *microstate* (i.e. an individual microscopic configuration of the system);
- The 21 different microstates all correspond to the same *macrostate* - the total energy of the system is $5 \hbar \omega_0$.

This is just one example – we could also have considered the distribution of 27 quanta of energy amongst 300 oscillators, or the distribution of 10^7 quanta of energy amongst 1 mole of oscillators. Regardless of the number of microstates we're considering, the following fundamental hypothesis is at the very core of statistical mechanics (and thus underlies thermodynamics):

FUNDAMENTAL ASSUMPTION OF STATISTICAL MECHANICS

Each microstate corresponding to a given macrostate is equally probable.

We can draw an analogy between a game of poker and the concept of microstates and macrostates. (NB *Do not take this analogy too literally*. We'll see later how it is dangerous to associate a concept such as entropy with everyday objects such as decks of cards, arrangements of socks in a drawer, or a messy ('disordered') bedroom.) Ask yourself what are the chances of being dealt the following hand of cards from a well shuffled, 52 card deck:



Now, take a new well shuffled deck of 52 cards and deal out five cards. What are the chances of being dealt the following hand?



NOTES

The probability of being dealt either of the hands of cards shown on the previous page is *exactly the same*. Why then are we so much happier to be dealt the royal flush rather than what might best be described as a ‘junk’ hand? This is because, as eloquently stated by a student during Lecture 10, “*the rules of the game state that some combinations of cards are worth more than others*”.

A total of over $2\frac{1}{2}$ million different possible hands of 5 cards may be drawn from a 52 card deck (make sure you can work out *precisely* how many combinations there are). Each one of these hands is analogous to a *microstate* – a single combination of 5 cards. However, we can define a variety of macrostates for the hands of cards. For example, we could have the following: “Royal Flush”, “Straight”, “4 of a kind”, “Pair”, “Two Pair”, “Junk” – where “Junk” is a ‘worthless’ hand of cards. Although every *microstate* is equally likely, the macrostate “Royal Flush” is associated with very many less microstates than is the macrostate “Pair” or the macrostate “Junk”. (You’ll explore this in more detail in Coursework Set 6). *Macrostates associated with low numbers of microstates are much less likely to be observed.*

Two interacting atoms: six 1D oscillators

Remember, we're ultimately trying to establish why the total thermal energy is shared uniformly between two blocks, originally of different temperatures, when they're brought into contact. Let's consider the smallest possible blocks – two interacting atoms. As each atom comprises three 1D oscillators this means we have six 1D oscillators in total. Try answering the following questions:

? *How many ways are there of distributing 4 quanta of energy amongst six 1D oscillators?*

? *If all four quanta of energy are given to one atom or the other, how many ways are there of distributing the energy?*

? *If three quanta are given to one atom, and one quantum to the other, how many ways are there of distributing the energy?*

? *If the four quanta are shared equally between the atoms, how many ways are there of distributing the energy?*

NOTES

The results from the questions on the previous page are shown as a histogram in Fig. 3.7. It is clear that *it is most probable that the thermal energy is shared equally between the two atoms.*

Note that there are two ways to consider Fig. 3.7:

(i) if frequent observations of the two atom system are made, in 29% of the observations (36 out of 126), the energy will be split equally;

(ii) for 100 identical two atom systems, at any given instant 29% of the systems will have the energy split equally between the two atoms.

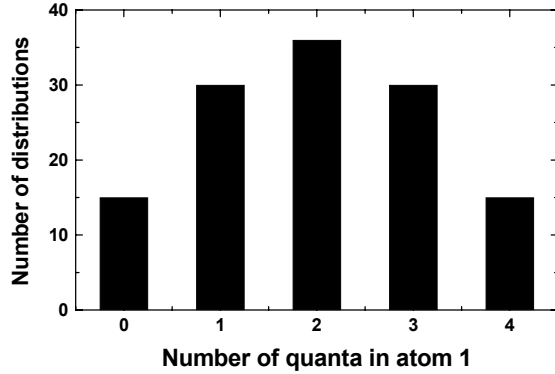


Fig. 3.7 A histogram showing the number of microstates associated with having 0, 1, 2, 3, or 4 quanta of energy on atom 1 of a two atom system.

Increasing the number of atoms

What happens if we increase the number of atoms in the system? If we consider only a few more atoms (say, 10) and a few more quanta of energy (again, let's choose 10) it turns out that there are 635 million ways of arranging the quanta amongst the oscillators. This is for only a few atoms! So you can see that the number of arrangements increases *very* quickly for small changes in the number of oscillators. For example, for 300 oscillators (i.e. 100 atoms), there are 1.7×10^{96} ways of distributing 100 quanta of energy. However, there is only 1 way of placing all the quanta on one *particular* oscillator (i.e. the quanta are given to one 'special' oscillator we've chosen).

The probability of finding all the energy 'concentrated' on one atom in a 100 atom ensemble is thus unimaginably small. For a mole of solid ($\sim 6 \times 10^{23}$ atoms), although it is *possible* that rather than finding that the energy is uniformly distributed throughout the system we observe that all the energy is concentrated on one atom (or a small group of atoms), we would have to wait on average for a period many times the age of the Universe to see this exceptionally unlikely event occur. (The phrase 'exceptionally unlikely' does not do justice to the staggeringly small odds associated with this possibility!).

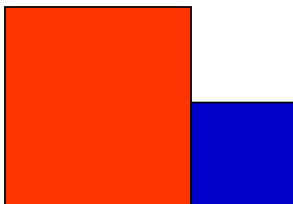


Fig. 3.8 Instead of single atom blocks, we now consider two blocks comprising 6 atoms and 3 atoms respectively. The total energy to be distributed amongst the oscillators in the blocks is 100 quanta.

Again, let's put this argument on a more quantitative footing and examine how the distribution of energy changes as the number of atoms is increased. Instead of using single atom 'blocks', let's first choose two slightly larger blocks – one comprising 6 atoms, the other comprising three atoms. 100 quanta of energy are placed in the blocks (which are, as before, in contact, see Fig. 3.8). Note also that the blocks are adiabatically isolated – i.e. they're not thermally coupled to their environment.

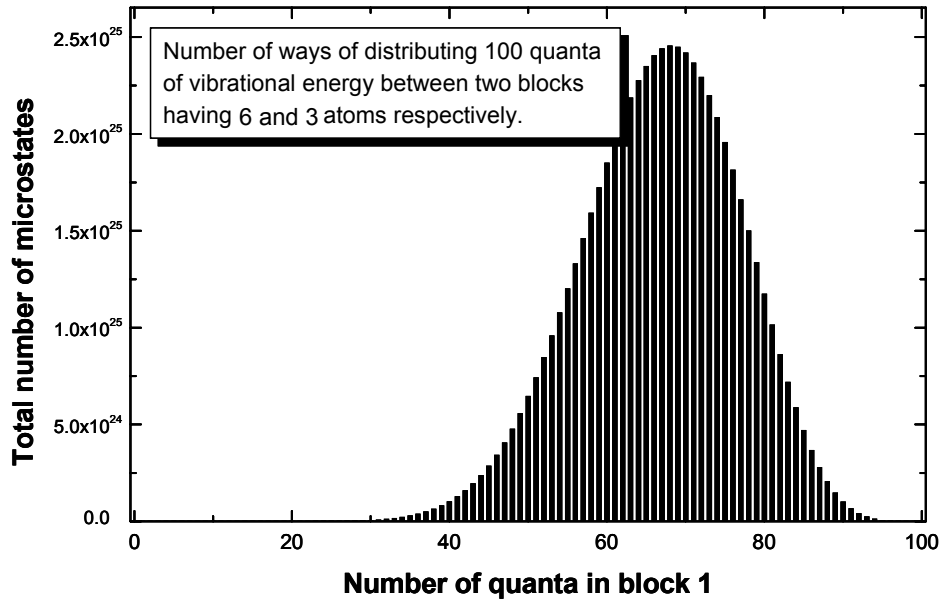


Fig. 3.9 A histogram showing the total number of microstates (arrangements of quanta of energy) vs. the number of quanta of energy in block 1. Note that the histogram has a well defined width and mean value. A total of 100 quanta of energy have been distributed between the blocks (which comprise six and three atoms (18 and 9 oscillators) respectively).

It is clear that a plot of the total number of microstates (i.e. W , where W is the product of the number of microstates associated with block 1 (Ω_1) and the number of microstates associated with block 2 (Ω_2)) vs the number of quanta of energy in block 1 is peaked at a certain value of energy.



In Fig. 3.9, to the nearest integer, where on the x-axis is the maximum of the distribution curve located? Why?

NOTES

Fig. 3.10 illustrates what happens when the number of atoms in each block shown in Fig. 3.8 is increased by an order of magnitude. Note that the distribution has narrowed appreciably. Fig. 3.9 represents a system containing less than 100 atoms. If we were to carry out this calculation for a typical macroscopic system comprising of the order of 10^{23} atoms, the distribution would be *extremely* narrow (..another understatement!). For a macroscopic system, the probability of finding the system in a state other than the most probable (which involves an equal sharing of the energy amongst all the oscillators) is an unimaginably small number. The width of the distribution is, in fact, proportional to $1/\sqrt{N}$ where N is the total number of oscillators.

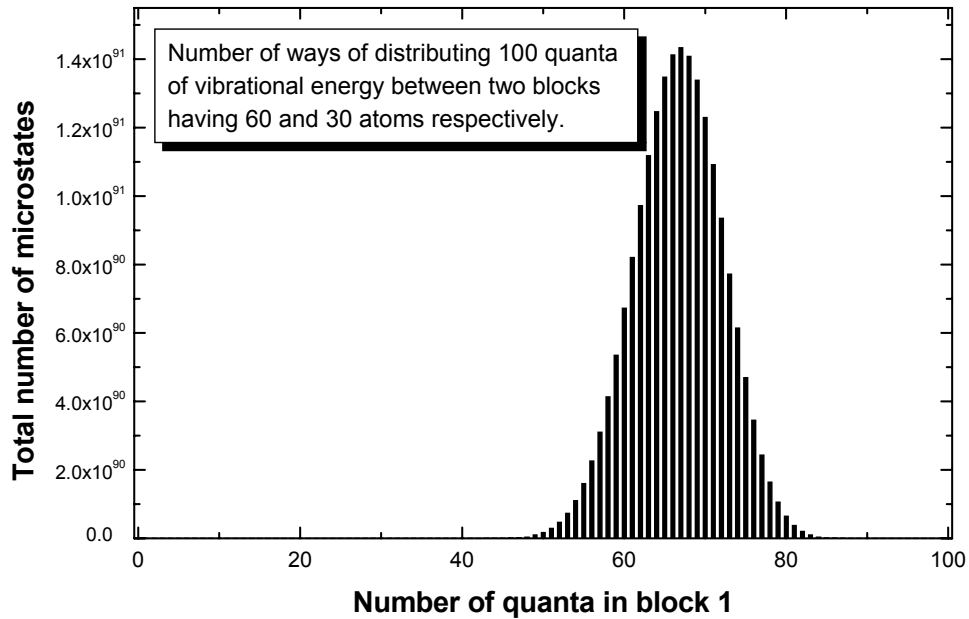


Fig. 3.10 When the number of atoms is increased by an order of magnitude, the mean of the distribution doesn't change but its width decreases considerably. This distribution is for a system containing less than 100 atoms. For a typical macroscopic system comprising $\sim 10^{23}$ atoms, the distribution will be extremely narrow. The probability of finding the system in a state other than that where the energy is shared equally between the two blocks is unimaginably small.

NOTES

3.4 Thermal equilibrium and entropy

For two systems that are not at thermal equilibrium, there will be a flow of energy until a balance is reached and the flow of energy ceases. Having considered the distribution of microstates for the two block system, we are now in a position to understand just why energy flows so that a balance is reached, i.e. so that both blocks reach the same equilibrium temperature (rather than one block ending up with all the energy).

In Fig. 3.11, the *logarithms* of Ω_1 (the number of microstates associated with Block 1), Ω_2 (the number of microstates associated with Block 2), and W , the total number of microstates ($= \Omega_1\Omega_2$) are plotted against the number of quanta of energy in Block 1. (Although one reason for the introduction of logarithms is that they make the consideration of very large numbers rather more straight-forward, there is a more fundamental reason which will be outlined below.) Note that the maximum of $\ln(\Omega_1\Omega_2)$ is located at the same position on the x-axis as was the peak in Fig. 3.10. This is not so surprising – if $\Omega_1\Omega_2$ has a maximum at x_{max} then so too will $\ln(\Omega_1\Omega_2)$.

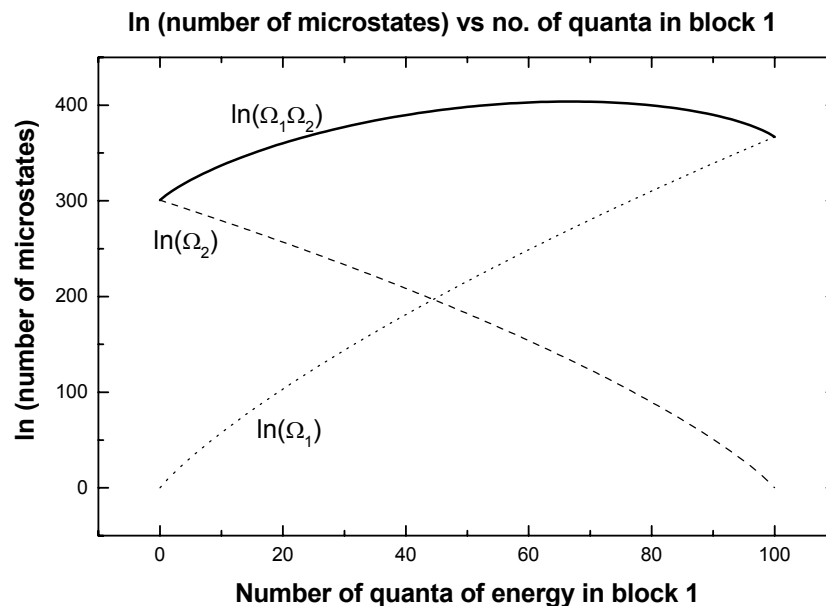


Fig. 3.11 Plot of natural log of microstates vs quanta of energy in Block 1.



If Block 2 were three times the size of Block 1, what value on the x-axis would correspond to the maximum of $\ln(\Omega_1\Omega_2)$?



A definition of entropy

Entropy is a measure of the number of possible microstates available to a system. Boltzmann's expression for entropy is a very simple (yet far-reaching) equation:

$$S = k \ln (W) \quad 3.2$$

where W is the total number of *accessible* microstates (note the word 'accessible' – we'll have more to say on this later!) and k is Boltzmann's constant.

As for the expression given for the Boltzmann factor in Section 2.3 of the notes, I strongly recommend that you commit Eqn. 3.2 to memory! In fact, as we'll soon see, the Boltzmann factor expression (i.e. the probability of occupying a state equals $\alpha \exp (-\Delta E/kT)$, where α is a constant and ΔE is the energy of the state above the ground state) and Eqn 3.2 are just two different ways of expressing precisely the same physical law.

Due to the properties of logarithms, we can get the total entropy of a system by simply adding up the entropies of the individual parts of the system:

$$S = k \ln(\Omega_1 \Omega_2) \Rightarrow \\ S = k \ln(\Omega_1) + k \ln(\Omega_2)$$

To summarise.....

If we now collate the various ideas outlined in this component of the module, we can write down the following important statement.

At thermal equilibrium, the most probable energy distribution is that associated with the greatest number of possible microstates. This distribution maximizes the total entropy of the system.

In the next set of lecture notes we'll focus on defining just what we mean by the term 'system', consider the importance of reversibility when considering entropy, introduce the concept of increasing entropy in a closed system, and discuss in some detail the 2nd law of thermodynamics.