Aims
In this chapter you will meet the concept of entropy and discover its connection with the state of disorder of a system. You will also be led to appreciate the evidence that natural changes involve an increase in disorder and hence, in the language of thermal physics, an increase in entropy.

Minimum Learning Goals
When you have finished studying this chapter you should be able to do all of the following.
1. Explain, interpret and use
   order/disorder, entropy, reversible and irreversible changes.
2. Describe the different ways of ordering molecules in a system and explain why well-ordered situations are unusual, whereas the "average" situation is the one likely to be found.
3. Recall the definition of $\Omega$ as the number of available states of a system and the definition of entropy as $k \ln \Omega$; hence discuss entropy as a measure of the randomness of a system and give examples to illustrate this.
4. Discuss naturally occurring irreversible changes in terms of increase of entropy.

PRE-LECTURE

Q4.1 Suppose you had an unbiased coin.
What is the chance of
(i) tossing a head;
(ii) tossing two successive heads;
(iii) tossing ten successive heads?

Q4.2 What is the chance of winning two 100,000-ticket lotteries in succession?
A certain event has one chance in $10^{20}$ of occurring; this is the equivalent of winning how many of these lotteries in succession?

Q4.3 A man jumps off a cliff and lands on the rocks below! Is there anything from the point of view of the conservation of energy (and the first law of thermodynamics) to prevent his bouncing back to the top of the cliff.

LECTURE

4.1 PROBABILITY
Card playing
Consider the following set of playing cards dealt to a group of four persons:

<table>
<thead>
<tr>
<th></th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
</tr>
</thead>
<tbody>
<tr>
<td>Clubs</td>
<td>AKQJ1098765432</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Diamonds</td>
<td>-</td>
<td>AKQJ1098765432</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Hearts</td>
<td>-</td>
<td>-</td>
<td>AKQJ1098765432</td>
<td>-</td>
</tr>
<tr>
<td>Spades</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>AKQJ1098765432</td>
</tr>
</tbody>
</table>

This set of cards is well-ordered; very few words are needed to unambiguously describe it.
The chance of this well-ordered arrangement of four sets of cards appearing at random is $1 \text{ in } 2 \times 10^{27}$. 
Consider another set of hands:

<table>
<thead>
<tr>
<th></th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
</tr>
</thead>
<tbody>
<tr>
<td>Clubs</td>
<td>AJ65</td>
<td>K97</td>
<td>1032</td>
<td>Q84</td>
</tr>
<tr>
<td>Diamonds</td>
<td>K75</td>
<td>QJ8</td>
<td>432</td>
<td>A1096</td>
</tr>
<tr>
<td>Hearts</td>
<td>Q62</td>
<td>J875</td>
<td>K109</td>
<td>A43</td>
</tr>
<tr>
<td>Spades</td>
<td>863</td>
<td>KJ4</td>
<td>A752</td>
<td>Q109</td>
</tr>
</tbody>
</table>

This set of cards is disordered: three of the hands have to be detailed card by card to unambiguously describe it.

The chance of this disordered arrangement of four sets of cards appearing at random is also 1 in $2 \times 10^{27}$.

Both sets have the same probability of being dealt, yet the first set looks peculiar and the second set looks normal.

Although the second set is, in terms of actual cards in the hands, as improbable as any other, it is representative of a large number of hands of the type 4 of one suit, 3 of the other suits.

A single such 4/3/3/3 hand can be obtained in any one of $1.7 \times 10^{10}$ ways. That is to say $1.7 \times 10^{10}$ hands of this 4/3/3/3 type, all containing different cards can be dealt: the total number of different single hands that can be dealt is $6.3 \times 10^{11}$.

This means that if we play many games of bridge we see many occurrences of this 4/3/3/3 distribution. That is why we call such a hand normal.

**Conclusion:**

(1) The well-ordered situation is unusual; the disordered situation is common.

(2) While all situations have an equal probability of occurring, there are so many more disordered situations than ordered situations that we expect to find disordered situations rather than ordered situations.

**Further Example of Probabilities**

(1) **Packing people into houses.**

Another illustration of common/uncommon situations coexisting with equal probabilities is given on the videotape.

(2) **Air molecules in box.**

Consider the situation with a large number of air molecules in a box. There are too many molecules to use the laws of motion to keep track of them: a statistical or probability approach must be used.

How do we expect the molecules to be spread out? All in one corner, or pretty evenly throughout the box?

There is no fundamental law of physics that says it must be an even spread: rather, it is a matter of equal probability of all arrangements but an overwhelming number of arrangements that correspond to even spreading.

In following calculation the box is considered to be divided into a large number of small cells: even-spreading corresponds to the same number of molecules in each cell; "all in one corner" corresponds to all the molecules being in a single cell.

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
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</tr>
</thead>
<tbody>
<tr>
<td>Number of molecules</td>
<td>$1 \times 10^{25}$</td>
</tr>
<tr>
<td>Box size</td>
<td>$1 \text{ m}^3$</td>
</tr>
<tr>
<td>Size of cell</td>
<td>$1 \times 10^{-6} \text{ m}^3$</td>
</tr>
<tr>
<td>Hence number of cells</td>
<td>$1 \times 10^6$</td>
</tr>
</tbody>
</table>

The number of ways of getting all the molecules into a single cell equals 1.

The number of ways of arranging molecules evenly among cells ($10^{19}$ in each cell) is about $(10^6)^{10^{25}}$, a number that can well be described as overwhelming.
4.2 DEFINITION OF ENTROPY

What we have done to date is to count the number of ways a system may be arranged and to note that very few of these arrangements correspond to a state of high organisation while the vast majority of them correspond to an average, disorganised state.

The number of ways a system can be organised can then be used as a measure of its disorder or randomness. The technical term we use for this measure is called the entropy of the system. Since the numbers we have been dealing with are extremely large, it is more convenient to deal with the logarithms of the numbers.

We write the number of available states of the system as $\Omega$ and proceed to define the entropy of the system as

$$S = k \ln \Omega.$$  

The symbol $k$ is called Boltzmann's constant and is used here so that we finish up with the same number and units for entropy as in the thermodynamic approach which will be used in TP5.

The value of Boltzmann's constant is $1.38 \times 10^{-23}$ J.K$^{-1}$.

4.3 SIMPLE CALCULATION OF ENTROPY

Air in Box

(i) all molecules in one particular cell (in the corner of the box)

$$\Omega = 1$$

and

$$S = k \ln \Omega = k \ln 1 = 0 \text{ J.K}^{-1}.$$  

(ii) molecules evenly distributed

$$\Omega = (10^6)^{10^{25}}.$$  

$$S = k \ln \Omega = 10^2 \text{ J.K}^{-1}.$$  

As expected the entropy is larger in the disordered system.

4.4 ENTROPY AND IRREVERSIBLE CHANGES

There is always a possibility that a system can be in a state that is well ordered and so considered abnormal, e.g. all the air molecules bunched in a corner of room or all the molecules in a human body moving in the same direction (levitation). The reason why we do not commonly observe such behaviour is that there are so many other equally possible states of the system, the vast bulk of them disordered. What we commonly observe is one of these disordered states.

It is possible to apply some constraint to a system to artificially order it; e.g. all the air molecules in a room might be pushed down into a corner. When the constraint is removed, the system changes from order to disorder and does not change back. This natural phenomenon of a system changing from a situation of order (few available states) to one of disorder (many available states) is termed irreversibility (e.g. mixing salt and pepper).

By definition irreversible changes involve an increase of entropy.
**Observation of film being run forwards and backwards**

We can use our familiarity with this tendency of nature for irreversible changes (process of increasing entropy) to judge whether a film showing real-life situations is being shown forwards or backwards in time.

Situations:
- Milk bottle breaking.
- Car being driven in traffic.
- Car reversing or traveling forwards
- Child on slippery-dip.
- Child on swing.
- Clock pendulum.
- Hands on clock face.
- Billiard balls colliding.

Such judgements are easy to make when going from very ordered to disordered situations. When the system is rather disordered to start with, a judgement as to the direction of time is more difficult. E.g. viewing of the diffusion analogue film (lecture FE4) at a time well after its starting point.

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**POST LECTURE**

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### 4.5 FORWARDS OR BACKWARDS

**Q4.4** In movies of the "Perils of Pauline" type, a scene often appears where the heroine is tied to the railway line and a train comes to a halt just before it cuts her into three. If you carefully watch such a scene you should pick up a clue to the fact the film is actually being shown in reverse (fewer heroines are lost that way). What is the clue?

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### 4.6 QUESTION ON PROBABILITY

**Q4.5** Suppose there are 44 keys on a typewriter board (exclude capitals). Calculate the probability of a monkey typing out the 10 character phrase

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    i love you.
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In the light of this answer, do you really believe the story of the monkeys sitting at typewriters and coming up with the complete text of Hamlet?

[Suppose $10^{10}$ monkeys - $10^{18}$ seconds - 10 keys hit per second - $10^5$ characters in Hamlet.]