PHYS1001  PHYSICS 1 REGULAR
Module 2 Thermal Physics

Second Law of Thermodynamics
a statement of what is impossible

• Direction of thermodynamics processes: Heat always flows spontaneously from a hot object to a cooler one.

• Impossible to convert heat completely into mechanical work. Max efficient of a real heat energy < 100%. It is impossible for any system to undergo a process in which it absorbs heat from a reservoir at a single temperature and converts the heat completely into work, with the system ending in the same state in which it began.

• It is impossible to make a refrigerator that transports heat from a colder body to a hotter body without the addition of work. A minimum energy input is required to operate a refrigerator. It is impossible for any process to have the sole result the transfer of heat from a cooler to a hotter body.

• *Irreversible processes* (processes that proceed spontaneously in one direction but not other) – inherent one-way processes in nature - perfume from an open bottle will spread throughout a room – the perfume molecules will never spontaneous gather back into the bottle; miscible liquids left to themselves always tend to mix, not to unmix.

• No engine can be more efficient than a Carnot engine operating between the same two temperatures.

• Perpetual motion machines can not be constructed.

• For an isolated system, the direction of spontaneous change is from a situation of lesser probability to a situation of greater probability. For an isolated system, the direction of spontaneous change is from order to disorder. The entropy of an isolated system increases or remains the same.
Entropy and disorder

Quantitative measure of disorder – when a gas is heated and expands, the gas is in a more disordered state after the expansion than before since the molecules are moving in a larger volume and have more randomness of position.

Infinitesimal reversible change \( dS = \frac{dQ}{T} \)

Reversible isothermal change \( \Delta S = \frac{Q}{T} \)

Entropy change in a reversible process \( \Delta S = \frac{\int_1^2 dQ}{T} \)

The entropy has a definite value for a particular state. When a change occurs from state 1 to state 2, the change in entropy is the same for all possible paths 1 to 2. This fact can be used to determine the entropy change for an irreversible process – simply invent a path from 1 to 2 that consists of entirely reversible processes.

Entropy changes

Reversible cyclic process \( \Delta S = \int \frac{dQ}{T} = 0 \)

All irreversible changes \( \Delta S > 0 \) \( \Rightarrow \) entropy is not a conserved quantity

Second law – when all systems taking part in a process are included, the entropy remains constant or increases \( \Leftrightarrow \) no process is possible in which the total entropy decreases, when all systems taking part in the process are included

For all processes \( \Delta S_{\text{total}} \geq 0 \)
Discerning the arrow of time

In the movies of the type, “Perils of Pauline”, a scene often appears where the heroine is tied to the railway tracks and a train comes to a halt just before it cuts her into three.

If you watch such a scene (diverting your attention from the heroine), you should pick up a clue to the fact the film is actually being shown in reverse (less heroines are lost this way). What is the clue?

There is no phenomena whereby an object will spontaneously leave a state of equilibrium. All natural processes proceed in such a way that the probability of the state increases – law of increasing entropy – it is on of the most important laws of nature – the Second Law of Thermodynamics.
Entropy – microscopic view

Much greater number of possible microscopic states $\Rightarrow$ much greater probability of macroscopic state $\Rightarrow$ much greater disorder $\Rightarrow$ much greater entropy.

Equilibrium state – most probable macroscopic state – most number of microscopic states – greatest disorder – greatest entropy.

Configurations associated with large numbers of microstates are said to be more complex or more disordered than those with fewer microstates. The equilibrium state of a system is the most disordered configuration available. The Austrian physicist Ludwig Boltzmann introduced a measure of disorder called the entropy defined by

$$S = k \ln(w)$$

$$\Delta S = S_2 - S_1 = k \ln \left( \frac{w_2}{w_1} \right)$$

$w$ is the number of possible microscopic states for a given macroscopic state, $k$ is the Boltzmann constant and $\ln$ is the natural logarithm ($\log_e$).

A closed system can never spontaneously undergo a process that decreases the total number of microscopic states.
**Card playing**

Consider the following set of cards dealt to a group of 4 persons

Arrangement 1

<table>
<thead>
<tr>
<th></th>
<th>Jill</th>
<th>Jack</th>
<th>Jan</th>
<th>John</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 and it would be very surprising to see such an arrangement. The chance of getting this arrangement is 1 in $2 \times 10^{27}$.

Arrangement 2

<table>
<thead>
<tr>
<th></th>
<th>Jill</th>
<th>Jack</th>
<th>Jan</th>
<th>John</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 and is the type of arrangement that one commonly sees. The chance of getting arrangement 2 is 1 in $2 \times 10^{27}$.

Both arrangements dealt have the same probability, but arrangement 2 is normal and arrangement 1 is very, very, … rare. Although the arrangement 2 is improbable as any other, it is representative of a large number of hands of the type 4 of one suit and 3 of the other suits. A single hand such as 4/3/3/3 can be obtained in any one of $1.7 \times 10^{10}$ ways. This means that if we play many games of bridge we see many occurrences of this 4/3/3/3 arrangement.
**Coin game**

Consider a game of throwing coins into the air and then counting the number of heads and tails. We can start with throwing 4 coins (5 macroscopic states and 16 microscopic states).

Macroscopic state 1: 4 H / 0 T, microscopic state \( w = 1 \), prob = 1/16, \( S = k \ln(1) = 0 \)

- Microscopic state 1: H H H H

Macroscopic state 2: 3 H / 1 T, microscopic states \( w = 4 \), prob = 4/16, \( S = k \ln(4) \)

- Microscopic state 2: H H H T
- Microscopic state 3: H H T H
- Microscopic state 4: H T H H
- Microscopic state 5: T H H H

Macroscopic state 3: 2 H / 2 T, microscopic states \( w = 6 \), prob = 6/16, \( S = k \ln(6) \)

- Microscopic state 6: H H T T
- Microscopic state 7: H T H H
- Microscopic state 8: T T H H
- Microscopic state 9: T H T H
- Microscopic state 10: H T T T
- Microscopic state 11: T H H T

Macroscopic state 4: 1 H / 3 T, microscopic states \( w = 4 \), prob = 4/16, \( S = k \ln(4) \)

- Microscopic state 12: T T T H
- Microscopic state 13: T T H T
- Microscopic state 14: T H T T
- Microscopic state 15: H T T T

Macroscopic state 5: 0 H / 4 T, microscopic state \( w = 1 \), prob = 1/16, \( S = k \ln(1) = 0 \)

- Microscopic state 16: T T T T
Most probable macroscopic state is the state with the greatest probability of occurrence, state with the greatest disorder and the state with the greatest entropy, it is macroscopic state 3 (2 H / 2 T).

For \( N \) coins, the total number of microscopic states = \( 2^N \)

For \( h \) heads and \( t \) tails, the number of microscopic states = \( (h + t)! / h! \ t! = N! / h! \ t! \)

Probability of a macroscopic state

\[
\text{Probability of a macroscopic state} = \frac{\text{no. of microscopic states}}{\text{total no. microscopic state}} = \frac{N!}{(h+t)!} \frac{1}{2^N}
\]

\( N = 4 \), macroscopic state (3 H / 1T): \( h = 3 \) and \( t = 1 \)

\[
\text{prob} = \frac{4!}{(3!+1!)} \frac{1}{2^4} = \frac{4}{16}
\]

\( N = 4 \), macroscopic state (2 H / 2T): \( h = 2 \) and \( t = 2 \)

\[
\text{prob} = \frac{4!}{(2!+2!)} \frac{1}{2^4} = \frac{6}{16} \quad \text{this is the most probable state}
\]

\( N = 160 \) \( h = 80 \) and \( t = 80 \) \( \Rightarrow \) prob = 0.063

\( N = 160 \) \( h = 70 \) and \( t = 90 \) \( \Rightarrow \) prob = 0.018

\( N = 160 \) \( h = 60 \) and \( t = 100 \) \( \Rightarrow \) prob = 0.000042
Macrostate: no. of heads

No. of microstates

\[ N = 160 \]

\[ N = 80 \]

\[ N = 40 \]

\[ N = 4 \]
Molecules of air in a box

For 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 spread out?* There is no fundamental law of physics that says they must be evenly distributed – rather, it is a matter of probabilities.

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Box size</td>
<td>1 m³</td>
</tr>
<tr>
<td>No. of molecules</td>
<td>$10^{25}$</td>
</tr>
<tr>
<td>Size of cell</td>
<td>$10^{-6}$ m³</td>
</tr>
<tr>
<td>No. of cells</td>
<td>$10^{6}$</td>
</tr>
</tbody>
</table>

No. of ways of getting all molecules into a single cell = 1

Entropy $S = k \ln(w)$  \( w = 1 \)  $S = 0$

No. of ways of arranging molecules evenly among cells ($10^{10}$ in each cell) is $\left(10^{6}\right)^{10^{25}}$

Entropy $S = k \ln(w)$  \( w = \left(10^{6}\right)^{10^{25}} \)  $k = 1.38 \times 10^{-23}$ J.K$^{-1}$

\[ S = (1.38 \times 10^{-23} \text{ J.K}^{-1})(10^{25}) \ln(10^{6}) = 2000 \text{ J.K}^{-1} \]