THERMAL & STATISTICAL PHYSICS
SSP3133

DENSITY OF STATE,
ENTROPY
AND
THE SECOND LAW

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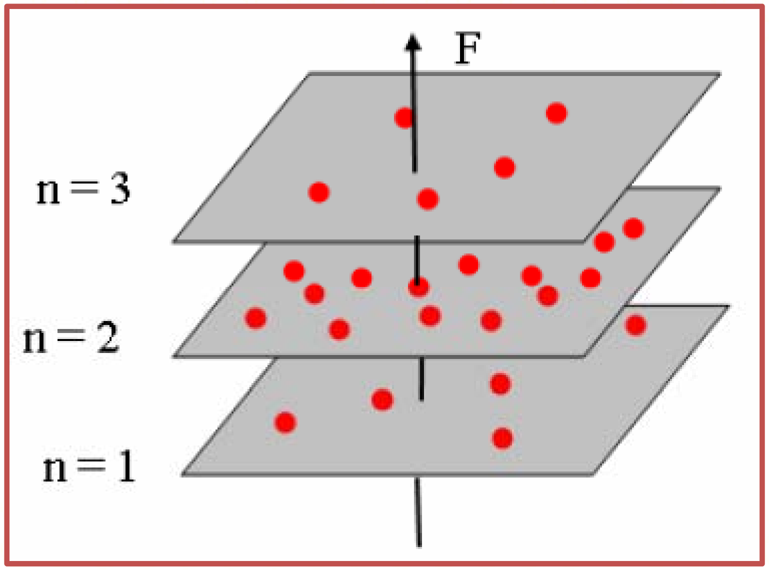
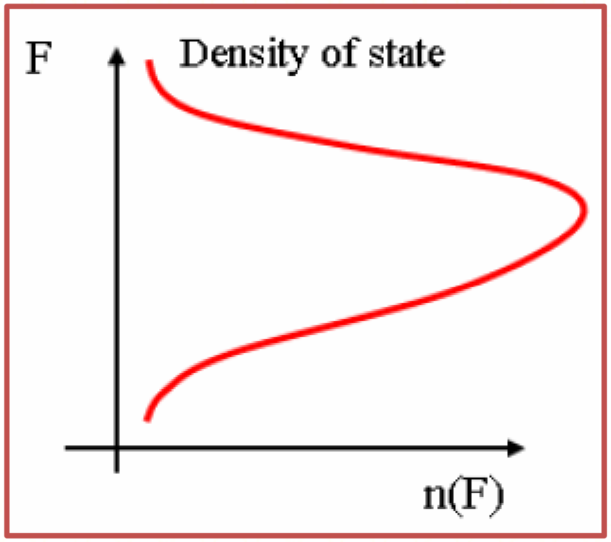
Acknowledgement : PROFESSOR DR RAMLI ABU HASSAN

Density of State





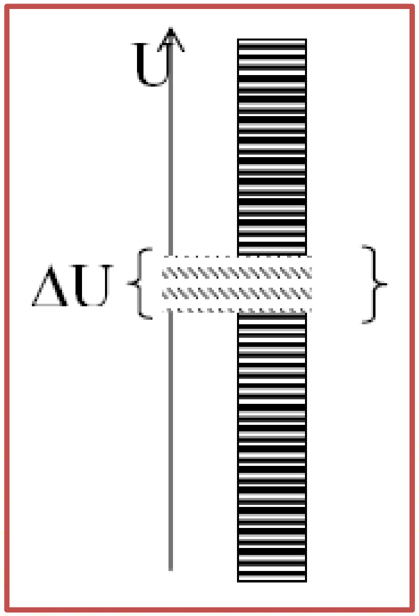
Let ΔU = energy range of finite width

Expect: number of states $\propto \Delta U$

If $\Omega(U, \Delta U)$: number of states between U and U+ΔU

$$\Omega(U, \Delta U) = g(U)\, \Delta U$$

g (U): density of state

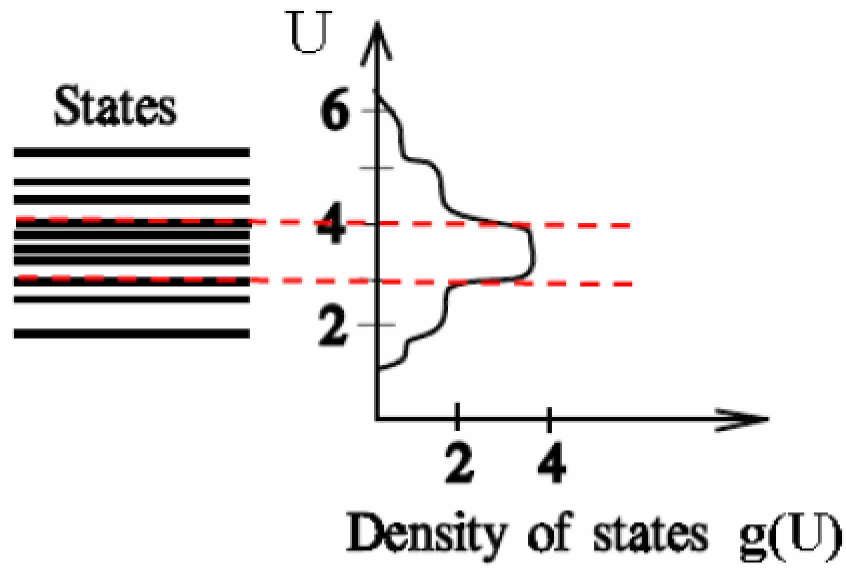


States available to the system

Definition

The energy density of states (EDOS) function measures the number of energy states in each unit interval of energy and in each unit volume of the crystal

$$g(U) = \frac{number\ of\ \ states}{Energy\ x\ volume}$$



The density of states at E

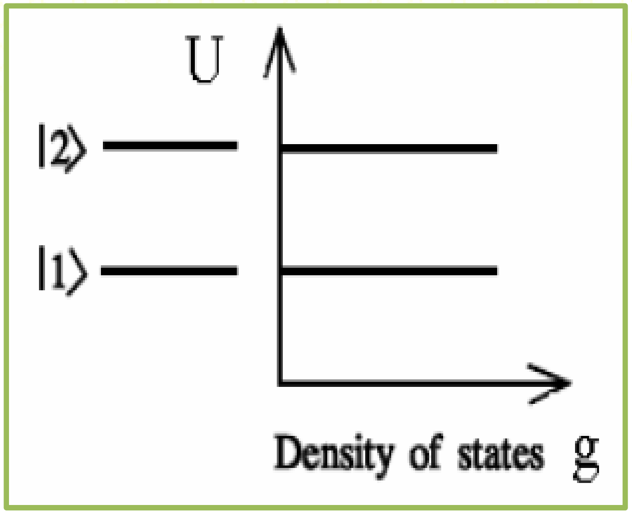
= (3 + 4) /2 = 3.5 eV

$$g(3.5) = \frac{number\ of\ \ states}{Energy\ x\ volume}$$

ΔE = 4 -3 = 1 eV → 4 energy states

$$= \frac{4}{1eV\ x\ 1cm^3} = 4$$

Example: Suppose a crystal has two discrete states (i.e. single states) in each unit volume of crystal.



The density-of-state function consists of two Dirac delta functions of the form

$$g(U) = \delta(U - U_1) + \delta(U - U_2)$$

Integrating over energy gives the number of states in each unit volume

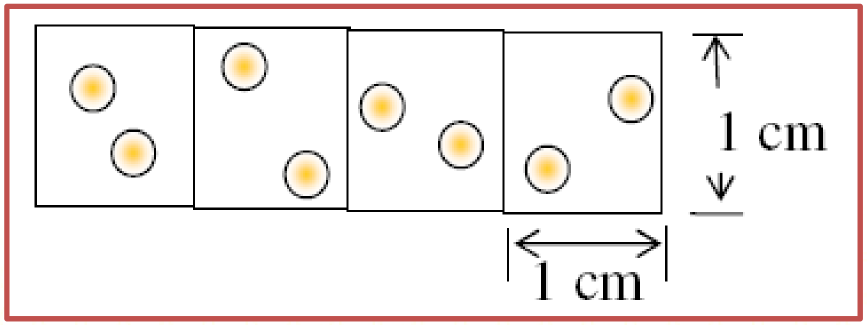
$$N_v = \int_0^\infty g(U)dU$$

$$= \int_0^\infty dU\{\delta(U - U_1) + \delta(U - U_2)\}$$

$$= 2$$

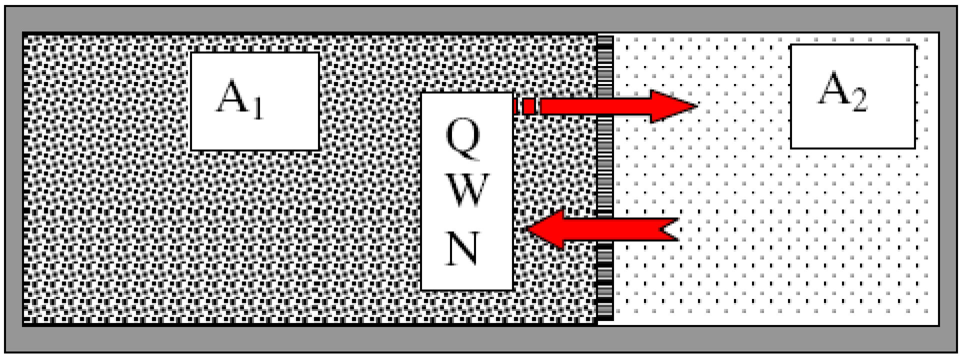
If the crystal has the size 1x4 cm^3 then the total number of states in the entire crystal must given by

$$N = \int_0^4 N_v dV = 8$$



Microstates of interacting systems

2 interacting systems, A_1 and A_2 – heat, work & particles



Let U_1: internal energy of A_1
U_2: internal energy of A_2

$$U_0 = U_1 + U_2 \quad \cong \text{constant}$$

The number of states

$$\Omega_0 = \Omega_1 \Omega_2$$

Let:

R for A_1 = 6 degrees of freedom

R for A_2 = 10 degrees of freedom

Therefore $\Omega_1 \propto (U_1)^3$

$\Omega_2 \propto (U_2)^5$

Assume $U_1 + U_2 = 5$ unit of energy

U_1	U_2	Ω_1	Ω_2	$\Omega_O = \Omega_1\Omega_2$
0	5	0	3125	0
1	4	1	1024	1024
2	***3***	***8***	***243***	***1944***
3	2	27	32	864
4	1	64	1	64
5	0	125	0	0
			Total	3896

Since every state is equaly likely, the most probable energy distribution

$U_1 = 2$ eu
$U_2 = 3$ eu

Note: $1944/3896 = 0.5$
-half of the time energy distribution is $U_1 = 2$ eu and $U_2 = 3$ eu

Now consider system with $R_1 = 12$ and $R_2 = 20$

$$\Omega_1 \propto (U_1)^6$$
$$\Omega_2 \propto (U_2)^{10}$$

Assume $U_1 + U_2 = 5$ unit of energy

Assume $U_1 + U_2 = 5$ unit of energy

U_1	U_2	Ω_1	Ω_2	$\Omega_O = \Omega_1\Omega_2$
0	5	0	9.77×10^6	0
1	4	1	1.05×10^6	1.05×10^6
2	***3***	***64***	$\boldsymbol{5.90\times10^6}$	$\boldsymbol{3.78\times10^6}$
3	2	729	1.02×10^6	0.744×10^6
4	1	4.1×10^3	1	0.004×10^6
5	0	1.56×10^4	0	0
			Total	5.57×10^6

For $U_1 = 2$ eu & $U_2 = 3$ eu

-the accessible states are 68%
-the system will have this energy distribution more than two-thirds of the time!!!

Let $R_1 = 120$ and $R_2 = 200$

$$\Omega_1 \propto (U_1)^{60}$$

$$\Omega_2 \propto (U_2)^{100}$$

U_1	U_2	Ω_1	Ω_2	$\Omega_O = \Omega_1\Omega_2$
0	5	0	7.9×10^{69}	0
1	4	1	1.6×10^{60}	1.6×10^{60}
2	***3***	***1.2×10^{18}***	***5.2×10^{47}***	***6.2×10^{65}***
3	2	4.2×10^{28}	1.3×10^{30}	5.5×10^{58}
4	1	1.3×10^{28}	1	1.3×10^{36}
5	0	8.7×10^{41}	0	0
			Total	6.2×10^{65}

For $U_1 = 2$ eu & $U_2 = 3$ eu

-the accessible states are 99.997%

-the system will have this energy distribution at any instant in time!!!

Marcoscopic system

Number of particles ~ 10^{24}
$R_1 = 6 \times 10^{24}$ and $R_2 = 10 \times 10^{24}$

$\Omega_1 \alpha (U_1)^{3x10^{24}}$

$\Omega_2 \alpha (U_2)^{5x10^{24}}$

U_1	U_2	Ω_1	Ω_2	$\Omega_O = \Omega_1 \Omega_2$
0	5	0	$10^{6.99x10^{24}}$	0
1	4	1	$10^{6.02x10^{24}}$	$10^{6.02x10^{24}}$
2	***3***	$10^{1.81x10^{24}}$	$10^{4.77x10^{24}}$	$10^{6.58x10^{24}}$
3	2	$10^{2.861x10^{24}}$	$10^{3.0x10^{24}}$	$10^{5.87x10^{24}}$
4	1	$10^{3.61x10^{24}}$	1	$10^{3.61x10^{24}}$
5	0	$10^{4.19x10^{24}}$	0	0
			Total	$10^{6.58x10^{24}}$

For $U_1 = 2$ eu & $U_2 = 3$ eu
-the accessible states are the most probable --- i.e $10^{0.56x10^{24}}$ times more probable than the other distribution.

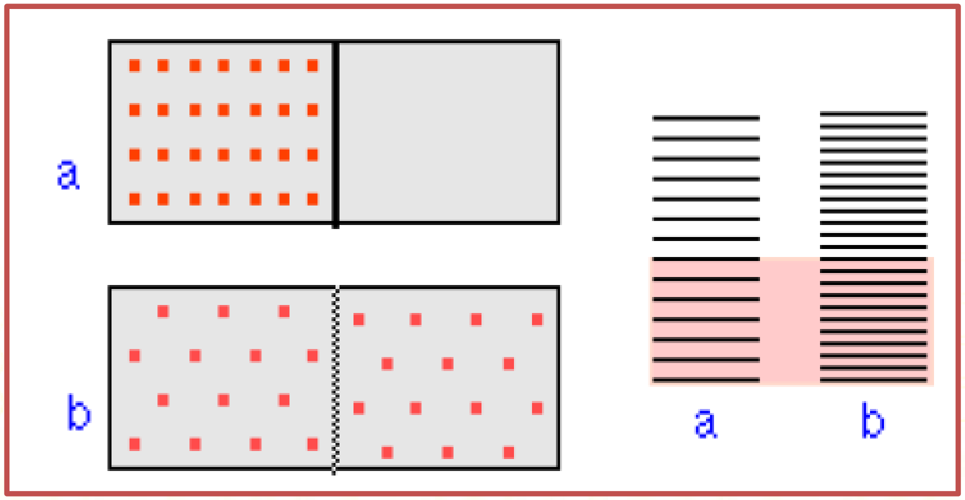
NOTE:
When 2 interacting macroscopic systems are in equilibrium, the values of the various system variables will be such that the

number of states available to the combined system is a maximum.

The second law of thermodynamics

As 2 interacting macroscopic systems approach equilibrium, the changes in the system variables will be such that the number of states available to the combined system increases. Or, in the approach to equilibrium,

$$\Delta\Omega_o > 0$$



Note: 1st Law: - reflect inviolable fact
-work for small system

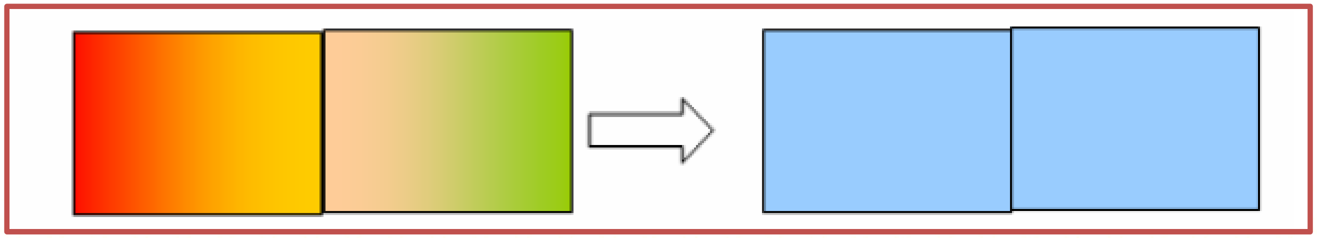
2nd Law: - based on probability
-for large system – there is some infinitesimal probability the law be violated!!!

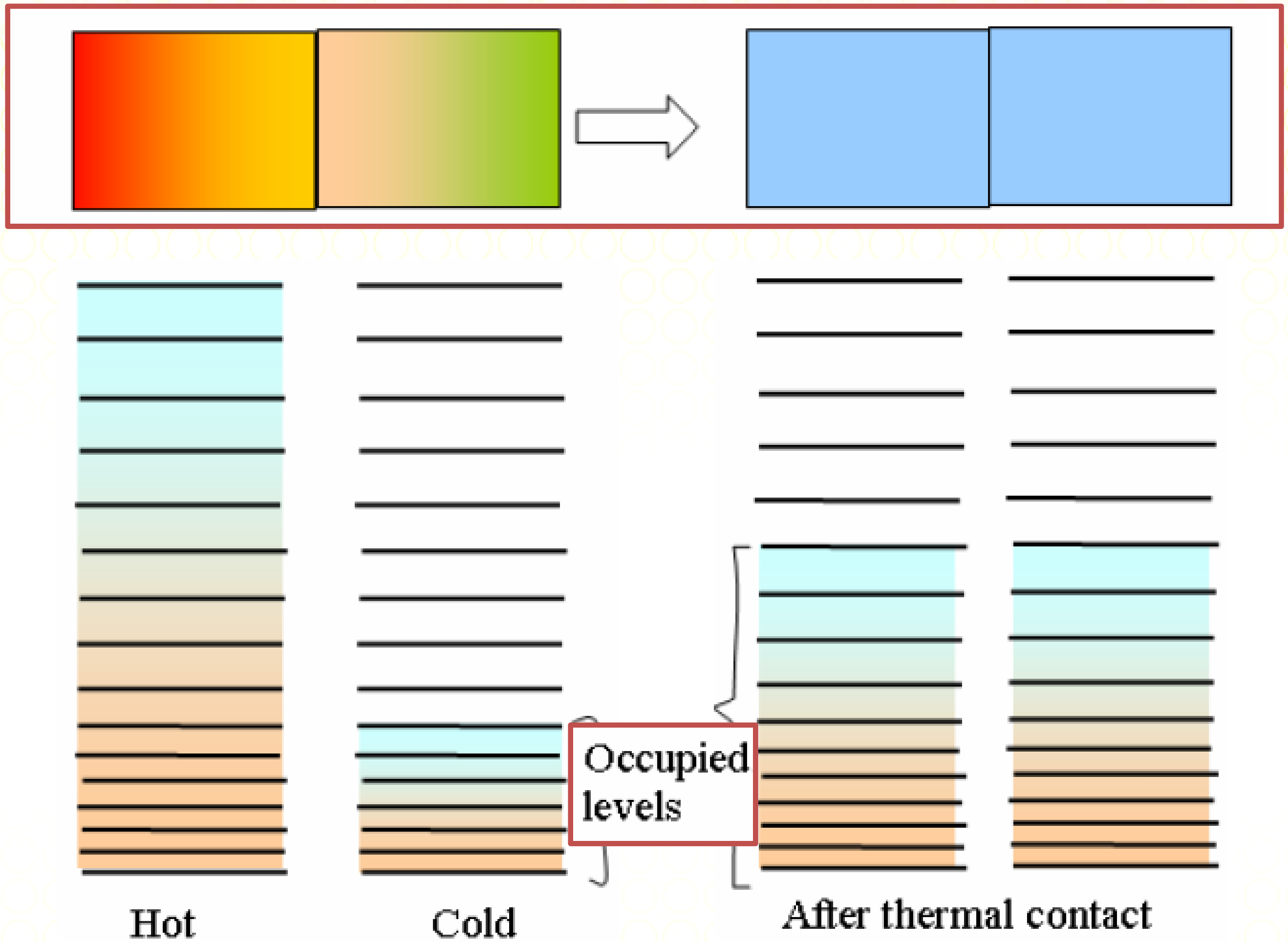
Heat flow and energy spreading

The fundamental science behind the second law:
Energy spontaneously disperses from being localized to becoming spread out if it is not hindered

Thermal contact:

-thermal energy flows from the higher occupied levels in the warmer object into the unoccupied levels of the cooler one until equal numbers are occupied in both bodies, bringing them to the same temperature.




Occupied levels
Hot
Cold
After thermal contact

The degree of dilution of the thermal energy is

$$Q / T$$

Cold body: T_{Cold} is low; few thermal energy states are occupied, so the amount of energy spreading can be very great.

When T_{Cold} near T_{Hot}, more thermal energy states are occupied

Entropy

Entropy – (Greek for **'turning into'**)

- Is a measure of the degree of disorder of a system.
- In a reversible process entropy remains constant.
- In an irreversible process, entropy MUST increase. Entropy can NEVER decrease in a closed system.
- In any cyclic process the entropy will either increases or remains the same

The 2nd **law of thermodynamics:**

Every time energy is transformed from one state to another, there is a loss in the amount of that form of energy, which becomes available to perform work of some kind. The loss in the amount of ***'available energy'*** *is known as* ***'entropy'***

Entropy –a state variable whose change is defined for a reversible process at T where Q is the heat absorbed

Entropy – a measure of the amount of energy which is unavailable to do work

Entropy – a measure of the disorder of a system.

Entropy – a measure of the multiplicity of a system

Definition

Entropy just measures the spontaneous dispersal of energy: how much energy is spread out in a process, or how widely spread out it becomes – as a function of temperature.

Or

$$\textbf{Entropy} = S \simeq k \ln \Omega$$

k: Boltzmann's constant
Ω very big number – take lnΩ

Combine system ($A_0 = A_1 + A_2$)

$$\Omega_0 = \Omega_1 \, \Omega_2$$

$$k \ln\Omega_0 = k \ln(\Omega_1 \, \Omega_2) = k \ln\Omega_1 + k \ln\Omega_2$$

$$S_0 = S_1 + S_2$$

2nd law can be stated in terms of the entropy (alternative)

As 2 interacting macroscopic systems have reached equilibrium, the changes in the system variables will be such that the entropy of the combined system increases.

$$\Delta S_0 > 0$$

When $A_0 = A_1 + A_2$ have reached equilibrium, then Ω_O will be maximized

$$\Delta S_0 \, (\text{equilibrium}) = 0$$

2^{nd} law (alternative)

For any 2 interacting systems (whether in equilibrium or not) the entropy of the combined system cannot decrease.

ΔS_0 > or = 0

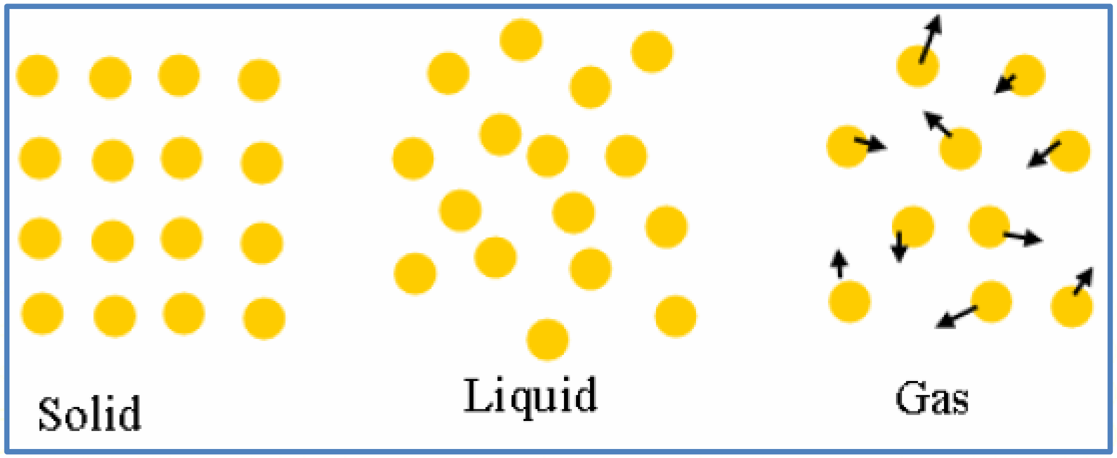
What is entropy? How is it related to the second law?

Entropy measures how much energy is dispersed in a particular process (at a specific temperature).

Energy spontaneously tends to flow only from being concentrated in one place to becoming diffused or dispersed and spread out.

e.g A hot frying pan cools down when it is taken off the kitchen stove.

The energy concentrated inside a chemical like oil or coal (or food) will spread out.



Cars rust, pendulums run down, people get old.
--Things like this don't happen backwards.
Like the flow of time (*time arrow*)
--they happen only in one sequence

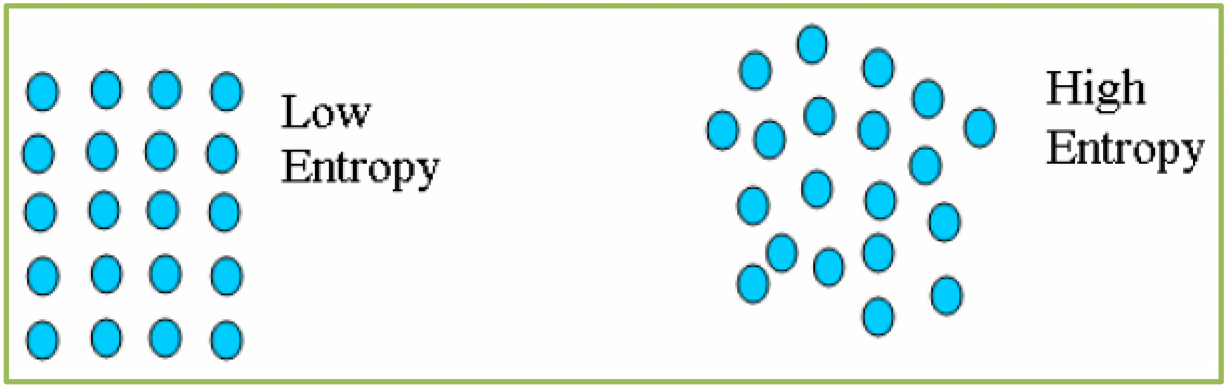
The 2nd law of **thermodynamics** (or the law of **entropy**)
*The **universe** and all of its **energy** systems will increase in disorder as time moves forward.*

Disorder means the breakdown of energy into useless **heat**, from which no **work** can be done.

Entropy is a measure of disorder
Chaos is a state of organized disorder

-entropy gives information about the evolution of an isolated system with time → gives the direction of "time arrow"

-State which is more disordered →this state came later in time



-The second law of thermodynamics --gives the direction of heat flow in any thermal process.

-Reasons -- why nature behaves in that way.

- *Any process either increases the entropy of the universe - or leaves it unchanged.*
  -Entropy is constant only in reversible processes
  -All natural processes are irreversible.

- *All natural processes tend toward increasing disorder*
  -energy is conserved
  -but iits availability is decreased.

- *Nature proceeds from*
  -simple to the complex
  -orderly to the disorderly
  -low entropy to high entropy.

- *The entropy of a system is proportional to the logarithm of the probability of that particular configuration of the system occuringm(*$\mathbf{S \cong k \ln \Omega}$)

Heat naturally flows from higher T to lower T.

No natural process has as its sole result the transfer of heat from a cooler to a warmer object.

No process can convert heat absorbed from a reservoir at one temperature directly into work without also rejecting heat to a cooler reservoir. That is, no heat engine is 100% efficient.

-more highly ordered the configuration of a system
-less likely it is to occur naturally
-hence the lower its entropy.

-The laws of Thermodynamics --wide range of applicatios
-Cosmology, History, Economics, Military, and to almost everything

The 2nd law of Thermodynamics:

-the **total entropy** in the world is **constantly increasing**
-decrease in **'available energy'**.
-the unavailable energy-form works as **pollution.**
-the world is moving towards a dissipated state
-the pollution is constantly increasing

-**entropy** (i.e. the 'unavailable' energy or pollution) tends towards a "**maximum**"

-In a closed system - ultimately reached a stage where there is no longer any difference in energy level --**'the equilibrium state'.**

-**Maximum** entropy -no longer 'free energy' is available for work

REFERENCES:

1. REAF, F : "Fundamentals Of Statistical And Thermal Physics", McGraw-Hill.

2. KITTEL & KROMER: "Thermal Physics", W.H. Freeman & Company.