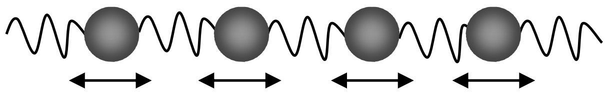
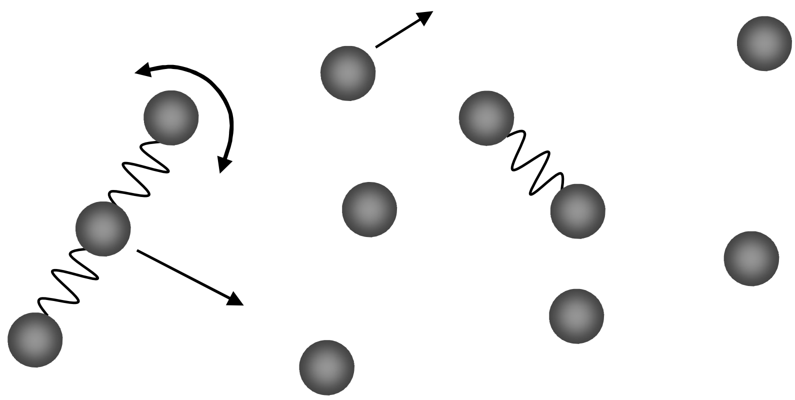
States of Matter and Entropy Change

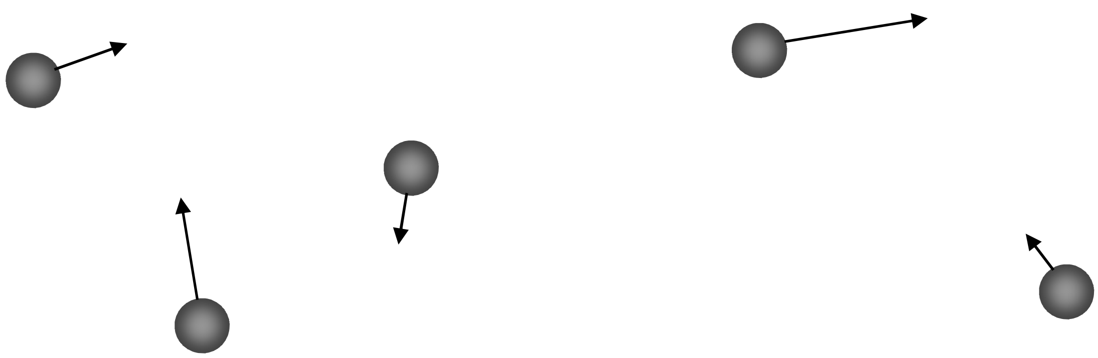
Solids: in a solid the particles (molecules/atoms) are held together in a rigid lattice and are free only to vibrate about their fixed positions (with only occasional changes in position) – we can imagine the bonds holding the particles together to be like tiny springs and there is long-range order in the substance:



Liquids: in a liquid the particles are more disordered and the average distance between them is greater than in a solid– small groups of them may be transiently bonded together in a sea of free particles that continually form and break bonds with one another. The particles / clumps of particles are more free to move around by translation and rotation. There is only transient and short-range order.



Gases: in an ideal gas the particles are completely free to move and spread far apart and do not bond at all to one another – they do not interact. In a real gas, there are some transient and very weak 'bonds' forming such as intermolecular van der Waals forces. The particles also interact by colliding with one another. The system



Entropy and the Sates of Matter

Solid	Liquid	Gas
Rigid - particles in fixed positions	Fluid – particles are free to move around	Fluid – particles are free to move around
Particles arranged in a regular lattice	Particles arranged randomly	Particles arranged randomly
Particles close together	Particles close together	Particles far apart
Volume depends only slightly on temperature and pressure (low compressibility)	Volume depends only slightly on temperature and pressure (low compressibility)	Volume depends strongly on temperature and pressure (high compressibility)
More or less fixed dimensions and shape	Expand to partly fill container or form drops	Expand completely to fill container
Highly ordered	Local order only	Highly disordered
Fewer ways of arranging the particles	More ways of arranging the particles	Virtually unlimited ways of arranging the particles
Entropy low	Entropy higher	Entropy highest

Entropy in Solutions:

When a solute dissolves into a solvent there is often an increase in its entropy, becomes the solute becomes more disordered as it spreads out and mixes with the solvent molecules (the number of ways of arranging the solute particles increases). For this reason, even if dissolving a solute is slightly endothermic, the increase in entropy can still ‘drive’ the process and the substance will dissolve spontaneously at room temperature. If the reaction is highly endothermic then the substance will not dissolve, even if entropy increases slightly. E.g. NaCl has a small positive $\Delta H_{solution}$, but its entropy increases enough when it dissolves to make it soluble in water.

However, for some substances dissolving actually decreases the entropy as water molecules cluster around the ions in a very ordered manner, and although the solute becomes more disordered upon dissolving, the solvent (water) becomes more ordered and overall the entropy decreases and such substances will not dissolve, e.g. $CaCO_3$.

Entropy and Internal Energy

A balloon of hot air floating upwards through the air has both external and internal energy. The external energy is the energy that the system as a whole possesses because the whole is moving – the balloon has kinetic energy as it rises and it also gains gravitational potential energy the higher it rises.

However, the air inside the balloon has its own internal energy which does not depend on the energy of the system as a whole – the air molecules possess their own energy, which can be of several types:

1. Translational kinetic energy – the kinetic energy of a molecule due to its translation (movement in a straight line) from one place to another (inside the balloon).
2. Rotational kinetic energy – due to the rotation of the molecules.
3. Vibrational energy – due to stretching and compression of bonds.
4. Electronic energy – due to electrons in atoms (atomic orbitals) and molecules (molecular orbitals) jumping up and down.

(5. Nuclear energy – their will be some radioactive molecules present).

You are used to thinking of electronic energy having only certain allowed values or energy levels – it is quantised – electronic energy is divided up into packets or quanta.

When an electron jumps between two energy levels it must absorb a quantum of energy corresponding to the exact difference in energy (ΔE) between the two energy levels:

$$\Delta E = E_2 - E_1.$$

This quanta could be a quantum of electromagnetic radiation (photon) or it could come from a collision between molecules or a collision with an electron, etc., so long as the energy supplied is exactly right.

More surprisingly, the translational, vibrational and rotational energies of molecules are also quantised – they can only take on certain allowed values corresponding to different energy levels.

(Note: Nuclear energy is also quantised).

Entropy can be defined as the number of ways of sharing out quanta of energy.

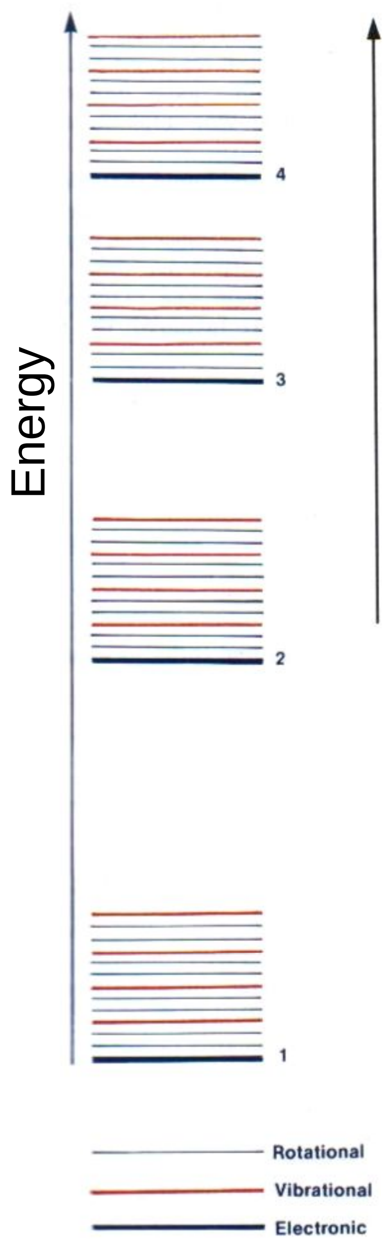
Quanta possessed by molecule 1	**Quanta possessed by molecule 2**
0	4
1	3
2	2
3	1
4	0

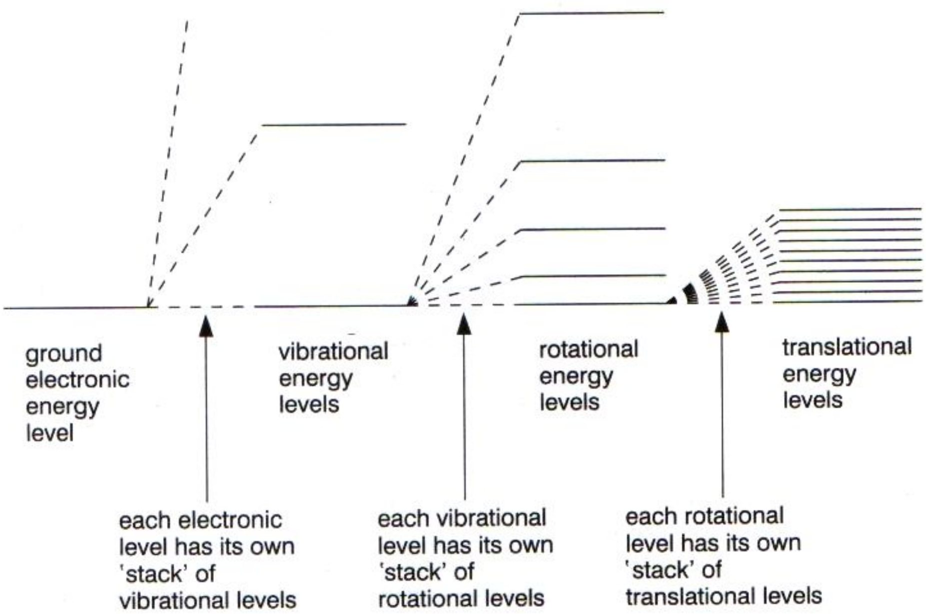
Left: there are 5 ways of dividing 4 quanta of energy between 2 molecules.

Q. How many ways are there of dividing a) 6 quanta between 2 molecules, and b) 4 quanta between 3 molecules?

Energy levels in a molecule.

Below: two different ways of showing the molecular energy level spectrum. Translational levels are even more closely spaced than rotational ones and are not shown on the left-hand diagram. Notice the vibrational levels are evenly spaced.





Kinetic energy levels in a diatomic molecule: