Energy and Matter

The Assumptions of Kinetic theory

Kinetic theory is a microscopic model of gases which predicts macroscopic quantities such as pressure and heat capacity.
It is based on six assumptions:

1. A gas is composed of a large number of molecules.
2. The molecules are small compared to their separation.
3. The molecules are uniformly distributed and move randomly.
4. The molecules obey Newton's laws of motion.
5. The molecules feel no force except during collisions with other molecules or the walls of the container (hard spheres)
6. Molecules collide elastically, and the walls are smooth.

Limitations of these assumptions:

1. A gas is composed of a large number of molecules.

2. The molecules are small compared to their separation.

3. The molecules are uniformly distributed and move randomly.

4. The molecules obey Newton's laws of motion.

5. The molecules feel no force except during collisions with other molecules or the walls of the container (hard spheres)

6. Molecules collide elastically, and the walls are smooth.

ok   not always   wrong

2. The molecules are small compared to their separation.

5. The molecules feel no force except during collisions with other molecules or the walls of the container
(hard spheres)

These conditions are only met at low densities

4. The molecules obey Newton's laws of motion.

Quantum mechanics rules!

quantum predictions tend to those of classical physics
if the de Broglie wavelength of the molecules,
λ = h/mv, is much less than their mean separation.

This is true if the temperature is high so that
the speed v is large on average, and
at low density when the mean separation is large.

Main message:

kinetic theory is approximate

and applies best to gases at

low density
and
high temperature

Ideal Gases

An ideal gas obeys the assumptions
of kinetic theory perfectly.

Real gases
approximate
ideal gases
in the limit of low density.

$$PV = NkT_I$$ is an equation of state

one has only two degrees of freedom in fixing the state of a gas.

One can fix the temperature and pressure,
but not also the volume

One can set the temperature and volume,
but not also the pressure

because given the first two, the third is fixed by the equation of state.

Temperature and average kinetic energy

Combining

$$PV = NkT_{\mathrm{I}}$$

and

$$P = \frac{1}{3}nm\bar{v^2}$$
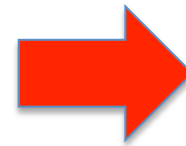
➡️ $$\frac{1}{2}m\bar{v^2} = \frac{3}{2}kT_{\mathrm{I}}$$

temperature is a measure of the average molecular kinetic energy for the ideal gas.

Boltzmann's constant k is the conversion factor between units of temperature and energy.

o Kinetic theory is an approximate theory which can be expected to apply to low density gases

o Internal energy $U = \dfrac{3}{2}PV$

o Equations of state $\boxed{PV = NkT_{\mathrm{I}}}$ $\boxed{P = nkT_{\mathrm{I}}}$ $\boxed{PV = n_m RT_{\mathrm{I}}}$

o Relation between pressure and kinetic energy

$$\boxed{P = \frac{1}{3}nm\bar{v}^2}$$

$$\frac{1}{2}m\bar{v}^2 = \frac{3}{2}kT_{\mathrm{I}}$$

o   Boltzmann factor $P(E) \propto e^{-E/kT}$

o   The equipartition theorem states that

for a classical system in thermal equilibrium, the total energy of the system is shared or *partitioned* equally among all the various degrees of freedom.

This means that the internal energy is

U = 3RT/2 per mole for a monatomic gas

U = 7RT/2 per mole for a diatomic gas

U = 13RT/2 per mole for a triatomic gas

U = 3RT per mole for solids

o The rate of increase in internal energy of a substance with increasing temperature
   or the increase in internal energy per unit rise in temperature
   is called its heat capacity (SI units of JK^{-1}).

Specific heat capacity per mole

$$C = \frac{dU}{dT} = \frac{3}{2}R = 12.5\,\text{J K}^{-1}\,\text{mole}^{-1}$$

o Equipartition failure:

In a classical system it is always possible for some atoms to be excited above the lowest energy level.

In a real system, if kT is much less than the energy needed to get to the first excited state, there can be no excitation at all, and no contribution to the specific heat.

Random walks
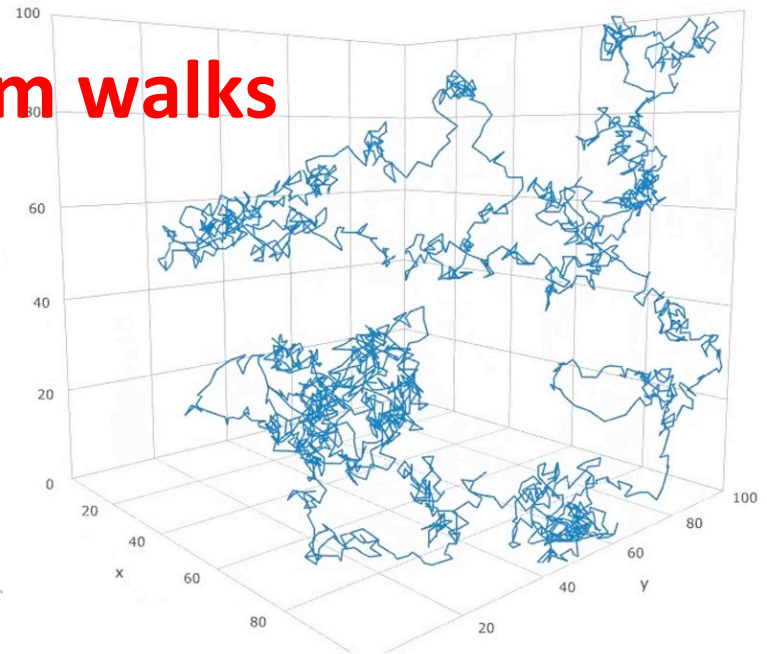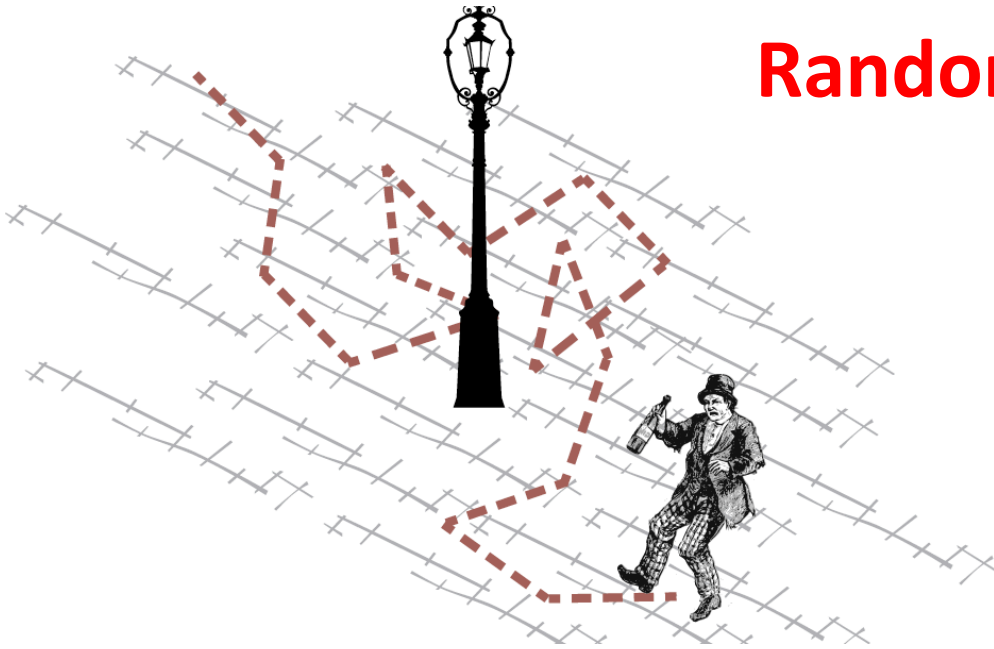
The paths of isolated molecules in a gas paths are called random walks.

o   how far molecules travel on average over given intervals of time?

o   how far do they travel before a collision occurs?

Before a collision we can describe a gas as if composed of many individual molecules.

When collisions occur, we need to consider a gas as composed of interacting molecules (the density will be a critical parameter).

The mean free path is the speed divided by the collision rate

speed = v   collision rate $\sqrt{2}\pi D^2 n v$

mean free path

$$\lambda = \frac{1}{\sqrt{2}\pi D^2 n}$$

For air at STP, $\lambda \approx 10^{-7}$ m
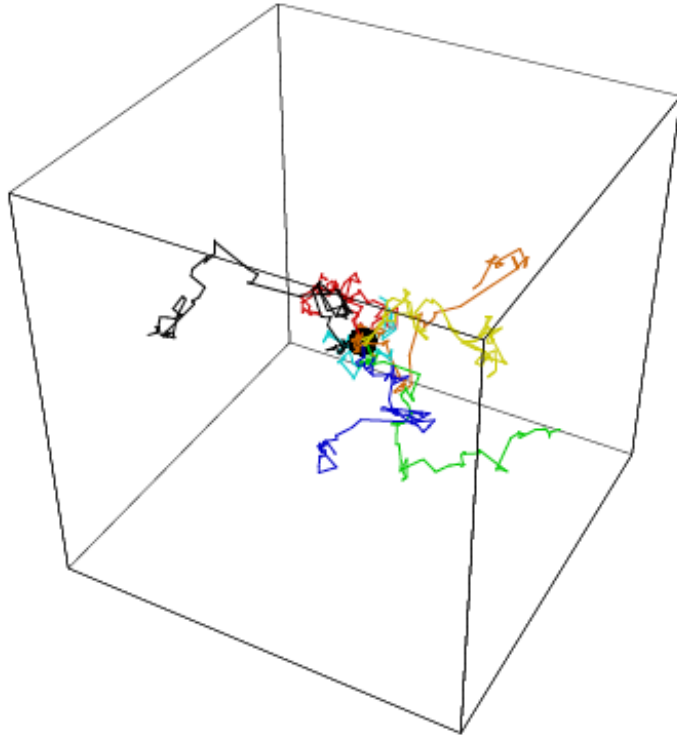
Seven random walks of a particle. Each walk comprises 100 steps with steplengths distributed according to the exponential distribution

$$P(r) = e^{-r/\lambda}$$

The distance travelled (displacement from the starting point) $r \approx \sqrt{N}\lambda$ and the path length can be hugely different,

since $\sqrt{N} \ll N$ for large N

Transport coefficients

	transported quantity	macroscopic law	kinetic theory estimate
diffusion	number density or 'identity'	$\frac{dN}{dt} = -DA\frac{dn}{dx}$	$D = \frac{1}{3}\lambda\bar{v}$
thermal conduction	thermal energy	$\frac{dQ}{dt} = -KA\frac{dT}{dx}$	$K = \frac{1}{3}\lambda\bar{v}c$
viscosity	momentum	$\frac{dp_x}{dt} = F_x = -\eta A\frac{dv_x}{dy}$	$\eta = \frac{1}{3}\lambda\bar{v}\rho$

Limitations of kinetic theory

Kinetic theory is successful in explaining, for instance, the pressure exerted by a gas, but it fails to describe:

- phase changes (boiling, melting),

- the existence of liquids and solids,

- deviations from the ideal gas law.

It is the neglect of interatomic forces which is most important (without them there could be no liquids).

We will now follow a more utilitarian approach in which we take some measured (macroscopic) properties and try to extrapolate physical (microscopic) theories from these.

This is the subject of classical thermodynamics.

Thermodynamics deals with quantities such as
work, heat and temperature.
It is concerned with **macroscopic**, not microscopic physics.

It is built from four fundamental laws deduced from experiments:

o Zeroth law: defines temperature.

o First law: defines internal energy and expresses the conservation of energy.

o Second Law: defines entropy and how efficiently one can convert heat to work.

o Third Law: establishes the unattainability of absolute zero.

Thermodynamic Definitions

In thermodynamics, we are often concerned with changes of a system but very often these must be considered in conjunction with changes in the surroundings.

The two are linked by a boundary which can come in several different varieties.

System	the piece of Universe under study. Its precise extent must be clearly defined.
Surroundings	anything that is not part of the system.
Boundary	whatever separates the system from its surroundings.

Closed	lets no matter in or out.
Open or permeable	can let matter pass.
Rigid	does not allow any change in the system by external forces, such as pressure.
Adiabatic	does not allow any heat to flow in or out.
Diathermal	opposite of adiabatic — does allow heat transfer.
Isolating	allows nothing in or out: closed, rigid and adiabatic.

What Joule found was that the amount of work required to change a system, when no heat is allowed to enter or escape, depends only upon the initial and final states of the system.

The First Law is nothing more than the conservation of energy.

The energy represented by the performance of the same amount of work causes the same change in a system.

This leads to the recognition of the concept of internal energy.

Examples of functions of state:

- o   pressure and volume
  the same state of a system must have the same volume by definition
- o   internal energy

NOT a function of state:

- Distance travelled
- Work
- Heat

The internal energy, U, is defined as:

$$W = U_{\text{final}} - U_{\text{initial}} = \Delta U$$

The work done on the system W changes its internal energy by W.

Note the sign convention: work done on the system is positive
work done by the system is negative

Heat

Heat is the transfer of energy between a system and its environment due to a temperature difference between them.

we can define the heat entering a system, Q, in the case of no work, as:

$$Q = \Delta U$$

Heat added to a system is positive.
Heat given up by a system is negative.

Joule showed that heat and work are two forms of the same thing, which we call energy.

$$1 \, \text{calorie} = 4.2 \, \text{J}$$

$$1 \, \text{Calorie} = 4200 \, \text{J}$$

the amount of heat needed to raise the temperature of 1 g of water by 1C.

the amount of heat needed to raise the temperature of 1 kg of water by 1C.

Mathematical expression of the First Law

If heat is added and work is performed on a system,
then the first law becomes:

$$\Delta U = Q + W$$

- energy is conserved,

- generalises conservation of kinetic + potential energy,

- defines heat as a form of energy.

Heat capacities

Let us consider the differential form of the first law:

$$đQ = dU - đW$$

And let us consider a change in temperature dT

We can define a heat capacity as
the heat input divided by the change in temperature:

$$C = \frac{đQ}{dT} = \frac{dU}{dT} - \frac{đW}{dT}$$

Note that the term heat capacity is inaccurate:
once heat enters a system, it loses its identity and should be thought of as energy.

The First Law is nothing more than the conservation of energy.

$$\Delta U = Q + W$$

Heat and work are *not* functions of state. They depend upon the path taken.

$$dU = đQ + đW$$

Heat capacity:

$$C = \frac{đQ}{dT} = \frac{dU}{dT} - \frac{đW}{dT}$$

Reversible changes

A process is reversible if the
system and surroundings return to their original state
when the process is reversed.

A reversible change can be carried out by making a tiny change, allowing the system to settle to equilibrium, making another tiny change, etc.
This is called a quasi-static change.

Reversible processes, although an idealisation, are at the heart of equilibrium thermodynamics, and lead to the evaluation of quantities of interest such as work.

For gases, we have shown that:
$$W_R = -P\,dV$$

For ideal gases and adiabatic changes:
$$PV^\gamma = \text{constant}$$

where γ is the ratio of the specific heat capacity at constant pressure to the specific heat capacity at constant volume.

$$\gamma = \frac{C_P}{C_V} = \frac{C_V + R}{C_V}$$

Statements of the Second Law

Clausius statement (from experimental evidence):

It is impossible to construct a device that, operating in a cycle, produces no effect other than the transfer of heat from a colder to a hotter body.

heat cannot of itself flow from a colder to a hotter body

Kelvin-Plank statement:

It is impossible to construct a device that, operating in a cycle, produces no effect other than the extraction of heat from a single body at uniform temperature and the performance of an equivalent amount of work.

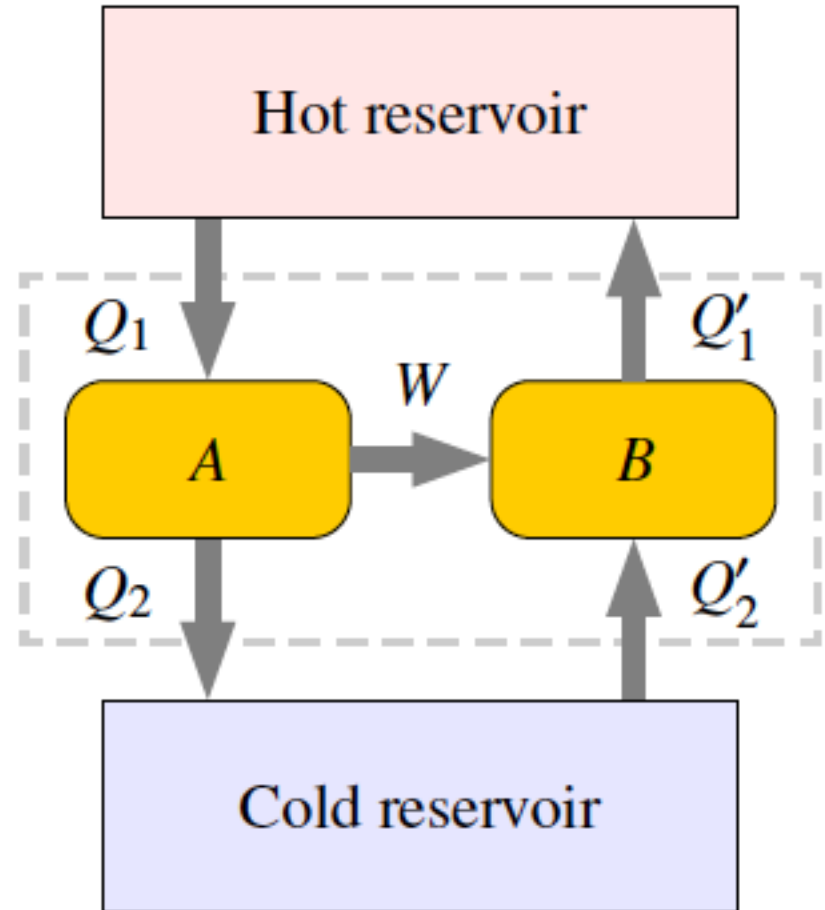heat cannot be completely converted into work without other effect

Carnot's theorem says that
reversible engines are the most efficient of all.

Let us consider two engines,
A and B.

Engine B is reversible and is run as a heat pump using the power generated by engine A, which may or may not be reversible.

Carnot's theorem states that
$$\eta_B > \eta_A$$
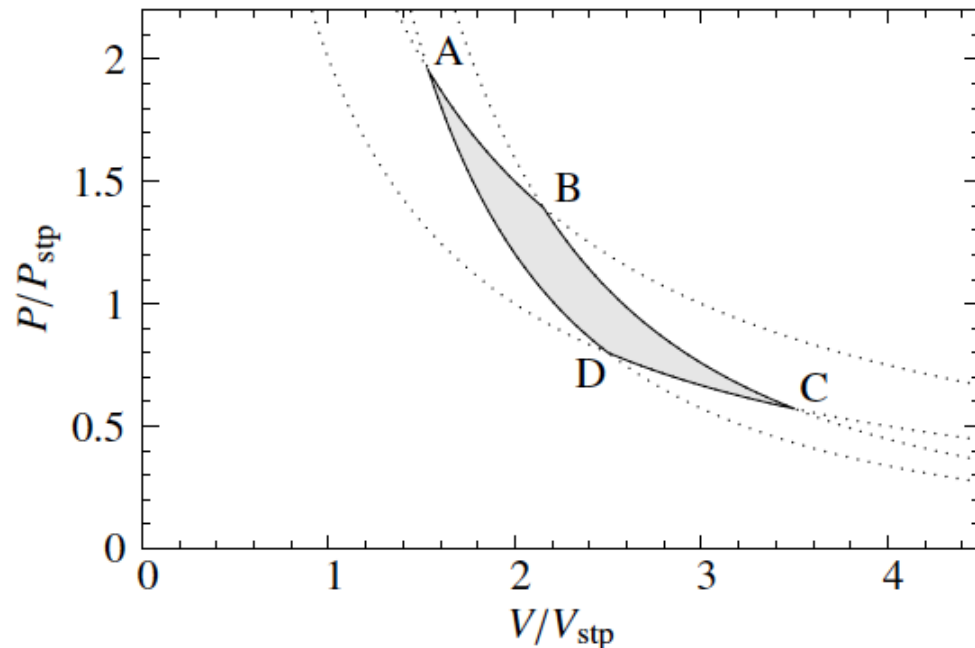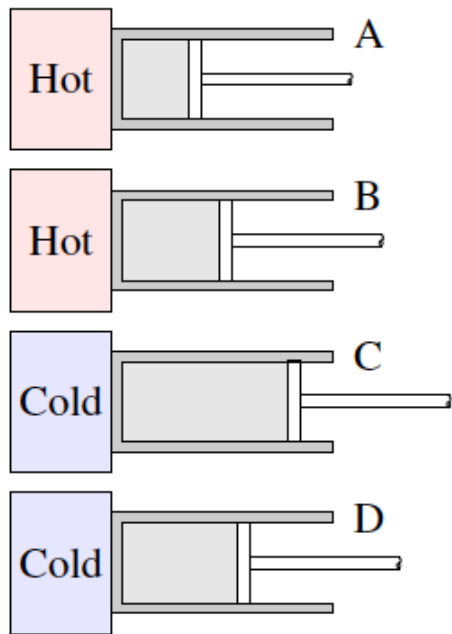
o Since areas in indicator diagrams represent work, the shaded area is the work extracted from one cycle of the Carnot cycle.

o The two lines representing the adiabatic changes, PV^γ = constant
rise more steeply than those representing the isothermal changes, PV = constant

o Isotherms cross the adiabatics, but isotherms do not cross each other, nor do adiabatics.
This should be obvious for isotherms since the same state cannot have two different temperatures.

- We need more than just the First Law of thermodynamics to describe the thermal behaviour of matter.

- There are some processes possible under the First Law which nevertheless never happen.

- The Second Law (in the form proposed by Clausius) is a statement of one such impossible process,
  the spontaneous transfer of heat from a cold to a hot body.

- This also leads to an equivalent statement to the effect that heat cannot be turned completely into work.
  The equivalence was established through the idea of a heat engine.

- Further the second law applied to such engines was used to establish that thermodynamically reversible engines are the most efficient

- All reversible engines running between the same reservoirs have the same efficiency.

Boltzmann's tomb with his definition of entropy engraved on it.

The second law of thermodynamics can be used
to prove the existence of
a new function of state known as entropy
which allows to determine quantitatively
- whether a process is reversible
- whether it can occur naturally or not

The Zeroth Law and Empirical Temperature

The zeroth law:

"if a system A is in thermal equilibrium with two other systems, B and C, then the systems B and C are in equilibrium with each other."

Two systems are in thermal equilibrium if
no heat is transferred between them
when they are placed in thermal contact

The Zeroth Law means that we can assign a label to any system, the label being the value shown on a thermometer when it is thermal equilibrium with the system.

We call the label temperature.

Temperature is a function of state which determines whether one system will be in thermal equilibrium with another.

The Increase of Entropy
and Heat Death of the Universe

For an isolated system $đQ = 0$, so Clausius' inequality becomes:

$$\boxed{đQ \leq T\, dS} \qquad \Longrightarrow \qquad dS \geq 0$$

the entropy of an isolated system can never decrease

This result imposes a direction in which processes can occur.
Applied to the Universe as a whole, the entropy will carry on increasing until it can no longer do so, by which point the Universe will be in a state of equilibrium and it will no longer be possible to extract work from any process.
This is the so-called heat death of the Universe.

The increase of entropy gives us another way to decide whether a process is reversible or not:

$$\boxed{\text{reversible processes do not change the total entropy of the Universe}}$$

Heat engines

In a heat engine, the hot reservoir has heat Q_1 removed so:

$$\Delta S_1 = -\frac{Q_1}{T_1}$$

Similarly:

$$\Delta S_2 = \frac{Q_2}{T_2}$$

So the total entropy change after a cycle is:

$$\Delta S = \frac{Q_2}{T_2} - \frac{Q_1}{T_1}$$

If the engine is reversible:

$$Q_1/T_1 = Q_2/T_2 \text{ and } \Delta S = 0$$

If the engine is irreversible, then it is less efficient,
or, equivalently, Q_2 is larger for a given Q_1
than in the case of a reversible engine

$\Delta S > 0$

Irreversible engines are therefore entropy sources

$$S = k \ln W$$

Boltzmann relation

entropy as a measure of the number of microscopic arrangements or microstates of a system W

The Universe is always changing to a more probable configuration, in the sense of more available microstates.
The new configurations are so much more probable that the change is irreversible.

o In the hands of Clausius and Kelvin, Carnot's theorem led to the definition of an absolute, as opposed to empirical, temperature scale.

o A new function of state was recognised, called entropy.
The entropy change of a system absorbing heat đQ, with the heat transfer occurring at temperature T, is Clausius' inequality in the form $dS \geq đQ/T$.

o When the change is reversible, this reduces to $dS = đQ_R/T$ where T is the temperature of the system.

o The important consequence of Clausius' inequality is that the entropy of an isolated system always increases.

o Following Boltzmann: a system always tends towards states of greater multiplicity given external constraints.

The Central Equation of Thermodynamics

The First Law of Thermodynamics can be written as:

$$đQ = dU − đW$$

and that for reversible pressure work we can write:

$$đQ_R = dU + P\,dV$$

We have seen that we can write: $$đQ_R = T\,dS$$

$$\boxed{T\,dS = dU + P\,dV}$$

This is the central equation: although derived for reversible changes only, it applies generally, because all variables are functions of state, so the method of change is not important.

However, it is essential that the system starts and ends in equilibrium so that it is meaningful to talk about pressure, temperature and entropy.38

Entropy of an ideal gas

For a mole of ideal gas we have P = RT/V
and dU = C_V dT (internal energy a function of temperature only). Therefore we can write:

$$T \, dS = dU + P \, dV \qquad \Rightarrow \qquad dS = C_V \frac{dT}{T} + R \frac{dV}{V}$$

integrating

$$S = S_0 + C_V \ln T + R \ln V$$

where S_0 is a constant of integration (note that this constant is not determined in classical thermodynamics but is by statistical thermodynamics).

This relation shows that the

entropy of an ideal gas increases with both T and V

increasing temperature increases the number of available states, since more energy states become available for the atoms.

Enthalpy

If a reaction occurs at constant volume, then the First Law states that:

$$-Q = -\Delta U$$

Let's consider a system in pressure equilibrium with its surroundings (at least at the start and at the end of the change), i.e. $P = P_0$:

$$\Delta U = Q - P_0 \Delta V$$

$$-Q = -(\Delta U + P_0 \Delta V) \qquad \text{the heat given off}$$

Given that $P = P_0$: $-Q = -(\Delta U + P\Delta V) = -\Delta(U + PV) = -\Delta H$

$$\boxed{H = U + PV}$$

a function of state
called the enthalpy

$$H = U + PV$$

-ΔH is the heat given off in chemical reactions at constant pressure.

The PV term in the enthalpy
corrects for work done during any volume change

In analogy to $\quad C_V = \left(\dfrac{\partial U}{\partial T}\right)_V \quad \Longrightarrow \quad C_P = \left(\dfrac{\partial H}{\partial T}\right)_P$

specific enthalpy capacity

Thermodynamic data books include enthalpies of formation, H_f

The enthalpy of formation of the elements themselves is defined as zero. For instance, both hydrogen in the form of H_2, and oxygen as O_2 have $H_f = 0$.
Water (H_2O) has $H_f = -242$ kJ mole^{-1}

Helmholtz free energy

$$F = \boxed{U} - \enclose{circle}{TS} \qquad\qquad \Delta F \leq 0$$

Equilibrium is reached therefore when F is a minimum
at which point dF = 0

The internal energy part enters to account for the heat transferred from the surroundings, in terms of the equivalent entropy change of the surroundings.

The TS part of F is the usual entropy part that gives
$\Delta S \geq 0$ for a thermally isolated system.

it is entropy which determines whether a change is possible or not, and F provides a convenient way of accounting for it.

Gibbs Free Energy

Experimentally it is easier to operate under conditions of
constant pressure rather than constant volume.

We have Q = ΔU, and Q = ΔH
Therefore rather than F = U - TS as the function that determines
whether changes can occur, we get:

$$\Delta G \leq 0$$

where
$$\boxed{G = H - TS = U - TS + PV}$$

Gibbs free energy

G is a minimum in equilibrium,
when dG = 0 for all possible changes

Thermodynamic potentials

o the internal energy U

o the enthalpy H = U + PV

o the Helmholtz free energy F = U - TS

o the Gibbs free energy G = U - TS + PV

like potential energy,
they are minimised in equilibrium.

- Central equation

$$T\,dS = dU + P\,dV$$

- Entropy

$$S = S_0 + C_V \ln T + R \ln V$$

- Boltzmann relation

$$S = k \ln W$$

- Enthalpy

$$H = U + PV$$

- Helmoltz Free energy

$$F = U - TS$$

- Gibbs Free energy

$$G = H - TS = U - TS + PV$$

Interatomic Forces

Interatomic forces are the forces that real atoms exert on each other

When very close they repel,
whereas at large distances the forces become weakly attractive.

The repulsion can be viewed in terms of the electrostatic repulsion of the nuclei in combination with the Pauli exclusion principle

The interaction between atoms can be represented by the potential energy $\Phi(r)$ between atoms separated by distance r.
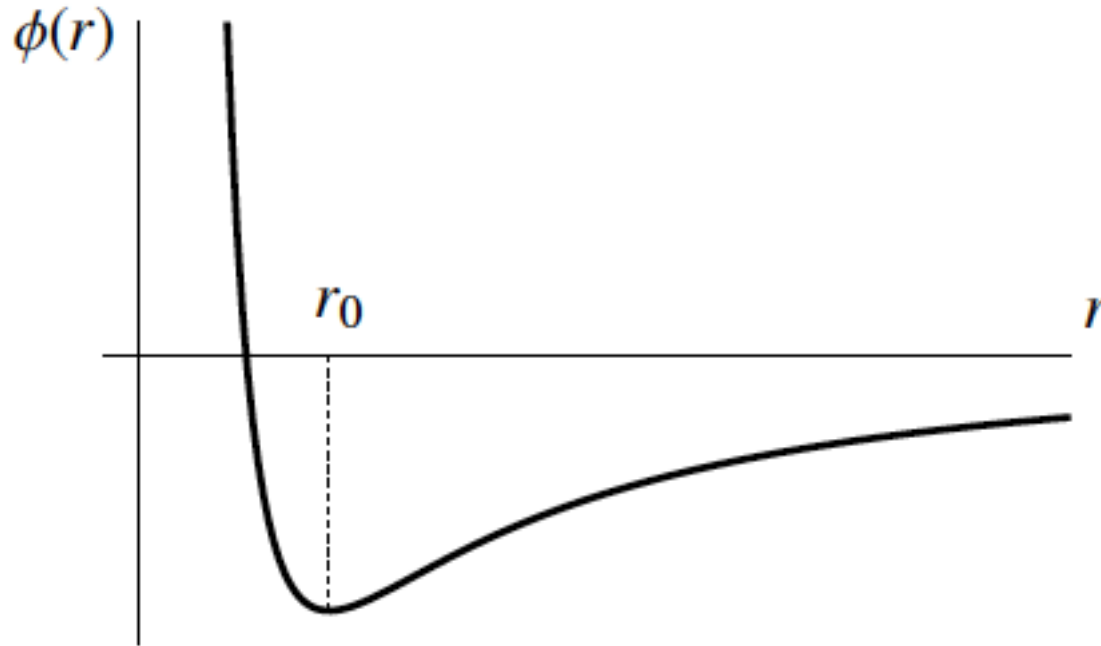The force f between atoms is related to the potential energy
by $f = -d\Phi/dr$
And $f > 0$ is a repulsive force,
so the negative gradient at short distance corresponds to repulsion.

potential energy *Φ(r)* between atoms separated by distance r

force f between atoms is f = -d*Φ*/dr

A schematic figure of the potential energy between two atoms as a function of distance between them.
r_0 denotes the equilibrium separation.

The constants *a* and *b* are the van der Waal's coefficients:

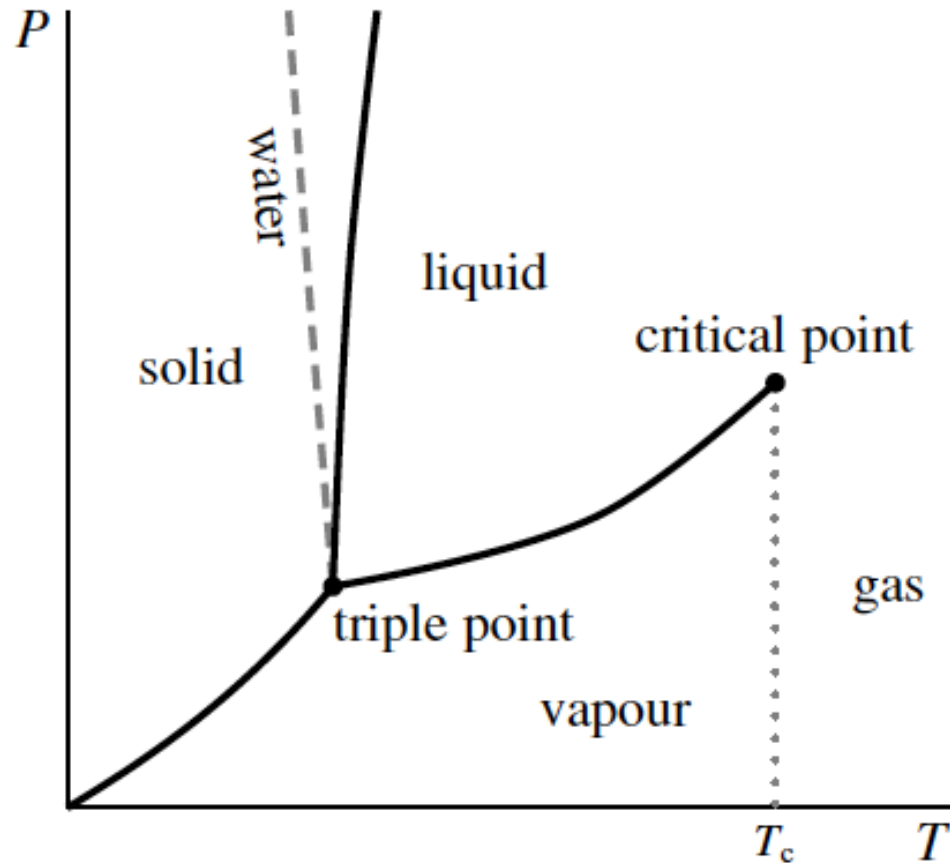*a* depends upon the long-range attractive forces,
b depends upon the short-range repulsive forces which define the "size" of an atom.

If we consider the number of moles n_m,
instead of the number of molecules N and rescale *a* and *b*
accordingly:

$$\left(P + n_m^2 \frac{a}{V^2} \right)(V - n_m b) = n_m RT$$

Phase diagrams

Given that P and T are the variables in G, it is useful to plot P-T diagrams:

The lines indicate the values of pressure and temperature for which the various phases are in equilibrium.

The key features of phase diagrams:

- The slopes of the lines come from the Clausius-Clapeyron equation:

$$\frac{dP}{dT} = \frac{L}{T(v_2 - v_1)}.$$

   The water/ice slope is negative: can "squeeze" ice into water

- The liquid/vapour line *stops* at the *critical point*: there is no continuation. There is no equivalent point for the solid/liquid line; solids and liquids appear to be intrinsically different and there is no way to make a smooth transition between them.

- The solid/vapour transition is called *sublimation*; iodine gives a nice example of this, subliming as a purple gas when heated in its solid form.

- The three lines meet at the triple point.

Classical thermodynamics can explain some of the features of phase diagrams, however, to understand the existence of phases we need to delve down to the microscopic level with the inclusion of interactions amongst atoms and molecules.

The van der Waals equations shows how even the simplest inclusion of the effects of interactions introduces features that can be identified with phase changes.

To explain the properties of liquids and solids, more sophisticated models are needed.