

Temperature, Thermal Expansion, and the Ideal Gas Law

System: a particular object or set of objects that is under consideration

Environment: Everything else

State: The condition the system is in (a set of tractable variables, that we can use to deduce the statics and dynamics of the system)

Microscopic description: Describe the state using microscopic variables, such as the trajectories of atoms and molecules

Macroscopic description: Describe the state using macroscopic variables that consist of an information reduced form of a collection of microscopic variables (i.e. pressure, temperature)

Thermodynamics: The description of processes in terms of macroscopic variables

→ The art of defining, understanding and using "state variables"

Atomic Theory of Matter

Smallest piece of matter that can not be divided further: **atom**

see "More is different" by P.W. Anderson

A useful simplification:

Unified atomic mass units

Set ^{12}C to 12.0000 u

$$\rightarrow 1 \text{ u} = 1.6605 \times 10^{-27} \text{ kg}$$

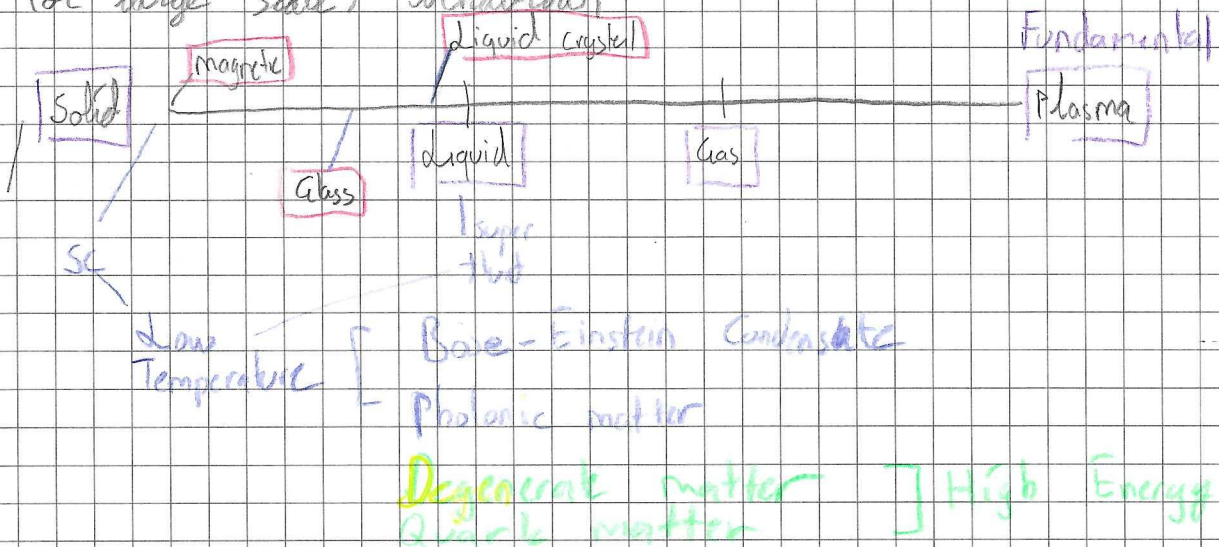
An important evidence for the atomic theory:
Brownian motion

Robert Brown 1827:

Although the pollen are not "alive" they move in seemingly self propelled motion on the surface of water this is due to "microscopic" H_2O although "macroscopic" water is "still"

Einstein: the diameter of a typical atom is 10^{-10} m

We define the "states of matter" based on microscopic (or large scale) behaviour



Transitions between states are "phase transitions"

In each "type of matter" there are distinct microscopic behaviours which lead to a distinct set of macroscopic "good" variables. This behaviour can be approached using the mathematical tool of "symmetries". See Emmy Noether.

Temperature and Thermometers

Temperature is a microscopic variable. We use the state of a "probe system" to measure the temperature of a system. These "probe" devices are called "thermometers".

Temperature of a system influences a number of macroscopic observables

→ Colour

→ Shape changes

Thermometers are devices that have "easy" and "consistently" measurable states, so that we can make precise quantitative measurements.

ex: thermal expansion of Mercury around ambient temperatures: linear and quite easy to read!

Thermal Equilibrium and the 0th Law of thermodynamics

Thermal equilibrium: Systems that are in thermal contact with each other (i.e. that can transfer thermal energy) will eventually be at same temperature

Zeroth law of Thermodynamics

If two systems are in thermal equilibrium with a third system, then they are in thermal equilibrium with each other.

This allows us a useful definition of temperature: when two systems are in equilibrium no thermal energy will be transferred between them, hence by definition they will be at the same temperature.

Thermal Expansion

A lot of materials expand when heated and shrink when cooled. When this expansion is linear to the temperature change, and assuming the material is thin enough, we can model it as

$$\Delta l = \alpha l_0 \Delta T$$

Δl — change in length
 α — coefficient of linear expansion
 l_0 — initial length
 ΔT — change in temperature

consequently

$$l = l_0 (1 + \alpha \Delta T)$$

length as a function of temperature

actually, the material is expanding in all directions

$$V = l_0 (1 + \alpha \Delta T) W_0 (1 + \alpha \Delta T) H_0 (1 + \alpha \Delta T)$$

$$\Delta V = V_0 (1 + \alpha \Delta T)^3 - V_0 = V_0 [3\alpha \Delta T + 3(\alpha \Delta T)^2 + (\alpha \Delta T)^3]$$

if $(\alpha \Delta T)$ (the amount of linear expansion in any direction) is much smaller than the original length $(\alpha \Delta T)^2$ and higher orders are even smaller, and can be ignored. Then

$$\Delta V \approx (3\alpha) V_0 \Delta T$$

Caveats:

- If the material is not isotropic (i.e. α for length, width and height are not the same) this equation is not valid
- linear behaviour is not a good model when the expansion is comparable to material length, or if the material is not crystalline
- Materials like water have some physico chemical alterations at certain temperatures (like the hydrogen bonds around 4°C in H₂O)

The Gas laws and Absolute Temperature

In gaseous materials, the state of the system is less obvious, we need to deal with a set of observables rather than one simultaneously!

Equation of state: is a thermodynamic equation relating state variables which describe the state of matter under a set of physical conditions

Equilibrium state: is an axiomatic concept where the variables that describe the state does not change in time or space

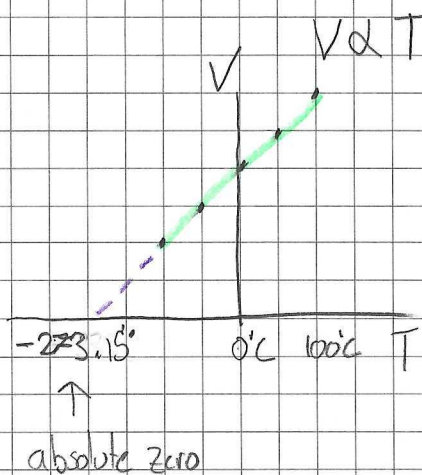
Robert Boyle
1627-1691

Boyle's law: (experiment) the volume of a gas is inversely proportional to the absolute pressure applied to it when the temperature is kept constant

$$V \propto \frac{1}{P} \text{ (constant } T) \quad \text{or} \quad PV = \text{constant (const. } T)$$

Jacques Charles
1746-1823

Charles law: (experiment) The volume of a given amount of gas is directly proportional to the absolute temperature when the pressure is kept constant



$V \propto T$ (constant P)

The above relationship reveals something peculiar: For any gas the V vs T graph projects to -273.15°C for $V=0$. This point is called the absolute zero. It is the basis of the Kelvin temperature scale

$$T(\text{K}) = T(^{\circ}\text{C}) + 273.15$$

Joseph Gay-Lussac
1778-1850

Gay-Lussac's law: (experiment) At constant volume, the absolute pressure of a given amount of gas is directly proportional to

the absolute temperature

$P \propto T$ (constant V)

note: The "law" naming scheme here is rather odd. these equations are only valid when the gas is in an "ideal" state, i.e. not too high pressure, temperatures where spontaneous symmetry breaking (a.k.a. phase change) may occur

The Ideal Gas Law

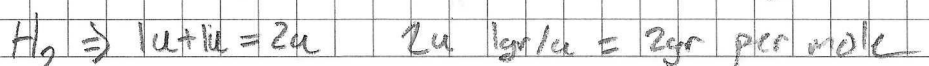
The gas laws of Boyle, Charles and Gay-Lussac tells us

$PV \propto mT$

where m is the total mass of the gas, and the proportionality constant is different for each gas.

Now here is something interesting: If we use moles instead of mass, the proportionality constant becomes the same for each gas!!

mole (1 mol) is defined as the amount of substance that contains as many atoms or molecules as there are in precisely 12 grams of carbon 12. Since carbon 12 is 12u, you can simply multiply the molecular mass of a gas with $1g/1u$ to obtain how many grams there are in one mol of that gas



$$\# \text{ moles} : n = \frac{\text{mass (grams)}}{\text{molecular mass (g/mol) (per mole)}}$$

Using moles, the combined EOS (equation of state of an ideal gas) becomes

$$PV = nRT$$

absolute Pressure
Ideal Gas Law
absolute Temperature (in K)

number of moles

R: universal gas constant (i.e. same for all gases)

$$R = 8.314 \text{ J/(mol}\cdot\text{K)}$$

Avogadro's Number

Avogadro's hypothesis: Equal volumes of gas at the same pressure and temperature contain equal number of molecules

Amedeo Avogadro (1776-1856)

Consequently the number of molecules in one mole of any pure substance is known as Avogadro's number (N_A)

Avogadro's Number $N_A = 6.02 \times 10^{23}$ (molecules/mole)

This enables a more useful form of ideal gas law

$$PV = NkT$$

Boltzmann Constant $k = \frac{R}{N_A} = \frac{8.314 \text{ J/mol}\cdot\text{K}}{6.02 \times 10^{23} / \text{mol}} = 1.38 \times 10^{-23} \text{ J/K}$