

Thermodynamics

Statistical Thermodynamics

- The idea of particles constantly undergoing **elastic** collisions leads to the idea of a static distribution of speeds.
- The probability that a state of energy E_i is occupied **in thermal equilibrium** is

$$p(E_i) = g(E_i)e^{-E_i/kT}$$

Where T is the absolute temperature and $g(E_i)$ is the **degeneracy** of energy E_i (the number of states of energy E_i which are accessible to the particle). In the continuous case:

$$p(E) dE = A g(E) e^{-E/kT} dE$$

There are two important components here – the **Boltzmann factor** and the **degeneracy** of each state.

- When seeking the distribution of energies, $g(E)$ is proportional to E . When seeking the distribution of velocities in three dimensions, $g(v)$ is proportional to v^2 – the surface area of the sphere of radius v in **velocity space** [ie: the volume of the small shell enclosing velocities v to $v + dv$ is $4\pi v^2 dv$].
- The **isothermal atmosphere** is an atmosphere
 - In a **gravitational field**, which we assume is constant.
 - In which the **temperature is the same everywhere**.

In our derivation of pressure and density distributions, we consider a cylindrical element in the atmosphere and note that:

- The pressure on the cylinder is **isotropic** at each point (the same in all directions), so we can write the pressure at the top surface as p and that at the bottom surface as $p + dp$.
- The weight of the element of atmosphere is balanced by the pressure difference.
- The weight of the element is $\rho(h)gAdh$.
- We can use the equation of state of the perfect gas in the form $pV = nkT$ and realise that if m is the average mass of a particle

in the gas, this becomes $p = \frac{\rho}{m} kT$ [this is where the constant pressure approximation comes into play].

- When working out how small particles of a solid **sediment** in a fluid, we use the following:
 - **Archimedes' principle** – the **upthrust** is equal to the **weight of displaced fluid**.
 - We use this to deduce the net force acting downwards in the tube (say f), and deduce the potential as $\phi(h) = \int_0^h f dh$ [this takes $h = 0$ as the datum].
 - Then, use the Boltzmann distribution, given that the degeneracy of each energy is 1.
 - This was verified experimentally by **J. Perrin** in 1908, and this can be used to determine Boltzmann's constant.
 - This can be used to separate out large molecules – by subjecting the particles to accelerations of 10^6g , the largest sediment out.
- **Phase equilibria**
 - The **structure of solids and liquids** is as follows:
 - There are some **intermolecular forces** which result in a **potential** with a **minimum** – this is the **equilibrium separation distance**.
 - If the particles are **spheres**, the closest way of packing them together is as a **close-packed array**:
 - The spheres are stacked as close to each other as they can be in a plane and their centres form **equilateral triangles**
 - In a plane, any atom is surrounded by its **six nearest neighbours**. The **interatomic forces** keep them all the same distance apart.
 - Planes are then stacked such that the centres of any three adjacent atoms form tetrahedra. Each atom is then surrounded by **12 neighbours** – we say that the **coordination number** $N = 12$.

- As the temperature increases above $T = 0$, the particles start gaining kinetic energy and “jiggle” around in their “cage”. If this gets too high, the lattice expands and occasional re-arrangements occur. If this happens enough time, the long-range crystalline order is lost and it becomes a **liquid** – the structure of the “cage” has changed.
 - There is still **short-range order**, and the coordination number $N = 10$ (for random close-packing). So we expect liquids to be ~20% less dense than solids.
- **Binding energies**
- If the depth of the potential well is Φ_0 , we note that this is the amount of energy needed to split up any two atoms.
 - In close-packed solids, where each atom is surrounded by its 12 closest neighbours [and we assume other binding forces are negligible], the binding energy per mole is

$$6N_A\Phi_0$$
 (Where we’ve used 6 instead of 12 because forces come in pairs).
 - Similarly, the binding energy of a liquid per mole is

$$5N_A\Phi_0$$
 - The binding energy of a gas is effectively 0, because there are no forces acting between particles.
- **Latent heats**
- Phase changes involve absorption or release of heat.
 - Ignoring the energies of materials associated with thermal motions, we can obtain the following expressions by conservation of energy:

$$L_{\text{sublimation}} = 6N_A\Phi_0$$

$$L_{\text{boiling}} = N_A\Phi_0$$

$$L_{\text{evaporation}} = N_A\Phi_0$$
 - These are simple estimates, but work well if not pushed too far.

Macroscopic Thermodynamics

- **Gas laws**

- **Boyle's Law** states that, experimentally [for gases of low density at high temperatures],

$$\boxed{pV = \text{constant}}$$

- **Charles' or Gay-Lussac's law** states that, at constant pressure

$$\boxed{V = V_0(1 + \alpha t)}$$

Where t is measured in degrees Celsius. This can be used to define the **perfect gas temperature scale**, in which the 0 is taken at the point where the gas has 0 volume. In Kelvins, where the zero is 0 K, we can write

$$\frac{V}{V_0} = \frac{T}{T_0}$$

Further analysis reveals that this is identical to the **thermodynamic temperature scale**.

- It is also found that at a constant volume, the pressure increases linearly with the temperature, with the same constant of proportionality as in Charles' law. Together, these give

$$\boxed{pV = nRT}$$

This is an **equation of state** [the relation which determines the pressure as a function of volume and temperature] of the perfect gas. Boltzmann's constant is the gas constant per molecule, so

$$k = \frac{R}{N_A} \text{ and } \boxed{pV = nkT}$$

- **Dalton's Law of Partial Pressures** states that **at a fixed temperature, the pressure of a mixture of gases is equal to the sum of the pressures which each gas would exert separately if the others were not there.**

- **First law**

- The **first law** is that “**energy is conserved when heat is taken into account**”.
- A system can acquire energy in two ways – as **heat** and as **work**. We write

$$dU = dQ + dW$$

Where these are all quantities done **ONTO** the system. [Heat is defined using this relation].

- We define the **heat capacities** at constant volume and pressure as

$$C_V = \left(\frac{\partial Q}{\partial T} \right)_V \quad \text{and} \quad C_p = \left(\frac{\partial Q}{\partial T} \right)_p$$

The latter is always larger because extra work is done in making the gas expand.

- We can easily deduce that $dU = C_V dT$ by noting that at constant volume, $dU = dQ$.
- By using the relation $dU = dQ + dW$ at constant pressure, and noting that $dQ = C_V dT$, and expressing the $p dV$ term using the ideal gas laws, one finds that

$$\boxed{C_p - C_V = R}$$

- A **reversible process** is one in which we pass from one state to another while passing through a **continuous set of equilibrium states**. There can be no unbalanced forces at any point in time, and so the process must happen **very slowly**, such that, if it were reversed, it would leave the universe exactly as it was before. This “gentleness” ensures that there is no loss of energy.
- **Isothermal expansions**
 - These occur at **constant temperature**.
 - In such a case, U stays constant. Therefore,

$$\boxed{dQ = p dV}$$

- and **Adiabatic expansions**

- **No heat** is transferred from our gas. Therefore, dQ is 0 and

$$dU = -p dV$$

- Now, we note two things:

- $dU = C_V dT$
- $pV = nRT \Rightarrow V dp + p dV = nR dT$
- We can therefore eliminate temperature, and get

$$V dp + p dV = \frac{nR}{C_V} dU$$

$$dU = \frac{C_V}{nR} (V dp + p dV)$$

- Substituting back into the above:

$$\frac{C_V}{nR}(V dp + p dV) = -p dV$$

And collecting terms in $p dV$ on one side

$$\begin{aligned}\frac{C_V}{nR}V dp &= -p\left(\frac{C_V}{nR} + 1\right)dV \\ \frac{C_V}{nR}V dp &= -p\left(\frac{C_V + nR}{nR}\right)dV \\ C_V V dp &= -p\overbrace{(C_V + nR)}^{\text{this is just } C_p}dV \\ C_V V dp &= -pC_p dV\end{aligned}$$

- If we then write the ratio of the heat capacities as γ and integrate, we end up with

$$\boxed{pV^\gamma = \text{constant}}$$

- Using $pV = nRT$, we can express this in terms of any two of p , V and T .
- We **define temperature** as the quantity that determines the direction of heat flow when two objects come into contact. The **second law of thermodynamics** states that no process exist whose sole effect is to transfer heat from a colder to a hotter body.

Kinetic Theory of Gases

- We would like to explain the macroscopic properties of gases in terms of molecule motions.
- The **definition of a perfect gas** is one that
 - Has the equation of state $pV = nkT$
 - Does not absorb or release any heat during a **Joule expansion** (expanding the volume of a gas). This implies that there are **no intermolecular forces** in the gas, or else we would have had to do work against these forces when expanding the gas.
- The **assumptions** underlying the kinetic theory of gases are as follows:
 - Gases consist of **particles in motion**. Each has **kinetic energy** $\frac{1}{2}mv^2$ and the velocities are in **random directions**.
 - The particles are modelled as **spheres**, which very small but finite diameters a .

- The **long-range forces** between atoms are **weak** (*cf.* Joule expansions), and any collisions are **elastic**.
- The origin of **pressure** on the walls is the **force per unit area** due to **elastic collisions** of a huge number of gas particles on the wall.
- The **temperature** is related to **average kinetic energy** of the **molecules** in the **gas**.
- The **distribution of velocities** follows the **Boltzmann Distribution**,

- The **one-dimensional** velocity distribution is

$$f_1(v_x) = \sqrt{\frac{m}{2\pi kT}} e^{-mv_x^2/2kT}$$

And the mean kinetic energy of such a component is $\frac{1}{2}m\overline{v_x^2} = \frac{1}{2}kT$. This is a crucial result!

- The three-dimensional velocity distribution can be obtained by multiplying all the 1D ones together to get the probability of finding a **particular** v_x , v_y and v_z , and then expressing it in terms of v , taking degeneracy into account.
- We then find, by integrating, that

$$\overline{v_x^2} + \overline{v_y^2} + \overline{v_z^2} = \overline{v^2} = \frac{3}{2}kT$$

- **Dalton's Law of Partial Pressures**

- If we have two different monoatomic gases of mass-per-particle m_1 and m_2 in a container, there will be collisions.
- In the ZMF, it's clear that, during each collision, no direction will be preferred. Call this velocity \mathbf{w} .
- The directions for \mathbf{w} are all equally likely relative to the motion of the CM, \mathbf{v}_{CM} [this is harder to prove!]
- Therefore:

$$\begin{aligned} \overline{\mathbf{w} \cdot \mathbf{v}_{\text{CM}}} &= 0 \\ \frac{m_1 \overline{\mathbf{v}_1} + m_2 \overline{\mathbf{v}_2}}{m_1 + m_2} \cdot (\overline{\mathbf{v}_1} - \overline{\mathbf{v}_2}) &= 0 \\ \frac{(m_1 \overline{v_1^2} - m_2 \overline{v_2^2}) + (m_2 - m_1)(\overline{\mathbf{v}_1} \cdot \overline{\mathbf{v}_2})}{m_1 + m_2} &= 0 \end{aligned}$$

- We can also reason that over the entire gas, there is as much chance of seeing a molecule move in one way than another. So:

$$\boxed{m_1 \overline{v_1^2} = m_2 \overline{v_2^2}}$$

In other words, the **kinetic energy** of both these gases is equal. This result can also be obtained using statistical methods.

- Since pressure is proportional to kinetic energy both in the individual gases and in the mix, this implies that the **pressure of the mixture** is equal to the **sum of the pressure of the parts**.

- **Temperature**

- The temperature of a gas was “defined” above by the relation $\frac{1}{2}m\overline{v^2} = \frac{3}{2}kT$.
- This, result can also be obtained by using the second-law definition – that temperature is the quantity that is equal in two bodies at equilibrium.
- If consider two gases in a box separated by a piston, it stands to reason that the energy imparted to the piston by each of the gases is proportional to the kinetic energy of each of the gases. So, at equilibrium, both these kinetic energies must be the same.
- **This** is the property which is equal in two gases at equilibrium, and so **this** is temperature! We just add a constant of proportionality of $\frac{3}{2}k$ to make our lives easier...

- **Pressure**

- The pressure is the force per unit area which arises from the rate of change of momentum of particles striking the walls elastically. The pressure is **isotropic**.
- We do this in two steps – first we calculate the change in momentum from the collision of one particle, and we then multiply by *all* the particles.
- For a particle hitting a wall, we need one component of the particle’s momentum multiplied by 2 (one there and one back) – in other words

$$\Delta p_x = 2mv_x$$

- Now, the number of particles:
 - In a time Δt , all particles which are moving towards the wall and for which $v_x\Delta t >$ distance from wall will collide with the wall.
 - The **fraction** of particles with a given speed v_x is $f_1(v_x) dv_x$.

- For a particle moving at v_x , we're interested in anything within $v_x \Delta t$ of the wall. If we assume the number of particles per unit volume is n , then the number of particles per unit area satisfying this condition is $nv_x \Delta t$.
- So, the total number of particles with velocity v_x hitting per unit area is $nv_x \Delta t f_1(x) dv_x$.
- The change of momentum per unit area due to the collisions of particles moving with speed v_x is therefore $2mv_x \times nv_x \Delta t f_1(x) dv_x$. The rate of change of momentum is therefore $2mv_x \times nv_x f_1(x) dv_x$.
- Averaging over *all* speeds to find the total force per unit area [but only taking positive speeds, of course!]

$$p = 2mn \int_0^\infty v_x^2 f_1(x) dv_x$$

$\underbrace{\hspace{1.5cm}}_{\text{even function}} \equiv mn \int_{-\infty}^\infty v_x^2 f_1(x) dv_x$
 $\underbrace{\hspace{1.5cm}}_{\substack{\text{rewriting the} \\ \text{integral as} \\ \text{what it means!}}} \equiv mn \overline{v_x^2}$

This is just a fancy way of saying that only 1/2 the molecules will be moving towards the wall.

- Since $\overline{v_x^2} + \overline{v_y^2} + \overline{v_z^2} = \overline{v^2}$, we can re-write this as

$$p = \frac{1}{3} nm \overline{v^2}$$

• **Internal energy**

- The **internal energy** of our ideal gas is the **kinetic energy** of its individual particles – $\frac{1}{2}mv^2$ [since they have no structure].
- Therefore, the average kinetic energy of the gas is

$$u = \frac{1}{2} nm \overline{v^2}$$

- From the distribution function for speeds in a gas, however, we know that

$$u = \frac{3}{2} nkT$$

- Combining these two results and the pressure, we recover the **ideal gas law**

$$p = nkT$$

- **Collisions**

- The number of particles with velocity v_x that will hit unit area of a wall in a time Δt is

$$v_x \Delta t \times n \times f_1(v_x) dv_x$$

- So the rate of collisions on a given unit area of wall is

$$\begin{aligned} J &= n \int_0^{\infty} v_x f_1(v_x) dv_x \\ &= n \sqrt{\frac{kT}{2m\pi}} \\ &= \frac{1}{4} n \bar{v} \end{aligned}$$