Chapter 1 - Energy in Thermal Physics

Two objects are in *thermal equilibrium* when they have been in contact for a sufficient amount of time. This time is called the *relaxation time* of the system. Equilibrium is achieved by an exchange of energy.

Equilibrium	Exchanged quantity
Thermal	Energy
Mechanical	Volume
Diffusive	Particles

In an **ideal gas** one imagines the particles to have no extent, and that they only interact with one another in elastic collisions. The density also has to be low, which means that the average distance between the molecules must be larger than each individual molecule. These criteria are often met at room temperature and 1atm of pressure. The properties of an ideal gas can be summarised by the **ideal gas law:**

$$PV = nRT = NkT$$

where n is the number of moles, $R = 8.31$J/mol $\cdot$ K is the universal gas constant, and N is the number of particles.

The allowed number of independent motions is called the **degree of freedom** of a system.

The **equipartition theorem** states that the energy of any quadratic degree of freedom has an average value of $\frac{1}{2}kT$. If a system has f degrees of freedom and only quadratic and temperature-dependent forms of energy, then the total thermal energy is $U = Nf \cdot \frac{1}{2}kT$.

Any spontaneous transfer of energy caused by a difference in temperature between objects is called **heat**. Any other kind of energy transfer in and out of a system is called **work**.

Heat transfers can happen in several different ways

- **Conduction:** transfer by molecular contact
- **Convection:** motion of the material, where a warmer material often expands and rises upwards
- **Radiation:** emission of electromagnetic waves

> 🔥 **The first law of thermodynamics:** Energy can neither appear nor disappear. $\quad \Delta U = Q + W$

Types of processes

- **Quasi-static:** a process which happens slowly enough to be considered reversible, since there will be no change in entropy
- **Isothermal:** constant temperature
- **Isobaric:** constant pressure
- **Isochoric:** constant volume
- **Adiabatic:** a process which happens quickly enough so that no heat can escape, meaning that energy is only exchanged as work. There is also no exchange of mass
- **Isentropic:** a process which is both adiabatic and quasi-static

Compression work

$$W = \vec{F} \cdot d\vec{r} = F\Delta x = PA\Delta x = -P\Delta V$$

The derivation above assumes a displacement in only the x-direction, and that the process is quasi-static**.** It is also based on a piston moving inwards, so expansion would require a positive sign on the change in volume.

Changing this to an integral yields $W = -\int_{V_i}^{V_f} P(V)dV$.

Isothermal compression

Using the ideal gas law, we find that $W = -NkT\int_{V_i}^{V_f} \frac{1}{V}dV$

Adiabatic compression

Using the equipartition theorem gives $dU = \frac{f}{2}NkdT = -PdV$. Using the ideal gas law to replace P yields $\frac{f}{2}\frac{dT}{T} = -\frac{1}{V}dV \Rightarrow V_f T_f^{f/2} = V_i T_i^{f/2}$. This means that $VT^{f/2}$ is constant. We can also rewrite the result to $V^{(f+2)/f}P = $ constant, where $(f+2)/f = \gamma$ is called the **adiabatic exponent.**

Heat capacities

The amount of heat required to increase the temperature of an object is called its **heat capacity**, and is given by $C = Q/\Delta T$. The heat capacity per unit mass is called the **specific heat capacity**, and is equal to $c = C/m$. If there is no work and a constant volume, it is sufficient to look at $C_V = \partial U/\partial T$. Similarly for constant pressure we have $C_P = \partial U/\partial T + P \cdot \partial V/\partial T$. For an ideal cas $C_P = C_V + Nk$.

Latent heat

At a **phase transformation**, the heat put into a system is not changing its temperature. Technically, this means that the heat capacity is infinite, which of course is very unphysical. What we look at instead is the **latent heat**, which is the amount of heat required to completely melt/boil the substance. We can also find the **specific latent heat** $l = L/m = Q/m$**.**

Enthalpy

The work needed to make room for a system under constant pressure is PV. This gives us the **enthalpy** $H = U + PV$, which is the total energy required to create the system out of nothing and put it into its environment. It is also the possible energy one could theoretically extract from the system when it is annihilated.

The change in enthalpy can be written as

$\Delta H = \Delta U + P\Delta V = Q + W_{\text{other}}$

This tells us that the enthalpy is the amount of heat added to a system if no work other than compression-expansion is being done. We can also use enthalpy to calculate $C_P = \partial H/\partial T$.

Rates of processes

Conduction - the transport of energy

For conduction through a window of thickness Δx and area A, we have

$$Q \propto \frac{A\Delta T\Delta t}{\Delta x}$$

The constant of proportionality is called the **thermal conductivity**, denoted k_t. Using it gives the **Fourier heat conduction law:**

$$\frac{Q}{\Delta t} = -k_t A \frac{dT}{dx}$$

The average distance traveled between collisions is called the **mean free path** l. We can derive this path by imagining a molecule in an ideal gas sweeping out a cylinder of radius $2r$ as it moves, where r is the radius of a molecule. If this volume is equal to the average volume per molecule, then we are likely to get a collision.

$$\pi(2r)^2 l \approx \frac{V}{N} \Rightarrow l \approx \frac{1}{4\pi r^2} \frac{V}{N}$$

For this ideal gas, we can also use this to calculate the thermal conductivity. We do this by imagining two boxes separated by a thin, penetrable wall. This yields $k_t = \frac{1}{2} \frac{C_V l}{A \Delta t} = \frac{1}{2} \frac{C_V}{V} l \bar{v} = \frac{f}{4} \frac{P}{T} l \bar{v}$, where l is the length of the box the molecules are departing from and $\bar{v}$ is the average speed of each molecule.

One could also calculate the **mean free time** τ with $\bar{v}/l$.

Viscosity - the transport of momentum

We can also look at the **viscosity** of a fluid. Its flow is said to be **laminar** if it moves in distinct smooth layers. For a fluid with macroscopic velocity u_x moving between two layers with area A, we have

$$F_x \propto \frac{A \Delta u_x}{\Delta z}$$

where Δz is the distance between the two layers. The constant of proportionality is called the **coefficient of viscosity**. Using this coefficient yields the **shear stress** on each plate:

$$\frac{|F_x|}{A} = \eta \frac{du_x}{dz}$$

Diffusion - the transport of particles

The **matter flux** $\vec{J}$ of particles across a surface is the net number per unit area per unit time.

$$\vec{J} = -D \frac{dc_n}{dx}$$

where D is the **diffusion coefficient**. This is **Fick's law**.

The macroscopic view of diffusion is simply transfer of energy and particles, while the microscopic view takes it one step further and explains this transfer by looking at the thermal motion and random collisions between the particles.