

# Thermodynamics

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# Preface

# Chapter 1

## Temperature & Heat

### 1.1 Thermal Equilibrium

When two systems are in **thermal contact**, they are able to exchange energy with each other. The one that loses energy is said to be hotter/higher temperature. If two systems are in **thermal equilibrium**, it means that there is no *net* energy transfer.

### 1.2 The 0<sup>th</sup> Law

**Definition 1.1** (0<sup>th</sup> Law of Thermodynamics). If two systems are each in thermal equilibrium with a third system, then they must be in thermal equilibrium with each other.

### 1.3 Measuring Temperature

To measure temperature, we can make use of the fact that properties of materials are often a function of temperature. We pick a property of a system, measure it, and compare to measurements made at other known temperatures. For example, the Kelvin temperature scale uses the triple point of water (defined as 273.16K) and absolute zero to define a scale. A good thermometer for calibrating is a fixed-volume gas thermometer, because there is a linear relationship between pressure and temperature (for an ideal gas).

### 1.4 The 1<sup>st</sup> Law

We denote the **internal energy** of a system  $U$ . Energy can be transferred into or out of the system by **heat** ( $Q$ ) or **work** ( $W$ ). Heat is the energy transferred due to a difference in temperature, and work is the usable mechanical energy.

**Definition 1.2** (1<sup>st</sup> Law of Thermodynamics). The change in internal energy of a system is equal to the sum of the change in heat and the work done on the system.

$$\Delta U = Q + W \quad (1.1)$$

If  $Q$  is positive, the system is being heated up, if  $Q$  is negative, the system is heating something else. Likewise, if  $W$  is positive, then work is being done on the system and if  $W$  is negative, then work is being done by the system.

## 1.5 Crystal Structure & Interatomic Forces

Without interatomic forces, everything would be a gas. In a solid, energy of the atoms is minimised by the bonding. For example, in ionic bonding, an electron is transferred from one atom to another, and the pair are held together by Coulomb's law. In covalent bonding, the energy of bonding electrons is minimised by sharing between atoms. There is also the van der Waals interaction which is due to dipole-dipole interactions.

Consider two atoms in a solid. When they get very close, there must be a repulsive force (otherwise matter would be infinitely dense). However, the force must become attractive further away (but still very close on a macroscopic scale). A simple model of an intermolecular force like this is the **Lennard-Jones potential**. It is given by

$$V(x) = 4\alpha \left[ \left( \frac{\beta}{x} \right)^{12} - \left( \frac{\beta}{x} \right)^6 \right] \quad (1.2)$$

This potential only really describes bonding between electrically neutral atoms or molecules, however the same is very similar for all types of bonding.

Close to the equilibrium separation, we can describe the Lennard-Jones potential can be approximated with a parabola.

$$V \propto (x - x_0)^2 \quad (1.3)$$

$$\implies F \propto -(x - x_0). \quad (1.4)$$

When looking at the stretching of materials, we can define two quantities. The **stress** is defined as the force per unit area.

$$\sigma = \frac{F}{A}. \quad (1.5)$$

The **strain** is defined as the proportional deformation of the material.

$$\varepsilon = \frac{\Delta L}{L}. \quad (1.6)$$

We can then define Young's modulus, which is a property that measures the stiffness of a solid material.

$$E = \frac{\sigma}{\varepsilon}. \quad (1.7)$$

## 1.6 Thermal Expansion

Near absolute zero, the average spacing of atoms is near  $x_0$ , but as energy is increased, more atoms will be sitting at higher energies so the average atomic separation will get larger (because of the asymmetry of the potential). Let  $L_0$  be the length of a solid bar at a temperature  $T$ . Suppose that the length of the bar increases linearly with temperature (first approximation). If the temperature increases by  $\Delta T$ , the length increases by  $\Delta L$  and we write

$$\frac{\Delta L}{L_0} = \alpha \Delta T. \quad (1.8)$$

$\alpha$  is called the **coefficient of linear expansion** and may be different at different temperatures. Analogously, if a volume  $V_0$  increases by  $\Delta V$ , then we can write

$$\frac{\Delta V}{V_0} = \beta \Delta T, \quad (1.9)$$

where  $\beta$  is the **coefficient of volume expansion**. How is  $\beta$  related to  $\alpha$ ?

$$V_1 = V_0 + \Delta V \quad (1.10)$$

$$= (1 + \beta \Delta T) V_0. \quad (1.11)$$

Similarly,  $L_1 = (1 + \alpha \Delta T) L_0$ , and using  $V_1 = L_1^3$ , we get

$$V_1 = L_0^3 (1 + \alpha \Delta T)^3 \quad (1.12)$$

$$1 + \beta \Delta T = (1 + \alpha \Delta T)^3 \quad (1.13)$$

$$1 + \beta \Delta T \approx 1 + 3\alpha \Delta T \quad (1.14)$$

$$\beta \approx 3\alpha. \quad (1.15)$$

Where in the third line we have used the approximation  $(1 + x)^n \approx 1 + nx$  for small  $x$ .

**Example 1.1.** Consider a doughnut-shaped block of material which expands linearly with temperature. It has an initial inner and outer diameter  $r_0$  and  $R_0$  respectively. Find the new area of the block in terms of  $r_0$  and  $R_0$  after a temperature increase of  $\Delta T$ , and hence show that they increase linear with the change in temperature.

## 1.7 Heat Transfer

The transfer of energy by heating is always due to a temperature difference. The specific mechanism depends on the material properties. For example, in a fluid the heating is caused by molecular collisions which transfer energy. In solids, energy is transferred by electrons or lattice vibrations known as phonons, depending on whether the material is electrically insulating or not. Fourier's heat conduction law states that

$$\frac{Q}{\Delta t} = P = -\kappa A \frac{dT}{dx}. \quad (1.16)$$

$P$  is the power transferred and  $\kappa$  is the thermal conductivity (measured in W/m/K). Under **steady state** conditions, meaning the temperature of the system and the surroundings at every point does not change with time (there may still be energy transfer), the law becomes

$$P = -\kappa A \frac{\Delta T}{\Delta x}. \quad (1.17)$$

An object that is so big that its temperature can be assumed to remain constant, no matter how much we heat or cool it, is known as a **thermal reservoir**. For example, a cup of tea will exchange heat with the air in the room that it sits in. It will cool down, but the room will not noticeably heat up.

**Example 1.2.** Consider three solid blocks between two thermal reservoirs which have temperatures  $T_1$  and  $T_2$  respectively.

**Example 1.3.** Consider two concentric cylinders.

## 1.8 Radiation

When it comes to heat transfer by radiation, the most important equation is the **Stefan-Boltzmann Law**,

$$P = \sigma \varepsilon A T^4. \quad (1.18)$$

$A$  is the surface area of the object,  $T$  is the surface temperature,  $\varepsilon$  is the emissivity, a dimensionless constant between 0 and 1 that determines how efficiently the object radiates energy, and  $\sigma$  is the Stefan-Boltzmann constant. A perfectly reflecting object has  $\varepsilon = 0$  and a perfectly absorbing and emitting object has  $\varepsilon = 1$ .

# Chapter 2

## Kinetic Theory

### 2.1 The Ideal Gas Law

An ideal gas is one where the particles can be considered point-like, meaning the average distance between particles is very large compared to particle size. We also assume that the particles interact only in perfectly elastic collisions (there are no intermolecular forces). This might sound like a very simplistic set of assumptions, but it turns out to be a very useful model. From these assumptions, we get the ideal gas law:

$$PV = nRT, \quad (2.1)$$

where  $R$  is the gas constant, equal to  $N_A K_B$ . Using this we can write the physicists version of the ideal gas law:

$$PV = NK_B T. \quad (2.2)$$

The ideal gas law is an example of an equation of state, one that relates state variables of a system to each other. Due to the assumptions that we have made, this equation only holds in the real world for gases that are in equilibrium (or very close to it). Note that a “state variable” is a property of the system that depends only on the current state, and not the past states.

Let’s focus on a single particle in an ideal gas in a container. If the particle hits the wall in the  $y - z$  plane, only the  $x$  component of the velocity will change since it is an elastic collision. Thus the pressure on the wall is due to the  $x$  component of the momentum. The particle’s momentum changes by  $\Delta p_{x,i} = -2mv_{x,i}$  so due to conservation of momentum there is  $\Delta p_{x,i} = 2mv_{x,i}$  imparted to the wall. The change in momentum is equal to the force multiplied by the time interval  $\Delta p = F\Delta t$ , so since pressure is defined as force per unit area, we get

$$\Delta p_{x,i} = P_i A \Delta t_i. \quad (2.3)$$

$P_i$  is the pressure due to particle  $i$  on the wall and  $\Delta t_i$  is the time interval between collisions for particle  $i$ . Now if we imagine the particle bouncing back and forth in the



box of width  $L$ , then the time between collisions is given by

$$\Delta t_i = \frac{2L}{v_{x,i}}. \quad (2.4)$$

Substituting this into the equation above we get

$$P_i V = m v_{x,i}^2, \quad (2.5)$$

where  $V = AL$ . The total pressure on the wall is simply equal to the sum of this quantity for all particles:

$$PV = \sum_{i=1}^N m v_{x,i}^2 = m \underbrace{\sum_{i=1}^N v_{x,i}^2}_{N \bar{v}_x^2} \quad (2.6)$$

The bar above the velocity denotes the mean. Now, note that

$$\bar{v}^2 = \bar{v}_x^2 + \bar{v}_y^2 + \bar{v}_z^2, \quad (2.7)$$

so assuming the velocity of the particles is **isotropic** (meaning there is not preferred direction),

$$\bar{v}_x^2 = \frac{1}{3} \bar{v}^2, \quad (2.8)$$

and hence by using the ideal gas law,

$$PV = \frac{1}{3} N m \bar{v}^2 = N k_B T \quad (2.9)$$

$$\implies \bar{v}^2 = \frac{3 k_B T}{m}. \quad (2.10)$$

If we take the square root of both sides, we get the **root mean square velocity**:

$$v_{\text{rms}} = \sqrt{\frac{3 k_B T}{m}}. \quad (2.11)$$

## 2.2 Equipartition Theorem

The internal energy of a gas is a state variable. It is the sum of all of the types of energy contained in the gas; kinetic, potential, mass, and chemical. For a monatomic ideal gas, we only have kinetic energy, and moreover the kinetic energy is purely translational:

$$U = \frac{1}{2} N m \bar{v}^2 = \frac{3}{2} N k_B T. \quad (2.12)$$

Note that this is a constant times  $N$ , meaning that on average each atom has an energy of  $\frac{3}{2} k_B T$ , or  $\frac{1}{2} k_B T$  for each translational degree of freedom. This is known as the **equipartition theorem**. In general, an ideal gas with  $N$  particles and  $f$  quadratic degrees of freedom will have an internal energy of

$$U = \frac{f}{2} N k_B T. \quad (2.13)$$

Note that a quadratic degree of freedom is one where the associated energy is proportional to the square of a position or momentum variable. For example, translation motion  $E = \frac{1}{2}mv^2$ , elastic potential energy  $E = \frac{1}{2}kx^2$ , or rotational kinetic energy  $E = \frac{1}{2}I\omega^2$ . A diatomic gas has 3 translational degrees of freedom, along with 2 rotational 2 vibrational (one for the kinetic energy and one for the potential energy). This makes 7 in total, however at lower temperatures some of these modes will not be excited and the degrees of freedom will be “frozen out”. For example, at room temperature, diatomic oxygen and nitrogen have 5 degrees of freedom.

Let’s look at the average distance between collisions, also known as the **mean free path**. A collision between two particles occurs if a particle comes within a diameter  $d$  of another. Identically, we can consider a particle with cross-sectional area  $2d$  and ask about the probability that a particle enters the volume traced out:

$$\pi d^2 \lambda \frac{N}{V} = 1 \quad (2.14)$$

$$\implies \lambda = \frac{V}{N\pi d^2}. \quad (2.15)$$

If we remember that all particles are moving, this gets reduced by a factor of  $\frac{1}{\sqrt{2}}$ :

$$\lambda = \frac{V}{\sqrt{2}N\pi d^2} = \frac{1}{\sqrt{2}n\pi d^2}. \quad (2.16)$$

Note that we have defined the number density  $n = \frac{N}{V}$ .

It can be shown that in an ideal gas, the velocities are distributed according to the **Maxwell-Boltzmann Distribution**. This takes the form

$$p(v) = \sqrt{\frac{2}{\pi}} \left( \frac{m}{k_B T} \right)^{\frac{3}{2}} v^2 \exp \left( -\frac{mv^2}{2k_B T} \right), \quad (2.17)$$

where  $p(v)$  is the probability density of a single particle having speed  $v$ . Note that this probability distribution is properly normalised so that  $\int_0^\infty p(v)dv = 1$ . At higher temperatures, the tail drops off much less i.e. there are a much wider range of velocities. From this distribution, we can measure some characteristic speeds. The most probable speed is found at the peak of the distribution, which is found by differentiating:

$$\frac{dp}{dv} = 0 = 2Ave^{-av^2}(1 - av^2) \quad (2.18)$$

$$\implies av_{\text{mp}}^2 = 1 \quad (2.19)$$

$$v_{\text{mp}} = \sqrt{\frac{1}{a}} = \sqrt{\frac{2k_B T}{m}}. \quad (2.20)$$

The mean speed will be to the right of the most probable speed since the distribution is asymmetric. It is found by integrating the distribution multiplied by  $v$ :

$$\bar{v} = \int_0^\infty vp(v)dv = A \int_0^\infty v^3 e^{-av^2} dv \quad (2.21)$$

$$= \frac{1}{2} A a^{-2} \quad (2.22)$$

$$= \sqrt{\frac{8k_B T}{\pi m}}. \quad (2.23)$$

Finally, we can calculate the root mean square speed just to check our answer from before:

$$v_{\text{rms}} = \sqrt{\int_0^\infty v^2 p(v)dv} = \sqrt{A \int_0^\infty v^4 e^{-av^2} dv} \quad (2.24)$$

$$= \sqrt{A \frac{3}{8} \sqrt{\pi} a^{-\frac{5}{2}}} \quad (2.25)$$

$$= \sqrt{\frac{3k_B T}{m}}. \quad (2.26)$$