PH2202

Thermal physics

Spring 2021

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Thermal physics deals with the topic of *temperature*. Temperature is a statistical property – thus, it makes no sense to talk of the temperature of one, two, or even a handful of particles.

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1 Kinetic Theory of Gases

1.1 The molecular picture of matter

Imagine looking into a container filled with steam, and magnifying by a factor of 10^{10}. A cubic metre might contain around 20 molecules, all of which are in constant motion, colliding with the walls and each other. Suppose that one of the walls is a piston. The molecules which collide with the piston and impart a force on it; in order to fix the piston in place, a counter force must be applied.

Definition 1.1 (Pressure)**.** The force per unit area applied by a gas on the walls of its container is called the pressure of the gas.

Now provide the system with heat. We know that the temperature of the gas must increase – what this means is that the speeds of the molecules increase, on average.

Definition 1.2 (Temperature)**.** The temperature of a gas is a measure of the average kinetic energy of the constituent particles.

Instead, consider an adiabatic container, which stops all flow of heat into and out of the gas. By compressing the gas with the piston, we observe that the temperature of the gas also rises.

Now, take away heat from the system. The temperature drops and the molecules tend to be close to each other. This is because of the dipolar attractive forces between the molecules (which varies as the inverse cube of the distance of the dipoles, and is hence comparatively short range). On the other hand, they cannot get too close, since once the electron clouds of the molecules start to overlap, a repulsive force is introduced. At a certain point, we reach a condensed form of matter: liquid water.

Liquid water is very much incompressible, yet the molecules freely move and slide around, without any periodic arrangement. The molecules at the surface are attracted by like molecules inside; this cohesive force keeps the liquid condensed. This tendency of a liquid to minimize its surface area is related to the phenomenon of surface tension. Some molecules on the surface are energetic enough to escape this cohesive attraction and leave the liquid – this is called evaporation. Heating a liquid simply increases the average kinetic energy of the molecules, thus increasing the rate of evaporation. When these energetic molecules leave the liquid, the average kinetic energy of the liquid drops, hence it cools down. This is the phenomenon of latent heat.

When this happens in a closed container, the process of evaporation cannot go on indefinitely, since the air has a limited capacity for holding moisture. Condensation is the process where these airborne molecules return to the liquid. At a certain point, the rates of evaporation and condensation become equal, and we obtain a saturated vapour.

Return to the liquid, and take away even more heat. Now, the motion of the molecules decrease to a point where they occupy fixed positions. They are still in motion, but their movement is restricted around their mean position. This is the crystal state. The lower the temperature, the smaller the oscillations and vibrations.

1.2 Basic assumptions

1. Gases are made up of a large number of molecules, and all molecules of one gas are identical.
2. Molecules of a gas are always moving. The number of molecules per unit volume remains constant, i.e. the density remains constant.
3. Molecules behave as elastic spheres during collisions. Kinetic energy and momenta are conserved, and the collision time is negligible compared to the free path time.
4. No force acts on any molecule, except during collisions. Intermolecular forces are only short ranged. Between collisions, the molecules continue moving with uniform velocity in a straight line.
5. The entire gas is isotropic; for all molecules, all directions are the same.

Remark. The collisions between molecules can be modelled as the elastic collision of hard spheres. The repulsive forces between molecules, governed by the Lennard-Jones potential, varies as $1/r^{12}$, which is very short range and very powerful. In comparison, gravity is a long range force since it varies as $1/r^2$.

1.3 Ideal gases

For an ideal gas, we make a few more assumptions. The gas molecules have negligible size, so are essentially point masses. Also, there are no forces on the molecules except during collisions, so they have no potential.

No real gases are ideal. We may look at the limit where the temperature T is very high and the density (or n) is very low. Here, the kinetic energy far exceeds any potential energies, and the mean free path becomes very high.

We look at some absurdities of this model.

1. How do point masses collide?
2. If two gases of different temperatures are mixed, how do they exchange heat?
3. Without intermolecular forces, are there any phase changes?
4. How do we explain properties such as viscosity and thermal conductivity?

1.4 Pressure

Suppose that a volume dV, located at (r, θ, ϕ), contains $n\,dV$ particles. If we consider a small flat, horizontal area ΔS, we can calculate the number of molecules moving towards ΔS, as

$$dN = \frac{n\cos\theta\,\Delta S}{4\pi r^2}\,dV.$$

Over a time Δt, we only consider the particles within the region $r = 0 \to c\Delta t$ above the xy plane. Integrating, we have

$$\int dN = \int_0^{c\Delta t}\int_0^{\pi/2}\int_0^{2\pi} \frac{n\cos\theta\,\Delta S}{4\pi r^2} r^2 \sin\theta\,d\phi\,d\theta\,dr.$$

Simplifying, we have

$$N = \frac{1}{2}n\,\Delta S\cdot c\Delta t\cdot\int_0^{\pi/2}\cos\theta\sin\theta\,d\theta = \frac{1}{4}nc\Delta S\,\Delta t.$$

Thus, the number of molecules hitting the wall per unit area per unit time is given by $nc/4$.

What if we have different molecules with different velocities? We can use this expression to conclude that if n_i molecules have velocity c_i, the average velocity is $\langle c\rangle = \sum n_i c_i/n$, $n = \sum n_i$, so

$$N = \frac{1}{4}n\langle c\rangle.$$

Now, each molecule can strike the walls of the container at some angle θ. For an elastic collision, the change in its momentum is $2mc\cos\theta$. Repeating the integration process, we write the momentum imparted as

$$\int 2mc\cos\theta\cdot\frac{n\cos\theta\Delta S}{4\pi r^2}dV = mnc^2\Delta S\cdot\int_0^{\pi/2}\cos^2\theta\sin\theta\,d\theta.$$

Simplifying, we have

$$\frac{1}{3}mnc^2\Delta S\Delta t.$$

For a velocity distribution, we deal with the RMS velocity where $c_{rms}^2 = \langle c_i^2\rangle = \sum n_i c_i^2/n$. Thus the pressure, which is the momentum imparted per unit area per unit time, is given by

$$\boxed{p = \frac{1}{3}\rho c_{rms}^2.}$$

Note that $\rho = mn$ is the density of the gas. Now, with knowledge of Boyle's Law and Charles' Law, we are forced to conclude that the temperature T is linearly dependent on c_{rms}^2.

For a volume V of gas, we see that

$$pV = \frac{1}{3}mnVc_{rms}^2 = \frac{1}{3}mNc_{rms}^2,$$

where $N = nV$ is the total number of molecules. Now, the average kinetic energy of these N molecules is

$$E = \sum \frac{1}{2} m n_i c_i^2 = \frac{1}{2} m N c_{rms}^2.$$

Combining these relations, we have

$$pV = \frac{2}{3}E.$$

Proposition 1.1 (Dalton's law of partial pressure)**.** *If there are multiple ideal gases in a container, then the total pressure of the mixture is the sum of partial pressures produced by each gas.*

$$p = p_1 + \cdots + p_n = \sum \frac{1}{3} \rho_i \langle c^2 \rangle_i.$$

Remark. This is a consequence of the assumption that the different gases do not interact with one another in any way, so the pressures they apply on the walls of the container simply add up. Similarly, the overall density is simply the sum $\rho = \rho_1 + \ldots \rho_n$.

Consider two gases at the same pressure. Thus, we have

$$n_1 \epsilon_1 = n_2 \epsilon_2,$$

where ϵ is the average kinetic energy of the gas. This is a measure of the temperature T of the gas. Since the gas molecules collide, the temperature T must be common between the two gases, so $\epsilon_1 = \epsilon_2$. This in turn means $n_1 = n_2$.

Proposition 1.2 (Avogadro's law)**.** *Equal volumes of two ideal gases at the same pressure and temperature will contain the same number of particles.*

Proposition 1.3 (Boyle's law)**.** *For isothermal expansion or contraction of a gas,*

$$pV = \textit{constant}.$$

For 1 mole of a gas, introduce the constant R such that

$$pV = \frac{2}{3}E = RT.$$

Putting $E = N_A \epsilon$, we write

$$\epsilon = \frac{3}{2} k_B T.$$

Here, $k_B = R/N_A$ is the Boltzmann constant. N_A is called Avogadro's number, which is the number of particles in 1 mole of a gas. We note that

$$N_A \approx 6.022 \times 10^{23}, \qquad k_B \approx 1.38 \times 10^{-23}\,\mathrm{J\,K^{-1}}.$$

Combining all these ideas leads to the ideal gas law.

Proposition 1.4 (Ideal gas law)**.** *The ideal gas law gives a relation between the pressure p, the volume V, the temperature T, and the number of moles n of an ideal gas.*

$$pV = nRT.$$

Here, the constant of proportionality R is called the ideal gas constant, with value

$$R \approx 8.314\,\mathrm{J\,mol^{-1}\,K^{-1}}.$$

Observe that the average energy of a molecule is

$$\epsilon = \frac{1}{2}mc_{rms}^2 = \frac{3}{2}k_B T.$$

This leads to

$$p = \frac{1}{3}mnc_{rms}^2 = nk_B T,$$

which shows that the pressure p of an ideal gas is a pure function of the intensive properties n and T.

1.5 Mean free path

We can relax the assumption that gas molecules are point masses, instead modelling them as hard spheres. If we know the molar mass M and the density ρ of the gas, the volume occupied per molecule is $M/N_A\rho$. In this way, we can approximate the 'diameter' of each molecule, say σ. If the molecules are packed tetrahedrally, say in the liquid state, each molecule occupies a volume $\sigma^3/\sqrt{2}$. Thus, we write

$$\frac{M}{N_A\rho} = \frac{\sigma^3}{\sqrt{2}}, \qquad \sigma = \left(\frac{\sqrt{2}M}{N_A\rho}\right)^{1/3}.$$

Definition 1.3. The mean distance travelled by a molecule between successive collisions is called the mean free path.

Consider a gas with identical molecules, each with diameter σ. Suppose that a particular molecule moves with relative speed v with respect to the other molecules. During each collision, the centres of the molecules are separated by σ. As this molecule moves, it sweeps out a cylindrical volume of influence, with area of cross section $\pi\sigma^2$ – any other molecules lying within this volume are vulnerable to collision. With respect to them, we see that within a time Δt, this volume is given by $\pi\sigma^2 v\Delta t$. Multiplying by the number density n, we see that $n\pi\sigma^2 v\Delta t$ molecules lie within this volume. We set this to be the number of collisions experienced by our molecule over the time Δt. If our molecule has an actual speed of u, it must have travelled a distance $u\Delta t$. This means that the average path length between collisions is given by

$$\lambda = \frac{u\Delta t}{n\pi\sigma^2 v\Delta t} = \frac{u/v}{n\pi\sigma^2}.$$

Now, if our particle of interest is moving significantly faster than all other surrounding molecules, we may write $u/v \approx 1$, so $\lambda \approx 1/n\pi\sigma^2$. Otherwise, set $u = c$, which is the common speed of all gas molecules. If two such molecules move with the same speed but in different directions, separated by an angle θ, their relative speed is given by

$$v = 2c \sin \frac{\theta}{2}.$$

To average this over θ, we first need to find the probability distribution for θ. Note that if we direct the velocity of one of the molecules along the axis of a sphere, the other velocity can pierce the sphere surface at any point with uniform probability; this is due to the isotropic nature of the gas. Recall that a differential surface element on a sphere is given by

$$dS = R^2 \sin\theta \, d\theta \, d\phi.$$

Thus, the annular ring at θ has area $2\pi R^2 \sin\theta \, d\theta$. Dividing by the total surface area $4\pi R^2$, we see that θ is distributed with the probability density function $f(\theta) = \sin\theta/2$. Thus, the average value of the relative speed v is given by

$$\langle v \rangle = \int_0^\pi 2c \sin\frac{\theta}{2} \cdot \frac{1}{2} \sin\theta \, d\theta = \frac{4}{3}c.$$

This gives the mean free path expression

$$\lambda = \frac{3}{4n\pi\sigma^2}.$$

This expression is contingent on the assumption that all molecules move with identical speed, in an isotropic fashion. A more nuanced calculation using the Maxwell distribution gives the expression

$$\boxed{\lambda = \frac{1}{\sqrt{2}n\pi\sigma^2}.}$$

Note that this doesn't show any explicit dependence on the temperature T. On the other hand, short range interactions between molecules become more significant at low T, which increases the effective diameter σ. Conversely, this attraction diminishes at higher T. We may write

$$\sigma^2 = \sigma_\infty^2 \left(1 + \frac{b}{T}\right),$$

where σ_∞ is the effective diameter as $T \to \infty$, and b is a measure of the molecular attraction. Thus,

$$\lambda \propto \frac{1}{1 + \frac{b}{T}},$$

which shows a marginal dependence on T.

Suppose that the probability that a molecule suffers no collisions over a distance x is given by $f(x)$. Now, the homogeneity and isotropy of the gas means that over a distance dx, the probability of a collision will be some pdx, irregardless of the direction of dx – the proportionality is given by a constant p when we consider very small dx. Now, the molecule suffers no collisions over a distance $x + dx$ with probability $f(x)(1 - p\,dx)$. However, this is just $f(x + dx)$, which we expand as a Taylor series and take only the first order terms to obtain $f(x) + f'(x)\,dx$. Thus,

$$f' = -pf,$$

which is solved by the exponential function e^{-px}. Since we want $f(0) = 1$, i.e. no collisions whatsoever over a distance 0, we set $f(x) = e^{-px}$. Now, we see that the probability of collision between x and $x + dx$ is $f(x)\, p\, dx$, so the mean free path is simply the expected value

$$\lambda = \int_0^\infty x\, e^{-px}\, p\, dx = \frac{1}{p}.$$

Thus, the probability density function f_λ of the free path is given as

$$f_\lambda(x) = \frac{1}{\lambda}\, e^{-x/\lambda}.$$

Note that this is an exponential distribution, with mean λ and variance λ^2. Around 37% of free paths are longer than λ; only 1% of paths are longer than 4.6λ.

1.6 Pressure, considering collisions

We recall that the number of molecules moving from a volume dV towards a surface ΔS was given by

$$dN = \frac{n \cos\theta\, \Delta S}{4\pi r^2}\, dV.$$

In our prior calculations, we neglected the effects of collisions. We show that these considerations do not in fact change the final result. Note that due to collisions, some of those molecules from dV directed towards ΔS are deviated from their path and do not reach their destination. Additionally, other molecules from outside dV can collide and reach ΔS.

Consider those molecules with speeds between c and $c + dc$, say dn_c many of them per unit volume. These molecules have a mean free path of λ_c, so any one of these will suffer $c\Delta t/\lambda_c$ collisions over a times Δt. Thus, within a volume dV, the number of collisions in which those dn_c molecules participate is given as

$$\frac{c\Delta t}{\lambda_c}\, dn_c\, dV.$$

Note that this must be the number of free paths which start over that time. From the isotropic nature of the gas, the fraction of those free paths which start towards ΔS is given as

$$\frac{\cos\theta \Delta S}{4\pi r^2}.$$

Of these, the e^{-r/λ_c} fraction of free paths are longer than r, and hence reach ΔS. Thus, the number of molecules which start from dV and reach ΔS has the distribution

$$dN_c = \frac{\cos\theta \Delta S}{4\pi r^2} \cdot \frac{c\Delta t}{\lambda_c} \cdot e^{-r/\lambda_c}\; dn_c\, dV.$$