Goals

- Understand the connection between thermodynamic pressure and velocity distributions.
- Learn how to calculate gas properties and describe effusion using the Maxwell velocity distribution.
- Gain understanding of the role of particle-particle collisions in kinetic theory.

Maxwell distribution

The fraction of particles of mass $m$ with velocities between $v = (v_x, v_y, v_z)$ and $v + dv = (v_x + dv_x, v_y + dv_y, v_z + dv_z)$ is given by $f(v) dv \propto e^{-mv^2/2k_B T} dv$, where $T$ is temperature, $k_B$ the Boltzmann constant, and $v = |v|$.

It follows that the speed distribution (normalized to $\int_0^\infty f(v) dv = 1$) is

$$f(v) dv \propto \frac{4}{\sqrt{\pi}} \left( \frac{m}{2k_B T} \right)^{3/2} v^2 e^{-mv^2/2k_B T} dv.$$

The average speed is $\langle v \rangle = \sqrt{8k_B T/\pi m}$ and $\langle v^2 \rangle = 3k_B T/2m$. You should work out higher order expectation values using general formulas for Gaussian integrals e.g. given in Appendix C2 of Blundell & Blundell. The maximum value of $f(v)$ is attained for $v_{\text{max}} = \sqrt{2k_B T/m}$.

For a given density $n$ of Maxwell distributed particles the number travelling at angles between $\theta$ and $\theta + d\theta$ to a chosen direction is given by $nf(v) dv \sin\theta d\theta/2$, and the number of particles hitting a wall of area $A$ orthogonal to the chosen direction over time $dt$ is $A n f(v) \sin\theta \cos\theta dv d\theta dt/2$.

Collisions

The mean scattering time is $\tau = 1/\sqrt{2n\sigma \langle v \rangle}$, where $\sigma = \pi d^2$ is the collision cross-section of a molecule of diameter $d$. The mean free path travelled between collisions is $\lambda = 1/\sqrt{2n\sigma}$.

Problems

1. Remind yourself how one calculates pressure from a particle distribution function. Let us consider an anisotropic system, where there exists one (and only one) special direction in space (call it $z$), which affects the distribution of particle velocities (an example of such a situation is a gas of charged particles in a straight magnetic field).

   (a) How many variables does the distribution function now depend on? (Recall that in the isotropic case, it depended only on one, $v$.) Write down the most general form of the distribution function under these symmetries – what is the appropriate transformation of variables from $(v_x, v_y, v_z)$?

   (b) What is the expression for pressure $p_\parallel$ (in terms of averages of those new velocity variables) that the gas will exert on a wall perpendicular to the $z$ axis? (It is called $p_\parallel$ because it is due to particles whose velocities have non-zero projections onto the special direction $z$.) What is $p_\perp$, pressure on a wall parallel to $z$?

   (c) Now consider a wall with a normal $\mathbf{n}$ at an angle $\theta$ to $z$. What is the pressure on this wall in terms of $p_\parallel$ and $p_\perp$?

2. (a) Show that the number of molecules hitting unit area of a surface per unit time with speeds between $v$ and $v + dv$ and angles between $\theta$ and $\theta + d\theta$ to the normal is

   $$d\Phi(v, \theta) = \frac{1}{2} n v \tilde{f}(v) dv \sin(\theta) \cos(\theta) d\theta$$

   where $\tilde{f}(v)$ is the distribution of particle speeds.
(b) Show that the average value of $\cos(\theta)$ for these molecules is $2/3$.
(c) Show that for a gas obeying the Maxwellian distribution, the average energy of all the molecules is $3k_B T/2$, but the average energy of those hitting the surface is $2k_B T$.

3. (a) A Maxwellian gas effuses through a small hole to form a beam. After a certain distance from the hole, the beam hits a screen. Let $v_1$ be the most probable speed of atoms that, during a fixed interval of time, hit the screen. Let $v_2$ be the most probable speed of atoms situated, at any instant, between the small hole and the screen. Find expressions for $v_1$ and $v_2$. Why are these two speeds different?

(b) You have calculated the most probable speed $v_1$ for molecules of mass $m$ which have effused out of an enclosure at temperature $T$. Now calculate their mean speed $\langle v \rangle$. Which is the larger and why?

4. A vessel contains a monatomic gas at temperature $T$. Use Maxwell’s distribution of speeds to calculate the mean kinetic energy of the molecules. Molecules of the gas stream through a small hole into a vacuum. A box is opened for a short time and catches some of the molecules. Assuming the box is thermally insulated, calculate the final temperature of the gas trapped in the box.

5. This question requires you to think geometrically.

(a) A gas effuses into a vacuum through a small hole of area $A$. The particles are then collimated by passing through a very small circular hole of radius $a$, in a screen a distance $d$ from the first hole. Show that the rate at which particles emerge from the circular hole is $nA v^2/4d^2$, where $n$ is the particle density and $\langle v \rangle$ is the average speed. (Assume no collisions take place after the gas effuses and that $d \gg a$.)

(b) Show that if a gas were allowed to leak into an evacuated sphere and the particles condensed where they first hit the surface they would form a uniform coating.

6. A closed vessel is partially filled with liquid mercury; there is a hole of area $A = 10^{-7}$ m$^2$ above the liquid level. The vessel is placed in a region of high vacuum at $T = 273K$ and after 30 days is found to be lighter by $\Delta M = 2.4 \times 10^{-5}$ kg. Estimate the vapour pressure of mercury at $273K$. (The relative molecular mass of mercury is 200.59.)

7. Consider a gas that is a mixture of two species of molecules: type-1 with diameter $d_1$, mass $m_1$ and mean number density $n_1$ and type-2 with diameter $d_2$, mass $m_2$ and mean number density $n_2$. If we let them collide with each other for a while (for how long? answer this after you have solved the rest of the problem), they will eventually settle into a Maxwellian equilibrium and the temperatures of the two species will be the same.

(a) What will be the rms speeds of the two species?
(b) Show that the combined pressure of the mixture will be $p = p_1 + p_2$ (Dalton’s law).
(c) What is the cross-section for the collisions between type-1 and type-2 molecules?
(d) What is the mean collision rate of type-1 molecules with type-2 molecules? (Here you will need to find the mean relative speed of the two types of particles, a calculation analogous to one in the lecture notes)

8. Consider particles in a gas of mean number density $n$ and collisional cross-section $\sigma$, moving with speed $v$ (let us pretend they all have exactly the same speed).

(a) What is the probability $P(t)$ for a particle to experience no collisions up to time $t$? Therefore, what is the mean time until it experiences a collision?
Hint: Work out the probability for a particle not to have a collision between $t$ and $t + dt$. Hence work out $P(t + dt)$ in terms of $P(t)$ and the relevant parameters of the gas. You should end up with a differential equation for $P(t)$, which you can then solve. [You will find this derivation in Blundell & Blundell, but do try to figure it out yourself!]

(b) What is the the probability $P(x)$ for a particle to travel a distance $x$ before having a collision? Show that the root mean square free path is given by $\sqrt{2} \lambda_{mfp}$ where $\lambda_{mfp}$ is the mean free path.

(c) What is the most probable free path length?

(d) What percentage of molecules travel a distance greater than (i) $\lambda_{mfp}$, (ii) $2\lambda_{mfp}$, (iii) $5\lambda_{mfp}$?
9. Given that the mean free path in a gas at standard temperature and pressure (S.T.P.) is about $10^3$ atomic radii, estimate the highest allowable pressure in the chamber of an atomic beam apparatus $10^{-1}$m long (if one does not want to lose an appreciable fraction of atoms through collisions).

Class Problems

10. The probability distribution of molecular speeds in a gas in thermal equilibrium is a Maxwellian: a molecule of mass $m$ will have a velocity in a 3-dimensional interval $[v_x, v_x + dv_x] \times [v_y, v_y + dv_y] \times [v_z, v_z + dv_z]$ (denoted $d^3v$) with probability

$$f(v) d^3v \propto e^{-v^2/2k_B T} \, d^3v,$$

where $v_{th} = \sqrt{2k_B T/m}$ is the thermal speed, $T$ temperature, $k_B$ Boltzmann’s constant, and I have used the proportionality sign ($\propto$) because the normalisation constant has been omitted (work it out by integrating $f(v)$ over all velocities).

(a) Given the Maxwellian distribution, what is the distribution of speeds, $\tilde{f}(v)$? Calculate the mean speed $\langle v \rangle$ and the mean inverse speed $\langle 1/v \rangle$. Show that $\langle v \rangle / \langle 1/v \rangle = 4/\pi$.

(b) Calculate $\langle v^2 \rangle$, $\langle v^3 \rangle$, $\langle v^4 \rangle$, $\langle v^5 \rangle$.

(c) Work out a general formula for $\langle v^n \rangle$. What is larger, $\langle v^{27} \rangle^{1/27}$ or $\langle v^{56} \rangle^{1/56}$? Do you understand why that is, qualitatively?

(d) What is the distribution of speeds $\tilde{f}(v)$ in an $n$-dimensional world (for general $n$)?

[These things are worked out in Blundell & Blundell, but we figure it out ourselves here!]

11. A gas is a mixture of $H_2$ and $HD$ in the proportion 7000 : 1. As the gas effuses through a small hole from a vessel at constant temperature into a vacuum, the composition of the remaining mixture changes. By what factor will the pressure in the vessel have fallen when the remaining mixture consists of $H_2$ and $HD$ in the proportion 700 : 1. ($H=$hydrogen, $D=$deuterium)

Now consider instead a thermally insulated container of volume $V$ with a small hole of area $A$, containing a gas with molecular mass $m$. At time $t = 0$, the density is $n_0$ and temperature is $T_0$. As gas effuses out through a small hole, both density and temperature inside the container will drop. Work out their time dependence, $n(t)$ and $T(t)$ in terms of the quantities given above.

Hint: Temperature is related to the total energy of the particles in the container. Same way you calculated the flux of particles through the hole (leading to density decreasing), you can now also calculate the flux of energy, leading to temperature decreasing. As a result, you will get two differential (with respect to time) equations for two unknowns, $n$ and $T$. Derive and then integrate these equations.

12. Consider a large system of volume $V$ containing $N$ non-interacting particles. Take some fixed subvolume $V \ll V$. Calculate the probability to find $N$ particles in volume $V$. Now assume that both $N$ and $V$ tend to $\infty$, but in such a way that the particle number density is fixed: $N/V = n = \text{const}.$

(a) Show that in this limit, the probability $p_N$ to find $N$ particles in volume $V$ (both $N$ and $V$ are fixed, $N \ll N$) tends to the Poisson distribution whose average is $\langle N \rangle = nV$.

(b) Prove that

$$\frac{\langle (N - \langle N \rangle)^2 \rangle^{1/2}}{\langle N \rangle} = \frac{1}{\sqrt{N}}$$

(so fluctuations around the average are very small as $\langle N \rangle \gg 1$).

(c) Show that, if $\langle N \rangle \gg 1$, $p_N$ has its maximum at $N \approx \langle N \rangle = nV$; then show that in the vicinity of this maximum,

$$p_N \approx \frac{1}{\sqrt{2\pi nV}} e^{-(N-nV)^2/2nV}.$$

Stirling’s formula for $N!$ will be needed. This is

$$N! \approx \sqrt{2\pi n} \left( \frac{n}{e} \right)^n.$$