

Chapter 7

Applications of the Boltzmann Distribution in Classical Physics

Topics

Examples of the use of the Boltzmann distribution in classical physics. Sedimentation. Chemical reactions. Phase equilibrium and vapour pressure. The Origin of helium in the Big Bang.

In this chapter, we apply the Boltzmann distribution to a variety of different problems in classical physics.

7.1 Sedimentation

A pleasant and important application of the Boltzmann distribution is to the phenomenon of the *sedimentation* of small particles in a fluid. We demonstrated the random motions of microspheres diffusing in distilled water as an example of the phenomenon of *Brownian motion*. The path was associated with the vast numbers of random encounters of water molecules with the microspheres. As we showed, the displacement of the particles was exactly as predicted by Einstein's theory of the process. The same process of molecular collisions

means that the tiny particles do not just settle at the bottom of a test-tube, but form an ‘atmosphere’ in the test-tube, just like that of molecules in the Earth’s atmosphere.

As in the case of the Earth’s atmosphere, we can work out how the potential energies of the microscopic particles vary with height within the test-tube. We suppose that the particles have density ρ_p and the fluid density ρ_f . The net force acting downwards is the difference between the downward force of gravity mg and the upthrust u due to the displaced fluid, that is, Archimedes’ principle. Therefore, the net downward force is

$$f = mg - u = mg - \rho_f \frac{m}{\rho_p} g = mg \left(1 - \frac{\rho_f}{\rho_p} \right), \quad (7.1)$$

where m/ρ_p is the volume of the particle. Therefore, the potential energy at height h from the bottom of the test-tube is

$$\phi(h) = \int_0^h mg \left(1 - \frac{\rho_f}{\rho_p} \right) dh = mgh \left(1 - \frac{\rho_f}{\rho_p} \right). \quad (7.2)$$

Therefore, just like the Earth’s atmosphere, the distribution of particles with height is expected to be

$$n(h) = n(0) \exp \left[-\frac{\phi(h)}{kT} \right], \quad (7.3)$$

$$= n(0) \exp \left[-\frac{mgh}{kT} \left(1 - \frac{\rho_f}{\rho_p} \right) \right], \quad (7.4)$$

$$= n(0) \exp \left(-\frac{h}{h_0} \right),$$

where $h_0 = (kT/mg)[1 - (\rho_f/\rho_p)]^{-1}$. This was historically an important calculation because Perrin validated this analysis by making observations of the height distribution of tiny particles and found the distribution shown in Figure 7.1. At a particularly fraught period in the history of physics, this was important evidence in favour of the molecular picture of the internal structure of matter. It can be seen from (7.3) that, if the sizes and masses of the particles are known, Boltzmann’s constant k can be estimated.

The process of sedimentation can be used to separate out large molecules in what is known as an

Archimedes Principle

The upthrust is equal to the weight of displaced fluid.

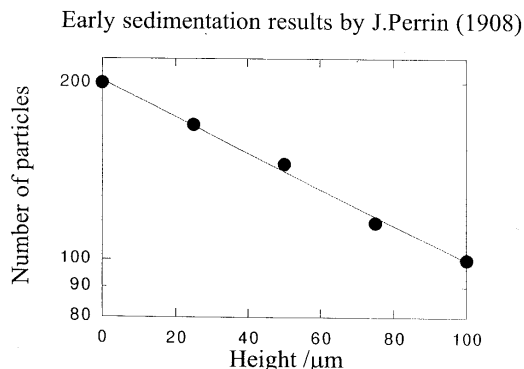


Figure 7.1. Perrin’s results for the height distribution of small particles in a test-tube. The vertical axis is plotted on a logarithmic scale.

ultracentrifuge. The lowest mass particles have the largest ‘atmospheric scale heights’. With accelerations of $10^6 g$, macromolecules such as proteins can be separated out.

7.2 Chemical Reactions

The Boltzmann distribution finds wide application in chemistry, particularly in understanding the rate at which chemical reactions take place. Typically, chemists mix two chemicals together so that the products of the reaction are in lower energy states than those of the reactants. In order for a reaction such as



to take place, two things must happen:

- The molecules A and B must collide;
- In order to react, they must overcome repulsive forces which lead to a potential energy or *activation energy* barrier, as illustrated in Figure 7.2.

Very often, it is a good idea to heat up the solution to speed up the reaction. Why does this help?

The diagram shows the potential barrier ϵ_f which has to be overcome before the reactants A and B can combine to reach a lower energy state in forming the product C. Equally, the reverse dissociation reaction



has a greater activation energy ϵ_b .

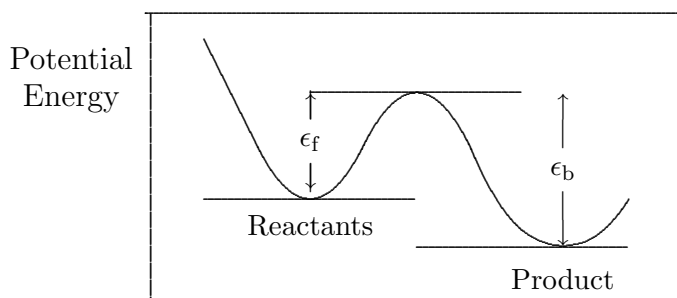
In chapter 5, we showed that the number of collisions, ΔN , which a particle makes in travelling a distance Δl is

$$\Delta N = n\sigma \Delta l,$$

where n is the number density of molecules and σ is the collision cross-section. If the particles have speed v , $\Delta l \approx v \Delta t$ and therefore the rate of collisions is

$$\frac{dN}{dt} = n\sigma v. \quad (7.5)$$

Figure 7.2. The potential energy associated with the atoms involved in a chemical reaction.



The origin of the activation energy is the kinetic energy of the colliding molecules. To make a simple estimate of what happens, let us assume that molecule A collides with a stationary molecule B. In order for the reaction to take place, the kinetic energy of molecule A must be at least $\frac{1}{2}mv_A^2 = \epsilon_f$ and so we need to estimate the fraction of atoms which have kinetic energies greater than this value.

As shown in (7.5), the probability of a collision is proportional to the speed v of the particles and so the fraction χ of atoms colliding with speed greater than $v_f = \sqrt{2\epsilon_f/m}$ is

$$\chi = \frac{\int_{\sqrt{2\epsilon_f/m}}^{\infty} v \times v^2 \exp\left(-\frac{mv^2}{2kT}\right) dv}{\int_0^{\infty} v \times v^2 \exp\left(-\frac{mv^2}{2kT}\right) dv} \quad (7.6)$$

$$= \exp(-\epsilon_f/kT) \left(\frac{\epsilon_f}{kT} + 1\right), \quad (7.7)$$

$$\approx \exp(-\epsilon_f/kT), \text{ if } \epsilon_f \ll kT.$$

This is a rather crude estimate and can be improved in many ways, but the calculations are lengthy. The final result is just the one we have derived

$$\chi = \exp(-\epsilon_f/kT), \quad (7.8)$$

which is again the simple form of the Boltzmann factor.

We need also to include the fact that, for each atom A, the collision rate is proportional to the number density of atoms B, n_B and that the number density of A atoms is n_A . Therefore the overall rate of the reaction must also be proportional to $n_A n_B$ and so

$$\frac{dn_C}{dt} \propto n_A n_B \exp\left(-\frac{\epsilon_f}{kT}\right) \quad (7.9)$$

Those of you doing chemistry will know all about this. The importance of heating up the reactants is that T is raised and so the probability of the reacting particles having enough energy to pass over the activation barrier increases exponentially, as ϵ_f/kT decreases.

Reminder - The Three-dimensional Maxwell Distribution

$$f(v) dv = \left(\frac{m}{2\pi kT}\right)^{3/2} 4\pi v^2 e^{-mv^2/2kT} dv$$

Optional practice in integration

Show that the ratio of the integrals in (7.6) gives the result (7.7).

Notice the other interesting point that the dissociation reaction is very much less likely to occur since $\epsilon_b/kT \gg \epsilon_f/kT$ and these terms appear in the exponential at the same temperature T . Notice also that the energy liberated in the reaction is $\epsilon_b - \epsilon_f$.

This formula can be tested by plotting the logarithm of the reaction rate against $1/T$, what is known as an *Arrhenius plot*. An example of such a plot for the decomposition of acetaldehyde is shown in Fig. 7.3.

This diagram illustrates the problems facing detergent manufacturers. One of the big challenges is to discover detergents which work at lower temperatures so that less energy is used in heating up the water and there is less chance of being scalded. The big problem they have is to beat the effects of the exponential in the Boltzmann distribution.

7.3 Phase Equilibrium and Vapour Pressure

7.3.1 The Structure of Solids and Liquids

Let us make a brief excursion into the structures of solids and liquids in order to understand the physics of melting and boiling. We represent the particles by hard elastic spheres. In the case of gases, we have assumed that interatomic or intermolecular forces can be neglected, but that cannot be the case for liquids and solids, which are held together by the attractive forces between particles. For simplicity, we assume that the force between particles is represented by the potential function $\Phi(r/a_0)$ shown in Figure 7.4, in which r is the separation of the particles and a_0 is their equilibrium separation.

When the atoms are far apart, the negative potential means that they are attracted to each other, whilst at short distances they are repelled by quantum mechanical forces. The equilibrium separation occurs at some separation a_0 , at which the attractive potential has a minimum of depth Φ_0 . Φ_0 is the amount of energy which would have to be sup-

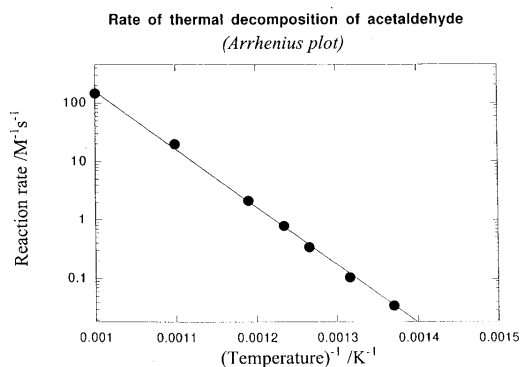
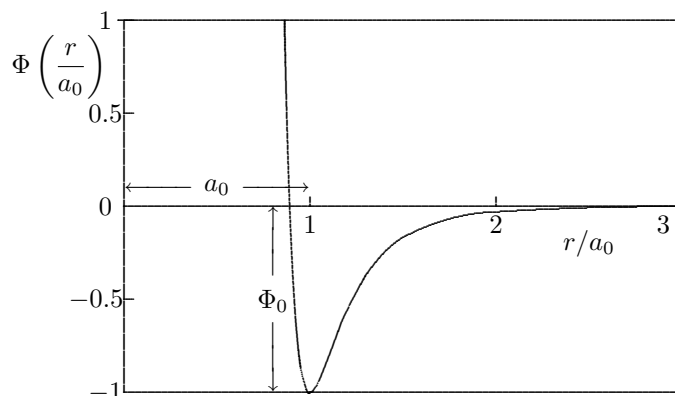


Figure 7.3. Arrhenius plot for the reaction rate of the decomposition of acetaldehyde.

Figure 7.4. The attractive potential between two atoms or molecules.



plied to dissociate the molecule, that is, separate the atoms to infinity.

If the particles were spheres, the closest way of packing them together in a solid is as a *close packed array*. This is the type of arrangement you find if you build a pyramid of identical oranges or billiard balls. A *close-packed plane* is shown in Figure 7.5. The spheres are packed as close together as they can be in a plane. Their centres all form *equilateral triangles* so that, in the plane, any atom is surrounded by *six nearest neighbours*. The interatomic forces keep all the atoms at the same distance apart.

Now, we have to place layers of close-packed planes one top of one another. The closest way of packing them in three-dimensions is to place a sphere on top of each triangle formed by a triplet of atoms, as shown in figure 7.6 for a pair of rows. Thus, in a close-packed array, the atoms form a continuous sequence of tetrahedra. When we place a second plane on top of the first as shown, and then a third on top of that, we can count up the number of atoms which are at the same distance from any atom. *In the plane*, there are 6 atoms at the same distance. In the *upper plane*, there are three at the same distance as those in the central plane and the same goes for the atoms in the *lower plane*. Therefore, each atom is surrounded by 12 atoms, all at the same distance. This is known as a *close-packed array* and we say that the *coordination number* $\mathcal{N} = 12$. The array forms a *crystal lattice* with *long-range crystalline order*.

The above picture represents a close-packed solid at $T = 0$ K. As the temperature is raised above $T = 0$, if we consider only the translational motions of the atoms of the array, they will acquire a kinetic energy of $\frac{3}{2}kT$ per atom and so they will randomly bang around within a small volume, or 'cage', defined by the 12 nearest neighbours. If the temperature is not too high, the crystal structure is not destroyed.

As the temperature is raised, however, the random thermal motions make the lattice expand, and, if this is not prevented by the application of an in-

Figure 7.5. A Close-packed Plane

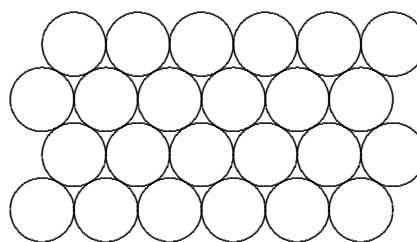
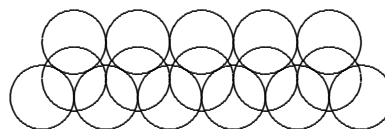


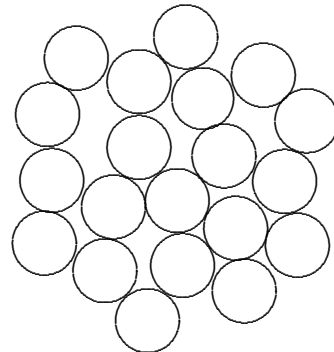
Figure 7.6. A Close-packed Plane with the Next Row on Top



creased external pressure, the molecules can move sufficiently far apart for occasional rearrangements of the crystal lattice to occur. If sufficient rearrangements take place, the long-range crystalline order is lost and the material becomes a *liquid*. Apart from the fact that these rearrangements can take place, the situation is not so different from that of a solid. Each molecule still bangs around in a cage formed by its nearest neighbours, but the structure of the cage is no longer a regular crystalline lattice.

For a liquid in the low temperature limit, this arrangement corresponds to *random close packing*, as illustrated in Figure 7.7. This structure is obtained if we stick the spheres together at the hard sphere separation, but at random orientations. The nearest neighbour distance remains the same as in the solid. There is some short-range order, but there is no longer any large-scale crystalline order. For random close-packing, the coordination number is $\mathcal{N} \approx 10$, rather than 12 for the close-packed array. We would therefore expect liquids to be typically about 20% less dense than solids.

Figure 7.7. Random Close-packing in a Liquid



7.3.2 The Binding Energies of Solids and Liquids

By *binding energy*, we mean the energy which has to be supplied in order to break up the solid into its component atoms or molecules at $T = 0$. From the shape of the inter-particle potential, it can be seen that the magnitude of the interaction potential energy decreases rapidly with increasing distance from a_0 and so we need only take nearest neighbour interactions into account. We can therefore estimate the binding energy by noting that, according to the close-packed model, most of the binding energy of a molecule is with its 12 nearest neighbours. Now, the potential refers to the interaction energy of *pairs* of molecules and therefore we share half the potential energy between each of them. Therefore, the total energy needed to disperse the molecules to infinity is $6N_A\Phi_0$ per mole, that is,

$$\text{Binding energy of solid} = 6N_A\Phi_0. \quad (7.10)$$

We can apply the same line of reasoning to the binding energies of liquids. The only difference is that there are only 10 nearest neighbours, each separated by a_0 . Again pairs of particles share the binding energy pair-wise and so the total binding energy per mole necessary to disperse the fluid to infinity is

$$\text{Binding energy of liquid} = 5N_A\Phi_0. \quad (7.11)$$

7.3.3 The Latent Heats of Solids and Liquids

Substances can exist as solids, liquids or gases (or vapours) and these are known as their different *phases*. The processes by which substances change phase are:

<i>Melting</i>	solid \rightarrow liquid	<i>Solidification</i>	liquid \rightarrow solid.
<i>Boiling</i>	liquid \rightarrow gas	<i>Condensation</i>	gas \rightarrow liquid.
<i>Sublimation</i>	solid \rightarrow gas	<i>Condensation</i>	gas \rightarrow solid.

At a given pressure, these *phase transitions* take place at a particular temperature. The processes on the left of the list involve the absorption of heat; those on the right involve the release of energy as the substance reaches a state of lower internal energy. The energies associated with these phase transitions are known as their *latent heats*.

We can estimate the latent heats associated with these processes by arguments based upon the principle of the *conservation of energy*. We assume that the transitions take place at a particular temperature and then estimate the total internal energies in the initial and final states of the phase transition. To do this, we need to estimate the *internal energies* U of the substance in both phases.

Let us give an elementary treatment in terms of the internal binding energies of the substance and ignore the energies associated with the thermal motions of the particles. To a good approximation, the internal energy in the solid phase is $-6N_A\Phi_0$ and $-5N_A\Phi_0$ in the liquid phase. In the gaseous phase, since we are ignoring thermal motions, we set the internal energy equal to zero.

Thus, the molar latent heat for the transition from the solid to the gaseous phase, a *sublimation* phase transition, is

$$L_{\text{sublimation}} \approx 6N_A \Phi_0. \quad (7.12)$$

A similar line of reasoning leads to an estimate of the latent heat associated with the liquid to gas transition. Hence the latent heat of boiling is

$$L_{\text{boiling}} \approx 5N_A \Phi_0. \quad (7.13)$$

By subtraction, we can find the *latent heat of melting*.

$$L_{\text{melting}} \approx N_A \Phi_0. \quad (7.14)$$

Thus, melting is a much less energetic process than boiling – this explains why scalding is so painful.

You should be aware that these are simple estimates, but they work well, provided they are not pushed too far.

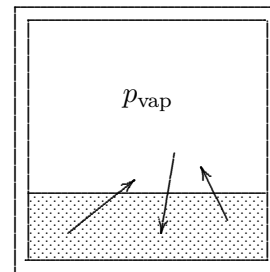
7.3.4 Boiling water

In equilibrium, molecules leave the surface of a liquid if they can overcome the potential barrier associated with their attraction for the bulk of the fluid. At the same time, molecules in the vapour phase can be absorbed into the liquid. Let us consider the equilibrium state within a closed vessel containing a liquid (Figure 7.8).

The simplest model is to consider an atom or molecule located at the surface. If it were within the body of the fluid, it would have on average 10 bonds linking it to the bulk of the fluid. At the surface it has only half the number of bonds, each with energy Φ_0 . Therefore, we would expect that the atom would have to acquire an energy $\epsilon = 5\Phi_0 = L/N_A$ from random thermal motions within the fluid in order to escape from the surface. We recognise that $5\Phi_0$ is just the latent heat per molecule. This is what is known as a *thermally activated process*.

The distribution of particle speeds perpendicular to the surface of the liquid is given by the one-

Figure 7.8. A Liquid in Equilibrium with its Vapour



dimensional Maxwell distribution

$$dn(v_z) = n_L f_1(v_z) dv_z = n_L \left(\frac{m}{2\pi kT} \right)^{1/2} \exp\left(-\frac{mv_z^2}{2kT}\right) dv_z. \quad (7.15)$$

The rate of arrival of particles with speeds v_z to $v_z + dv_z$ at the surface is $v_z dn(v_z)$ particles m^{-2} and so the rate of escape of molecules from the surface with energies greater than ϵ is

$$\begin{aligned} n(\geq \epsilon) &= \int_{\sqrt{2\epsilon/m}}^{\infty} v_z dn(v_z) \\ &= n_L \left(\frac{m}{2\pi kT} \right)^{1/2} \int_{\sqrt{2\epsilon/m}}^{\infty} v_z \exp\left(-\frac{mv_z^2}{2kT}\right) dv_z, \\ &= n_L \left(\frac{kT}{2\pi m} \right)^{1/2} \exp\left(-\frac{\epsilon}{kT}\right) \end{aligned} \quad (7.16)$$

In equilibrium, the loss of particles from the surface of the liquid is balanced by the return of particles from the vapour to the liquid state. The rate of arrival of particles from the vapour phase to the surface is given by the usual formula $\frac{1}{4}n_V\bar{v}$, where $\bar{v} = \sqrt{8kT/\pi m}$ and n_V is the number density of particles in the vapour phase. Therefore, when the processes of escape and return are in balance, we expect

$$n_L \left(\frac{kT}{2\pi m} \right)^{1/2} \exp\left(-\frac{\epsilon}{kT}\right) = \frac{1}{4}n_V \times \left(\frac{8kT}{\pi m} \right)^{1/2}, \quad (7.17)$$

that is,

$$\frac{n_V}{n_L} = \exp\left(-\frac{\epsilon}{kT}\right) = \exp\left(-\frac{L}{RT}\right). \quad (7.18)$$

We see that we have recovered another expression involving the Boltzmann factor. What this expression means is that the atoms or molecules in the vapour phase have average energy ϵ greater than those in the liquid phase and this makes sense since they must have at least energy ϵ to escape from the surface of the liquid.

Now, as we change the temperature, the number density of atoms in the liquid phase scarcely changes

at all and so the pressure of the vapour in equilibrium with the liquid is

$$p = n_V kT \propto T \exp\left(-\frac{L}{RT}\right). \quad (7.19)$$

The variation of the vapour pressure with temperature is dominated by the exponential term. We see that, as the temperature changes from 0 to 30°C (273 to 303 K), the pre-exponential factor changes by a factor of 1.1, while the exponential changes by a factor of about 6.

Figure 7.9 shows how the vapour pressure changes with temperature for water. Often, the term *saturated vapour pressure* is used for the vapour pressure since the pressure is as great as it can be at that temperature. When the pressure of the vapour becomes equal to local atmospheric pressure, the liquid boils. It can therefore be understood from Figure 7.9 why the boiling point of water decreases at high altitude. The saturated vapour pressure of the water vapour reaches local atmospheric pressure at a lower temperature.

7.4 The Origin of Helium - Non-examinable

Let us complete this study by working out the basic physics of the Big Bang and, in particular, the origin of helium. Everywhere we look in the Universe, the abundance of helium, ${}^4\text{He}$, is at least 23% by mass. This is too large a percentage to have been produced by nucleosynthesis in stars, but it comes naturally out of the early phases of the Big Bang. This important result depends only upon fundamental physics and the Boltzmann distribution.

First, we need the thermal history of the Universe. This turns out to be remarkably simple. The cooled remnant of the hot early phases of the Big Bang are all around us as microwave background radiation. This radiation is incredibly uniform over the sky and has a perfect black body spectrum at a temperature of 2.726 K (Figure 7.10). Now, the Universe is expanding uniformly on the very large scale and so we can work out how the temperature and energy density of the radiation change as

Exercise Check this calculation for yourself, given that the latent heat of vaporisation of water is $L = 4.06 \times 10^4 \text{ J mol}^{-1}$.

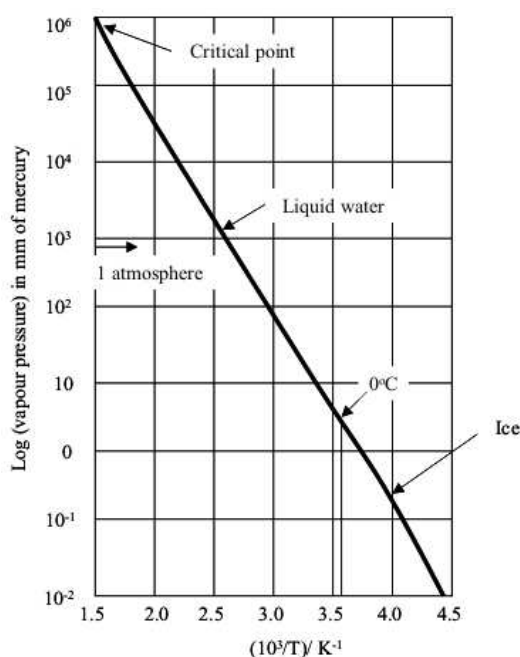


Figure 7.9. The variation of vapour pressure of water with temperature. Notice that the horizontal axis shows $1000 T^{-1}$.

the Universe expands. In fact, the radiation simply cools adiabatically as the Universe expands. Let us work out the consequences of this expansion for the temperature history of the Universe.

7.4.1 The Equation of State for a Photon Gas

Just as we can write $p = nkT$ for a perfect gas, so we can find a relation between pressure and temperature for a gas of electromagnetic waves or photons. Let us do this as an example.

Example: Show that the equation of state of a photon gas is $p = \frac{1}{3}u = \frac{1}{3}aT^4$, where u is the energy density of the radiation.

First, we ask,

‘What is the probability of particles having velocity vectors pointing at an angle θ with respect to a chosen direction?’

We soon realise that there will be *none* coming in at precisely θ . Rather, we should have asked,

‘How many particles are there with velocity vectors pointing between the angles θ and $\theta + d\theta$ with respect to the chosen direction?’

Remember that we can make $d\theta$ as tiny as we like. The way of working out the probability is shown in Figure 7.11.

Because of the effect of collisions, the velocity vectors of the particles are randomised and so there is an equal probability of the velocity vectors pointing in any direction. Therefore, we can consider the probability of the particles having velocity vectors lying within some solid angle $d\Omega$ in terms of the element of area dA on a sphere in that direction (see Section 9 of the Maths Handbook). Thus, the probability is the ratio of the area of dA to the total surface area of the sphere

$$p(dA) = \frac{dA}{4\pi r^2} \tag{7.20}$$

This result is quite general for an isotropic distribution of directions. In our case, we want to know the probability of the particles having velocity vectors within angles

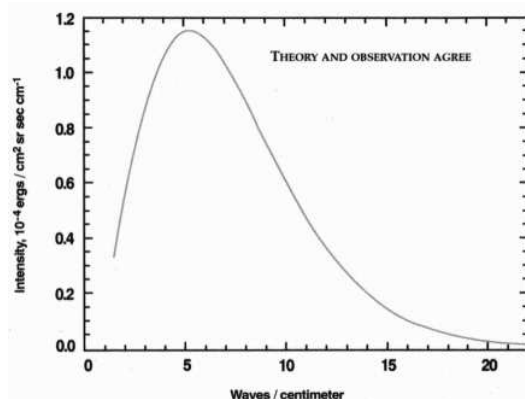
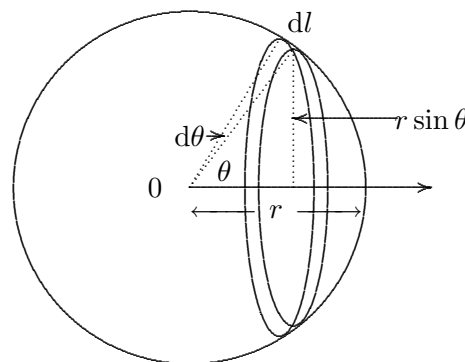


Figure 7.10. The spectrum of the Cosmic Microwave Background Radiation as measured by the COBE satellite. The spectrum is that of a perfect black-body at a temperature of 2.726 K.

Figure 7.11. Probability Distributions on a Sphere



θ to $\theta + d\theta$ of our chosen direction. It can be seen from the diagram that the tips of the vectors could lie anywhere within the circular annulus shown on the sphere and they would satisfy that criterion. Thus, we need to work out the surface area of that annulus and insert it into (7.20). Since the annulus is very thin, we simply multiply the circumference of the annulus by its thickness dl , as shown on the diagram. The radius of the annulus is $r \sin \theta$ and so its circumference is $2\pi r \sin \theta$. The thickness of the annulus is $dl = r d\theta$. Therefore, its surface area is $dA = 2\pi r \sin \theta r d\theta = 2\pi r^2 \sin \theta d\theta$. The probability of the velocity vectors lying within the angles θ to $\theta + d\theta$ with respect to the chosen direction is therefore

$$p(dA) = \frac{dA}{4\pi r^2} = p(\theta) d\theta = \frac{2\pi r^2 \sin \theta d\theta}{4\pi r^2} = \frac{1}{2} \sin \theta d\theta \tag{7.21}$$

It immediately follows that, if we have N particles, the number with velocity vectors between angles θ to $\theta + d\theta$ is

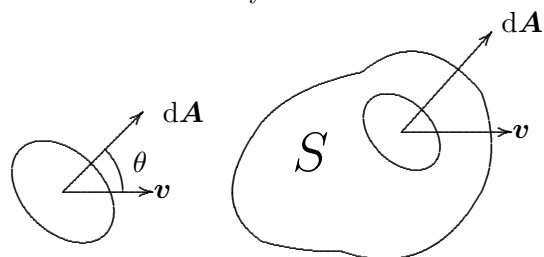
$$N(\theta) d\theta = Np(\theta) d\theta = \frac{1}{2} N \sin \theta d\theta \tag{7.22}$$

Next, we need the *flux of particles arriving from a particular direction, that is, the number of particles moving with velocity \mathbf{v} through an elementary of surface area $d\mathbf{A}$ per second*. We recall how we define the vector area $d\mathbf{A}$ (see Section 6 of the Maths Handbook). The number density of the particles is n .

The component of velocity parallel to the plane of the elementary area is $|\mathbf{v}| \sin \theta$, but this results in no flow through the area $d\mathbf{A}$. The component of velocity parallel to the vector $d\mathbf{A}$, that is, perpendicular to the surface, is $|\mathbf{v}| \cos \theta$ and so the number of particles passing through $d\mathbf{A}$ per second is $n|\mathbf{v}||d\mathbf{A}| \cos \theta = n\mathbf{v} \cdot d\mathbf{A}$ (Figure 7.12).

We now combine these results to relate the pressure to the energy density of a photon gas. Suppose the number density of photons is n . Consider those photons propagating towards the wall of the vessel at angle of incidence θ . Then, the change in momentum when the photon is reflected from the wall is $2h\nu \cos \theta/c$, using $p = h\nu/c$. The flux of such photons is $n\mathbf{v} \cdot d\mathbf{A} = nc \cos \theta dA$. The number of photons arriving within angle θ to $\theta + d\theta$ is $\frac{1}{2} N \sin \theta d\theta$ and so the rate of change of momentum per

Figure 7.12. The Flux of Particles though an elementary area $d\mathbf{A}$



unit area, or the *pressure* of the gas of photons, is

$$\begin{aligned} p &= \int_0^{\pi/2} \frac{2h\nu \cos \theta}{c} \times nc \cos \theta \times \frac{1}{2} \sin \theta \, d\theta, \\ &= nh\nu \int_0^{\pi/2} \cos^2 \theta \, d(\cos \theta), \\ &= \frac{1}{3}nh\nu = \frac{1}{3}u. \end{aligned} \quad (7.23)$$

Hence, for isotropic radiation in general and black-body radiation in particular, we find $p = \frac{1}{3}u$.

Now, let us use this result to work out the adiabatic expansion of a spherical volume V with radius R for a gas of photons. The system is thermally isolated and so

$$dU = -p \, dV. \quad (7.24)$$

For the photon gas, we need an expression for the energy density of radiation at a given temperature in thermal equilibrium. This is given by the Stefan-Boltzmann law, $u = aT^4$, where a is known as the Stefan-Boltzmann constant – we will study this law in detail later in the course. Therefore, the total energy density is $U = VaT^4$, and $p = \frac{1}{3}aT^4$. Substituting into (7.24), we find

$$\begin{aligned} dU &= -p \, dV, \\ d(VaT^4) &= -\frac{1}{3}aT^4 \, dV, \\ 4VT^3 \, dT + T^4 \, dV &= \frac{T^4}{3} \, dV, \\ 4VT^3 \, dT &= -\frac{4}{3}T^4 \, dV, \\ \frac{dT}{T} &= -\frac{1}{3} \frac{dV}{V}, \\ \ln T &= -\frac{1}{3} \ln V, \\ T &\propto V^{-1/3} \propto R^{-1}. \end{aligned} \quad (7.25)$$

We have implicitly worked out the ratio of specific heats for a photon gas. You will recall that we showed that the expression (6.20) for the adiabatic expansion of any gas was

$$TV^{\gamma-1} = \text{constant}.$$

It follows immediately that $\gamma = 4/3$ for a photon gas.

The equation of state of a photon gas

$$p = \frac{1}{3}u.$$

The Stefan-Boltzmann Law

The energy density of radiation in thermal equilibrium at temperature T is

$$u = aT^4,$$

where $a = 7.566 \times 10^{-16} \text{ J m}^{-3} \text{ K}^{-4}$ is known as the Stefan-Boltzmann constant. This law will be discussed in detail in the quantum physics half of the course. It can be found by integrating the energy under the black-body curve, which was quoted in Figure 1.11.

Ratio of specific heats for a photon gas

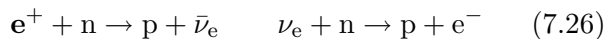
$$\gamma = \frac{4}{3}.$$

Now, we can use (7.25) to work out the temperature of the radiation when it was squashed much closer together than it is today. When we work out the dynamics of the expanding Universe, it turns out that the thermal history of the early Universe is given by

$$T \approx 10^{10} t^{-1/2} \text{ K},$$

so that, when the Universe was only 1 second old, the temperature was 10^{10} K. Since $T \propto R^{-1}$, the Universe was squashed by a factor of $10^{10}/2.726 \approx 3.5 \times 10^9$ relative to its present size. This is such a high temperature that all nuclei were broken up into their constituent protons and neutrons. At earlier times, the Universe was a sea of elementary particles which were in thermal equilibrium at a very high temperature, which continued to increase, roughly as (7.25) into the very early Universe. This is why the particle physicists regard the very early Universe as a laboratory for particle physics.

Let us now run the clocks forward from an equilibrium state when the temperature was about 10^{11} K. At that stage, the electrons e^- , positrons e^+ , neutrons n , protons p , electron neutrinos ν_e and antineutrinos $\bar{\nu}_e$ were all present in their equilibrium abundances. The reactions which maintain the protons and neutrons in thermal equilibrium are the following weak interactions



Now, the equilibrium abundances of neutrons and protons is given by the standard Boltzmann relation

$$N \propto \exp - \left(\frac{E}{kT} \right) \quad (7.27)$$

where $E = mc^2$ is the mass of the neutron or the proton. Since the mass of the neutron is slightly greater than the mass of the proton, $m_n = 1.674929 \times 10^{-27}$ kg and $m_p = 1.672623 \times 10^{-27}$ kg, the ratio of abundances of neutrons to protons decreases as

the temperature drops

$$\frac{N_n}{N_p} = \exp - \left(\frac{m_n c^2}{kT} \right) \exp \left(\frac{m_p c^2}{kT} \right) \quad (7.28)$$

$$= \exp \left(- \frac{\Delta m c^2}{kT} \right) \quad (7.29)$$

where $\Delta m c^2 = (m_n - m_p) c^2 = 1.28$ MeV is the mass difference between the neutron and the proton.

The relative abundances of neutrons to protons is described by this formula until the time when the time-scale for the weak interactions described by (7.26) becomes greater than the age of the Universe at these early times. Detailed calculations show that this occurred when the Universe was about 1 second old, when the temperature of the Universe was $T = 10^{10}$ K or $kT = 1$ MeV. Therefore, inserting this value into (7.29), the neutron to proton ratio was frozen at a value of roughly 0.21. In the subsequent reactions, the neutrons combine with protons to form helium nuclei by a sequence of reactions in which first deuterium is formed by the combination of a neutron and a proton. The deuterons then combine with protons to form ^3He which then combine with other ^3He nuclei to form ^4He . A more detailed calculation shows that about 24% by mass of ^4He is formed by this process Figure 7.13). Remarkably, this is precisely the minimum value of the helium abundance we find wherever we can detect helium in the Universe. Thus, the abundance of helium acts as a thermometer to tell us the temperature at which the neutrons and protons decoupled in the very early Universe. In addition, the abundances of the other light elements such as deuterium (D), helium-3 (^3He) and lithium-7 (^7Li) can be accounted for by the same process of primordial nucleosynthesis.

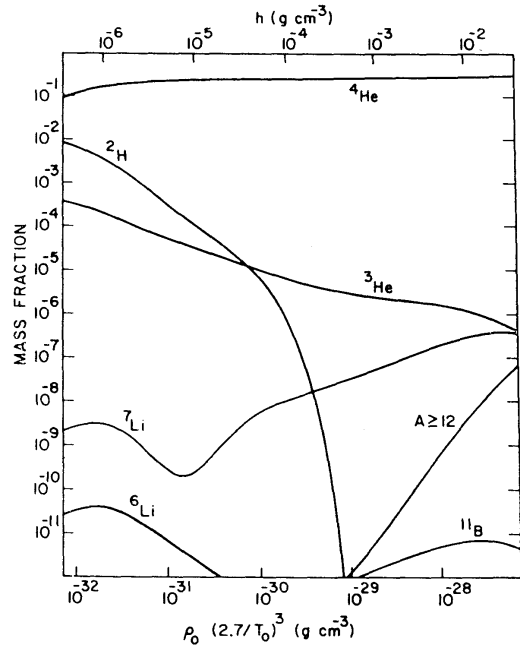


Figure 7.13. The predicted primordial abundances of the light elements created during the early phases of the Big Bang as a function of the present baryon density of the Universe.