

## Chapter 3

# THE LAW OF DETAILED BALANCE

Molecular motion can be looked upon as a sequence of reactions and the reactions cause changes. The collision of the molecules causing a change of momentum is a kind of reaction. If the structure of the molecules is changed by the reaction, this is then a chemical reaction. Detailed balance implies that in equilibrium, the number of occurrence of each reaction in the forward direction is the same as that in the reverse direction. That is to say, we have equilibrium not only macroscopically, but also for each microscopic reaction. Detailed balance can be understood from the symmetry of the arrow of time. If time is reversed, the law of the molecular motion is unchanged. Equilibrium is an unchanged state and looks the same whether time flows forwards or backwards. Hence the number of reactions in the forward and backward directions must be the same.

Detailed balance can be applied directly to analyse the ideal gas, including a dense quantum gas. The density in the so-called quantum gas is so high that the wave nature of the particles must be considered. The reaction in an ideal gas is very easy to analyse. If we add some plausible assumptions, we can calculate the density distribution of the particles from detailed balance and it can explain the relationship of temperature and chemical potential with the conserved quantities of the various reactions. Detailed balance can be applied in reverse, i.e. we can determine some properties of the reactions from the known density distribution of the particles. This is the main content of this chapter.

Detailed balance can be used as the starting point of statistical mechanics. In principle it is capable of analysing any equilibrium state. The now commonly used Monte Carlo method is based on detailed balance for calculation. This

method utilises numerical calculations on the computer to simulate various reactions. We shall discuss this in Chapter 25.

Detailed balance cannot take the place of the basic assumption in Chapter 5, because we are as yet unable to make careful analysis on more complicated reactions. Even for the ideal gas case, we have to assume the independence of all the reactions. In using detailed balance, we cannot avoid introducing the basic assumption. However, it may appear in different forms.

### 3.1. The Energy Distribution of the State

Each state is a trajectory, e.g. the state of the electrons in an atomic model is the most familiar. Each state is specified by a group of quantum numbers  $(n, l, m, \sigma)$ . The energy of a state in a hydrogen-like atom is

$$-\frac{Z^2 R}{n^2}, \quad n = 1, 2, \dots,$$

$$R = 13.6 \text{ eV}, \quad (3-1)$$

where  $Z$  is the charge of the nucleus (in units of electron charge). The quantum numbers  $l, m$  are respectively the angular momentum and its projection in a certain direction, and  $\sigma$  is the projection of the spin of the electron in a certain direction.

Each state can accommodate one electron, because electrons are fermions and must obey the exclusion principle, i.e. two particles cannot occupy the same state. The above atomic model is to put  $Z$  electron into the  $Z$  lowest energy states which are determined by the electrostatic potential of the nucleus. In most problems, the state of the particles are determined by the potential energy. We review the simplest situation and calculate the energy distribution of the states.

#### A. The statistics of the energy distribution

Let us first look at the states of a free particle. This particle is confined in a cube of volume  $L^3$  and obeys periodic boundary conditions, i.e.  $x = 0$  and  $x = L$  are the same side, and similarly in the  $y, z$  directions. Hence this is a three dimensional ring-shaped container without boundaries. The results of a quantum mechanical analysis are as follows. The state of the particle is specified by three integers  $(n_x, n_y, n_z) \equiv \mathbf{n}$ . (For the moment we do not consider the spin

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of the particle or its other internal states.) The energy for  $\mathbf{n}$  is

$$\begin{aligned}\epsilon_{\mathbf{p}} &= \frac{p^2}{2m} \quad , \\ \mathbf{p} &= \frac{2\pi}{L}(n_x, n_y, n_z) \quad , \\ n_x, n_y, n_z &= 0, \pm 1, \pm 2, \dots \quad .\end{aligned}\tag{3-2}$$

The wavefunction in the  $\mathbf{n}$  state is a plane wave

$$\phi_{\mathbf{n}} = \frac{1}{L^{3/2}} e^{i\mathbf{p} \cdot \mathbf{r}}\tag{3-3}$$

(We take  $\hbar = 1$  to simplify the formula.) Each configuration is a state. The energy distribution of the states is

$$L^3 g(\epsilon) = \sum_{n_x=-\infty}^{\infty} \sum_{n_y=-\infty}^{\infty} \sum_{n_z=-\infty}^{\infty} \delta \left[ \epsilon - \frac{1}{2m} \left( \frac{2\pi}{L} \right)^2 (n_x^2 + n_y^2 + n_z^2) \right] \quad .\tag{3-4}$$

If  $L$  is very large, and  $\epsilon$  not small, the configurations in (3-4) have very large  $n_x, n_y$  and  $n_z$ , so they can be treated as continuous variables, and  $\Sigma$  is replaced by an integral:

$$\sum_{n_x} \sum_{n_y} \sum_{n_z} = \int dn_x \int dn_y \int dn_z \quad .\tag{3-5}$$

Finally the integration over  $n$  can be changed to that over  $p$ . (See (3-2).) Hence (3-4) becomes

$$\begin{aligned}L^3 g(\epsilon) &= \frac{L^3}{(2\pi)^3} \int d^3 p \delta \left( \epsilon - \frac{p^2}{2m} \right) \\ &= \frac{L^3}{2\pi^2} m \sqrt{2m\epsilon} \quad .\end{aligned}\tag{3-6}$$

Notice that if we use the hard wall boundary condition, i.e. the wavefunction  $\phi_{\mathbf{n}}(\mathbf{r})$  is zero at the boundary, then  $\mathbf{n} = (n_x, n_y, n_z)$ ,

$$\phi_{\mathbf{n}} = \left(\frac{2}{L}\right)^{3/2} \sin x p_x \sin y p_y \sin z p_z \quad ,$$

$$\mathbf{p} = \frac{\pi}{L} (n_x, n_y, n_z) \quad ,$$

$$\epsilon = \frac{p^2}{2m} \quad , \quad n_x, n_y, n_z = 1, 2, 3, \dots \quad . \quad (3-7)$$

Equations (3-7) and (3-2) are not the same.

However, the reader can prove that the  $g(\epsilon)$  calculated from (3-7) is the same as (3-6). Provided  $L$  is very large, then the boundary condition does not affect  $g(\epsilon)$ .

*B. The statistics of the energy in the short wavelength approximation*

In the short wavelength approximation (WKB approximation) the trajectory of the particle can be calculated from classical mechanics, but each trajectory must satisfy a quantum condition. Let us look at the situation of a particle in one dimension. The quantum condition is

$$\oint p(x) dx = nh \quad , \quad (3-8)$$

$$\epsilon_n = \frac{p(x)^2}{2m} + U(x) \quad . \quad (3-9)$$

where  $U(x)$  is the potential energy of the particle,  $p(x)$  is the momentum,  $h$  is Planck's constant and  $n$  is an integer. The integration in (3-8) is along a trajectory in phase space. (Fig. 3-1)

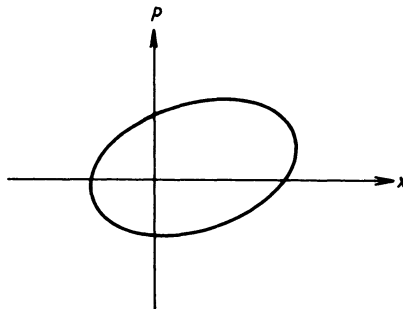


Fig. 3-1 A trajectory in phase space.

The quantum condition (3-8) determines the various  $\epsilon_n$  and the trajectories. Each integer specifies a trajectory and each trajectory a state. This method is valid for short wavelength, i.e. over a distance of  $h/p$ ,  $U(x)$  changes very little. Here  $h/p$  is the wavelength of the particle and the integral of (3-8) is just the area bounded by the trajectory.

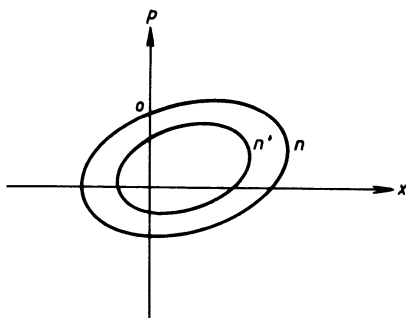


Fig. 3-2 Two trajectories  $n$  and  $n'$  in phase space.

The annulus region in Fig. 3-2 is specified by two trajectories  $n$  and  $n'$ . In this region, there are  $n - n'$  trajectories. According to (3-8)

$$n - n' = \frac{1}{h} \int dp dx \quad . \quad (3-10)$$

That is to say, the area of the region divided by  $h$  is the number of trajectories in the region. Therefore, to calculate the states we only need to find the area and then divide it by  $h$ . At the same time we can think of the state as points uniformly distributed in phase space with density  $1/h$ . Therefore,

$$L^3 g(\epsilon) = \frac{1}{h} \int dp dx \delta\left(\epsilon - \frac{p^2}{2m} - U(x)\right) \quad . \quad (3-11)$$

This integral (3-11) has the merit that it does not require solution of the trajectories or the value of each  $\epsilon_n$  of (3-8). We only need  $U(x)$ . Hence the short wavelength approximation is very convenient, but we must remember the limitation on its range of validity, namely  $U(x)$  must be nearly constant within a distance  $h/p$ . Generally speaking, this approximation is only true for states of high energy.

If space is three dimensional, (3-11) can be generalised to

$$L^3 g(\epsilon) = \frac{1}{h^3} \int d^3 p d^3 r \delta\left(\epsilon - \frac{p^2}{2m} - U(x)\right) \quad . \quad (3-12)$$

If the spin of the particle is not zero, we must add a spin quantum number to specify the state. Bosons have integer spins (in units of  $\hbar$ ) while the spins of fermions are half integers (integer +  $\frac{1}{2}$ ). The most usual fermions are electrons with spin  $\frac{1}{2}$ , while bosons include photons (spin 1) and  $^4\text{He}$  (spin 0), etc.

In some solids or liquids, certain motions of small amplitude can be described by special “particles”, e.g. phonons (for crystal vibration), spin wave (or magnons, for oscillation of magnetic moment), etc. These particles are usually bosons. (Notice that these particles do not exist in vacuum, but only in matter. Ordinary matter is not homogeneous, but has a crystal structure. Hence the concept of “spin” must be replaced by the symmetry property of the structure of the matter.)

### 3.2. The Energy Distribution of Fermions

We now use the law of detailed balance to calculate the energy distribution of the particles. This illustrates the content of the law and also emphasises collision as a basic ingredient of the ideal gas; without collisions there would be no thermodynamics.

A gas may be said to be ideal if the collision time (the time the particles are in contact) is very short, and the radius of contact (i.e. the effective interaction distance of the particles) is very small.

Each collision is a reaction. We assume that each reaction is an independent event and there is no relation between successive reactions. This is a rather effective hypothesis, making the analysis much simpler.

Consider a fermionic gas and let  $f_k$  be the average number of particles in the  $k$  state, where  $k$  denotes the momentum and spin of the particles. Because of collisions, each particle continually changes its state, e.g.



i.e. the states 1 and 2 interact to change to states 3 and 4. The rate of this reaction is

$$f_1 f_2 (1 - f_3) (1 - f_4) R \quad , \quad (3-14)$$

where  $f_1$  and  $f_2$  are the probability that there is one particle in the states 1 and 2 respectively and  $(1 - f_3)$ ,  $(1 - f_4)$  are the probability that there are no particles in the states 3 and 4. Because the gas is fermionic, if states 3, 4 are occupied, the reaction cannot proceed. This rate must be equal to that in the reverse direction, i.e.

$$f_1 f_2 (1 - f_3) (1 - f_4) R = f_3 f_4 (1 - f_1) (1 - f_2) R' \quad . \quad (3-15)$$

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According to quantum mechanics  $R = R'$ , because the equations of quantum mechanics are invariant under time reversal

$$\begin{aligned} R &= |M|^2 \quad , \\ R' &= |M^*|^2 = R \quad . \end{aligned} \quad (3-16)$$

Here,  $M$  is the matrix element of the scattering operator between states  $|1, 2\rangle$  and  $|3, 4\rangle$ . If time is reversed  $|1, 2\rangle$  and  $|3, 4\rangle$  are interchanged, and  $M$  becomes  $M^*$ . From (3-15) we get

$$\frac{f_1}{1-f_1} \cdot \frac{f_2}{1-f_2} = \frac{f_3}{1-f_3} \cdot \frac{f_4}{1-f_4} \quad . \quad (3-17)$$

If there is a reaction of three particles

$$1 + 2 + 3 \rightarrow 4 + 5 + 6 \quad ,$$

detailed balance will give results similar to (3-17), namely

$$\frac{f_1}{1-f_1} \cdot \frac{f_2}{1-f_2} \cdot \frac{f_3}{1-f_3} = \frac{f_4}{1-f_4} \cdot \frac{f_5}{1-f_5} \cdot \frac{f_6}{1-f_6} \quad . \quad (3-18)$$

Equations (3-17) and (3-18) are very stringent conditions, to be satisfied for all  $f_k$ . We can obtain  $f_k$  from (3-17) and (3-18). Of course, if all the  $f_k$  satisfy

$$\frac{f_k}{1-f_k} = \text{constant} \quad , \quad (3-19)$$

then (3-17) and (3-18) are certainly satisfied. But this means that each  $f_k$  is the same independent of the energy of the states, which is unreasonable. To solve (3-17) and (3-18) we also have to consider the conserved quantities of the reaction. Before and after the reactions (3-17) and (3-18), the energy and the particle number are conserved.

$$(3-17): \quad \text{particle number} = 2, \quad \text{energy} = \epsilon_1 + \epsilon_2 = \epsilon_3 + \epsilon_4$$

$$(3-18): \quad \text{particle number} = 3, \quad \text{energy} = \epsilon_1 + \epsilon_2 + \epsilon_3 = \epsilon_4 + \epsilon_5 + \epsilon_6 \quad .$$

(3-20)

Hence, there is another solution to (3-17) and (3-18), i.e.

$$\frac{f_k}{1-f_k} = e^{-\alpha - \beta \epsilon_k} \quad , \quad (3-21)$$

where  $\alpha$  and  $\beta$  are constants. To see that this is a solution, substitute (3-21) into (3-17) and (3-18), and use (3-20) to get

$$\begin{aligned} e^{-2\alpha-\beta(\epsilon_1+\epsilon_2)} &= e^{-2\alpha-\beta(\epsilon_3+\epsilon_4)} \\ e^{-3\alpha-\beta(\epsilon_1+\epsilon_2+\epsilon_3)} &= e^{-3\alpha-\beta(\epsilon_4+\epsilon_5+\epsilon_6)} \end{aligned} \quad (3-22)$$

Equation (3-21) of course means

$$f_k = \frac{1}{e^{\alpha+\beta\epsilon_k} + 1} \quad (3-23)$$

This is the particle distribution satisfying the condition of detailed balance. The parameters  $\alpha$  and  $\beta$  are constants shared by all the particles and should be related to the temperature and chemical potential. The relations of the total energy  $E$  and the particle number  $N$  with  $f_k$  are

$$\begin{aligned} E &= \sum_k \epsilon_k f_k = V \int d\epsilon g(\epsilon) \frac{\epsilon}{e^{\alpha+\beta\epsilon} + 1} \quad , \\ N &= \sum_k f_k = V \int d\epsilon g(\epsilon) \frac{1}{e^{\alpha+\beta\epsilon} + 1} \end{aligned} \quad (3-24)$$

If the gas is very dilute, i.e.,  $f_k \ll 1$ , then

$$f_k \simeq e^{-\alpha-\beta\epsilon_k} \quad (3-25)$$

This is the familiar result of the ideal gas, i.e. the Boltzmann distribution, and can be directly calculated from the energy of the states. Because  $g(\epsilon) \propto \sqrt{\epsilon}$  (see (3-5)), we get

$$\frac{E}{N} = \frac{3}{2\beta} \quad (3-26)$$

We discover that  $1/\beta$  is the temperature  $T$ , because in thermodynamics we know that  $E/N = \frac{3}{2}T$ . The parameter  $\alpha$  can be calculated from (3-24). Using (3-25) for  $f$ , we get

$$\begin{aligned} \frac{N}{V} &= e^{-\alpha} \int d\epsilon g(\epsilon) e^{-\beta\epsilon} \\ &= e^{-\alpha} (2s+1) (2\pi mT)^{3/2} / h^3 \quad , \end{aligned} \quad (3-27)$$

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i.e.

$$\alpha = \ln \left[ (2s + 1) (2\pi mT)^{3/2} \frac{V}{Nh^3} \right] , \quad (3-28)$$

where  $s$  is the spin of the particle. The chemical potential  $\mu$  of the ideal gas can be obtained from the results in thermodynamics (2-36)

$$\begin{aligned} -\frac{\mu}{T} &= \left( \frac{\partial S}{\partial N} \right)_E = \ln \frac{V}{N} \left( \frac{CE}{N} \right)^{3/2} - \frac{5}{2} \\ &= \ln \frac{V}{N} + \ln \left( \frac{3}{2} TC \right)^{3/2} - \frac{5}{2} . \end{aligned} \quad (3-29)$$

Equations (3-28) and (3-29) are identical except for an undetermined constant  $C$ . We can define

$$\frac{\mu}{T} = -\alpha \quad . \quad (3-30)$$

This fixes the value of  $C$ . Equation (2-36) becomes

$$S = N \ln \left[ \frac{V}{N} \left( \frac{4\pi mE}{3Nh^3} \right)^{3/2} (2s + 1) \right] + \frac{5}{2} N \quad . \quad (3-31)$$

Substituting (3-30) into (3-23) we get the familiar Fermi distribution

$$f_k = \frac{1}{e^{(\epsilon_k - \mu)/T} + 1} \quad . \quad (3-32)$$

Notice that in the above we have used the known ideal gas results to determine the meaning of  $\alpha$  and  $\beta$ . The ideal gas can be looked upon as a device to measure the temperature and the chemical potential of the gas. To express this idea more clearly: We can make the potential energy  $U(\mathbf{r})$  very high in one corner of the container so that the density becomes very low in this corner, so the ideal gas law is applicable. But  $\mu, T$  are quantities shared by all parts of the body because the various reactions involve all the particles. Hence once we measure  $\mu$  and  $T$  in this corner, then we know the  $\mu$  and  $T$  for the whole gas.

For general densities the entropy can be obtained by integrating the heat capacity:

$$S = \int^T \left( \frac{\partial E}{\partial T} \right)_V \frac{dT}{T} \quad . \quad (3-33)$$

The integration constant can be determined by the value at  $T \rightarrow \infty$ , i.e. the ideal gas result (3-31).

Hence, from detailed balance and the results of thermodynamics in Chapter 2, we determine the particle distribution and all the equilibrium properties of a fermionic gas. The constant  $C$  in the definition of entropy is determined by (3-30). This is a convenient choice. We shall discuss this at the end of the next section. The most important fermions are the electrons, which we shall discuss in the next chapter.

### 3.3. Conservation Laws, Chemical Potential and the Constant Term in the Entropy

The above analysis clearly shows the power of the conservation laws. Equation (3-21) is derived using the conservation of particle number and the conservation of energy. Hence  $T$  and  $\mu$  are the forces fixing the total energy and the total particle number.

If there are other conserved quantities, then (3-17) and (3-18) can have more solutions. For example, if momentum is conserved, i.e.

$$\mathbf{p}_1 + \mathbf{p}_2 = \mathbf{p}_3 + \mathbf{p}_4 \quad \text{in (3-17),}$$

$$\mathbf{p}_1 + \mathbf{p}_2 + \mathbf{p}_3 = \mathbf{p}_4 + \mathbf{p}_5 + \mathbf{p}_6 \quad \text{in (3-18) .} \quad (3-34)$$

then this allows a more general solution of (3-17) and (3-18):

$$\frac{f_k}{1-f_k} = e^{-\alpha - \beta \epsilon_k - \beta \mathbf{v} \cdot \mathbf{p}_k} , \quad (3-35)$$

i.e.

$$f_k = \frac{1}{e^{(\epsilon_k - \mathbf{v} \cdot \mathbf{p}_k - \mu)/T} + 1} , \quad (3-36)$$

where  $\mathbf{v}$  is the velocity of the whole gas. But if the container is stationary, collisions of the particles with the wall makes momentum nonconserved, and  $\mathbf{v}$  must be 0.

If the spins are unchanged during collisions, then

$$f_k = \frac{1}{e^{(\epsilon_k - \mu - \mathbf{s} \cdot \mathbf{h})/T} + 1} , \quad (3-37)$$

where the parameter  $\mathbf{h}$  can be looked upon as the force maintaining the total spin. If  $s = \frac{1}{2}$ , then  $\mathbf{s} \cdot \mathbf{h} = \pm \frac{1}{2} h$ .

Each conservation law will introduce a “force”. The above “forces”  $1/T$ ,  $-\mu/T$ ,  $\mathbf{v}/T$  and  $\mathbf{h}/T$  are obvious examples. Conversely, if a conservation law is broken, it will cause a force to become zero, e.g. the walls of a container cause momentum not to be conserved, and  $\mathbf{v} = 0$ . If the particle number is not conserved, i.e. it can change because of reactions,  $\mu$  must be zero. More complicated examples are found in chemical reactions. For example, three molecules  $A$ ,  $B$  and  $C$  mixing together undergo the reaction



The particle numbers of  $A$ ,  $B$  and  $C$  are not conserved, but are completely independent. Applying detailed balance to (3-38), then the generalisation of (3-17) is

$$\frac{f_A}{1-f_A} \cdot \frac{f_B}{1-f_B} = \frac{f_C}{1-f_C} \quad . \quad (3-39)$$

Equation (3-21) is still applicable, but the  $\alpha$ 's must satisfy

$$\alpha_A + \alpha_B = \alpha_C \quad . \quad (3-40)$$

From (3-30), we get

$$\mu_A + \mu_B - \mu_C = 0 \quad . \quad (3-41)$$

Because of the reaction (3-38), the three originally independent chemical potentials are reduced to two, with remaining one determined by (3-41). Each chemical reaction results in a relation between the chemical potentials.

The result (3-41) can be understood from another point of view. In equilibrium the chemical reaction (3-38) cannot perform any work, i.e.

$$\mu_A dN_A + \mu_B dN_B + \mu_C dN_C = 0 \quad . \quad (3-42)$$

But according to (3-38),  $dN_A = dN_B = -dN_C$ , and we immediately get (3-41). This is a result in thermodynamics and does not require (3-39) for its derivation.

We can see from this that (3-30) is a very ideal choice. If we do not use (3-30), but instead write

$$\frac{\mu}{T} = -\alpha + \eta \quad , \quad (3-43)$$

with  $\eta$  being a constant, then from (3-40) and (3-41) it can be seen that  $\eta$

cannot be any arbitrary constant but must satisfy

$$\eta_A + \eta_B = \eta_C \quad . \quad (3-44)$$

We have to consider all other possible chemical reactions. Each chemical reaction gives a relation similar to (3-44), and each  $\eta$  must satisfy all these relations. Of course, to choose such a  $\eta$  one must start from the conservation laws. All chemical and nuclear reactions must conserve nucleon number  $A$  (the total number of protons and neutrons). Hence  $\eta_A$  must be chosen to be

$$\eta_A = \text{constant} \times A \quad . \quad (3-45)$$

This constant must be the same for all molecules. If we further extend the definition of chemical potential to the case that the number of nucleons may not be conserved, the only possible choice is to set all the  $\eta$  to zero.

Hence, from the principle of detailed balance and the concept of states in quantum mechanics we obtain  $\alpha$ ,  $\beta$  and the distribution function (3-23). From the statistics of the states, Planck's constant  $h$  enters into  $\alpha$ . (See (3-28).) Then from the consideration of conservation laws,  $h$  naturally enters into entropy, completing its definition.

### 3.4. Distribution of Bosons and Black Body Radiation

Bosons are not restricted by the exclusion principle and hence have different reaction rates. The factors  $(1 - f_3)$ ,  $(1 - f_4)$  in (3-14) are the results of the exclusion principle and are not valid for bosons. According to quantum mechanics, the reaction of (3-13) should now be

$$f_1 f_2 (1 + f_3) (1 + f_4) R \quad , \quad (3-46)$$

i.e. we simply change the negative signs in (3-14) to positive ones. This result is not obvious and requires some calculations to obtain it. We regard this as known. Equation (3-46) says that if states 3 and 4 are already occupied, other states would be more inclined to go to them. Now we only need to change the negative signs in (3-14) – (3-18) to obtain the distribution function for the bosons. Equation (3-32) now becomes

$$f_k = \frac{1}{e^{(\epsilon_k - \mu)/T} - 1} \quad . \quad (3-47)$$

The low density case is independent of the statistics and  $f_k$  is again the Boltzmann distribution

$$f_k \simeq e^{(\mu - \epsilon_k)/T} \quad . \quad (3-48)$$

This can be called the *classical distribution*, while (3-47) and (3-32) are the quantum distributions. All the results of the last section can be reproduced for the boson case.

Photons are bosons and the photon gas in equilibrium is called the black body radiation. Photons are continually absorbed and emitted by the walls of the cavity. If there are molecules in the cavity, these molecules can also absorb or emit photons. The number of photons is not conserved, and hence its chemical potential is zero. The distribution of the photons is

$$f_k = \frac{1}{e^{\omega_k/T} - 1}, \quad (3-49)$$

where  $\omega_k$  is the frequency or the energy of the photon ( $\hbar = 1$ ), i.e.  $\epsilon_k = \hbar\omega_k$ . The energy distribution of the states of the photons can be calculated by the method in Sec. 3.1, and we only have to change  $\epsilon_p = p^2/2m$  in (3-6) to  $\epsilon_p = cp$ , where  $c$  is the speed of light, and also include the two polarisations. Thus

$$g(\omega) = \frac{2}{(2\pi)^3} \int d^3p \delta(\omega - cp) = \frac{\omega^2}{\pi^2 c^3}. \quad (3-50)$$

Hence the frequency distribution of the black body radiation is

$$\epsilon(\omega) = g(\omega) \frac{\omega}{e^{\omega/T} - 1} = \frac{\omega^3/\pi^2 c^3}{e^{\omega/T} - 1}. \quad (3-51)$$

This is the *Planck distribution*. The discovery of this distribution is a prelude to the birth of quantum mechanics, and precedes the reaction rate considerations in (3-46). Einstein used this together with the principle of detailed balance to derive some properties of the rates of absorption and emission of light as mentioned below.

Let molecule  $A$  absorb light of frequency  $\omega$  to become the excited state  $A^*$ . The energy of  $A^*$  is higher than that of  $A$  by  $\omega$ . In equilibrium, the ratio of the population  $N$  of  $A$  to the population  $N^*$  of  $A^*$  is

$$\frac{N^*}{N} = e^{-\omega/T}. \quad (3-52)$$

This formula can be derived by the principle of detailed balance. (See Prob. 10.) The absorption rate of light is proportional to  $N$  and  $\epsilon(\omega)$  and its emission rate is proportional to  $N^*$ . They must be equal. Therefore,

$$RN\epsilon(\omega) = R'N^* \quad (3-53)$$

where  $R'$  is the emission rate of one  $A^*$  and  $R$  is the absorption rate of the interaction of one  $A$  with one photon of energy  $\omega$ . From (3-52) and (3-53) we get

$$\begin{aligned} R' &= R \frac{N}{N^*} \epsilon(\omega) = R \frac{\omega^3}{\pi^2 c^3} \frac{e^{\omega/T}}{e^{\omega/T} - 1} \\ &= R \frac{\omega^3}{\pi^2 c^3} [1 + f(\omega)] \\ &= R \frac{\omega^3}{\pi^2 c^3} + R \epsilon(\omega) . \end{aligned} \quad (3-54)$$

The factor  $1 + f$  is naturally the same as the  $1 + f$  in (3-46).

Equation (3-54) shows that:

(1) Even if  $\epsilon(\omega) = 0$ , i.e. in the case of no photons,  $A^*$  can spontaneously emit a photon and become  $A$ , with a rate

$$r = R \frac{\omega^3}{\pi^2 c^3} , \quad (3-55)$$

i.e. the half life of  $A^*$  is  $\ln 2/r$ .

(2) If  $f \neq 0$ , the emission by  $A^*$  is faster and this is stimulated emission. This is a property special to bosons.

(3) The absorption and emission rates are determined by  $R$ , which depends on the structure of the molecule and the details of its interaction with photons.

These results are related to the interaction of molecules with light, and are obtained by detailed balance plus the Planck distribution. They are rather unexpected. Detailed quantum mechanical calculation must involve a complicated analysis of the interaction of  $A$ ,  $A^*$  and the photon, so as to obtain (3-54) (and the value of  $R$ ).

### 3.5. Chemical Reactions and the Law of Concentrations

In discussing the conservation laws in Sec. 3.3, we have mentioned chemical reactions. Each chemical reaction involves one conservation law and results in a relation between the chemical potentials like (3-41), which we now use to derive relations between the concentrations of the various molecules.

We start from the reaction (3-38), assuming that  $A$ ,  $B$  and  $C$  mix as an ideal gas, each distributed according to the classical formual (3-48). Besides the kinetic energy, the total energy of each molecule also includes the energy of

internal motion such as rotation and vibration

$$\begin{aligned}\epsilon_k &= \frac{p_k^2}{2m} + \omega_k \quad , \\ f_k &= e^{(\mu - \epsilon_k)/T} \quad .\end{aligned}\tag{3-56}$$

The total population of molecule  $A$  is

$$\begin{aligned}N_A &= \sum_k f_{kA} \\ &= V e^{\mu_A/T} \frac{1}{(2\pi\hbar)^3} \int d^3p e^{-p^2/2m_A T} \sum_\alpha e^{-\omega_{A\alpha}/T} \\ &\equiv V e^{\mu_A/T} e^{-\phi_A/T} \quad ,\end{aligned}\tag{3-57}$$

where  $\phi_A$  is a function of the temperature and is related to the mass  $m$  and the internal energy  $\omega_{A\alpha}$  of the molecules. Let  $n_A \equiv N_A/V$  be the concentration of  $A$ , then

$$\begin{aligned}\mu_A &= \phi_A + T \ln n_A \quad , \\ \mu_B &= \phi_B + T \ln n_B \quad , \\ \mu_C &= \phi_C + T \ln n_C \quad .\end{aligned}\tag{3-58}$$

From (3-14) we get

$$0 = \phi_A + \phi_B - \phi_C + T \ln \frac{n_A n_B}{n_C}\tag{3-59}$$

or

$$\frac{n_A n_B}{n_C} = e^{-(\phi_A + \phi_B - \phi_C)/T} \quad .$$

This is a theorem on equilibrium concentrations. The right hand side of (3-59) can be calculated from the properties of the molecules and is only a function of temperature. In other words, if we know the structure of the molecules we can obtain information on the concentrations. This is very useful for a chemical engineer. If the concentrations of the various molecules can be measured but the structure of the molecules is not clear, then (3-59) can be used to deduce the structure of the molecules. The reader can consult books on chemistry for a deeper understanding of this topic.

**Problems**

1. The concept of a distribution is the most common in statistical data, for example the age distribution, the income distribution or the grade distribution in an examination. A distribution can be represented by a curve. Figure 3-3 is an age distribution  $f(x)$  (say in units of ten thousands).

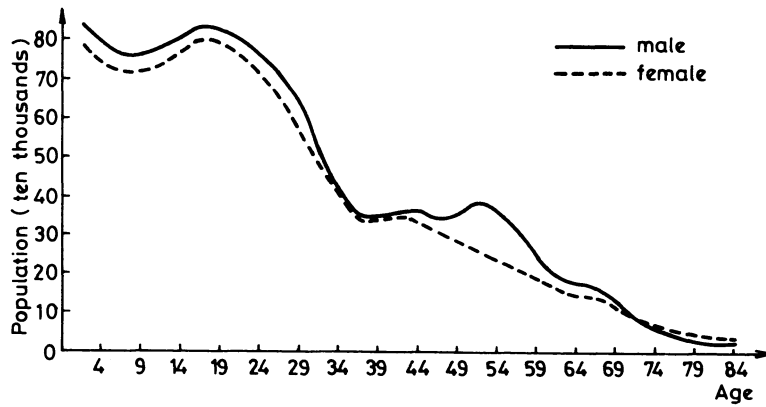


Fig. 3-3 Population distribution plotted against age.

The total area under the curve is the total population.

$$\int_0^{\infty} f(x) dx = \text{total population} \quad (3-60)$$

The population with age less than  $x'$ , denoted as  $N(x')$ , is the area under the curve to the left of  $x = x'$ .

$$N(x') = \int_0^{x'} f(x) dx \quad (3-61)$$

$$f(x) = \frac{dN(x)}{dx} \quad (3-62)$$

The meaning of this distribution function is:  $f(x) dx$  is the population between ages  $x$  and  $x + dx$ . To count the population with age less than  $x'$ , we can search through the census to collect the names of the people whose age is less than  $x'$  and then count the number:

$$N(x') = \sum_s \theta(x' - x(s)) \quad (3-63)$$

where  $s$  is the name of each person and  $x(s)$  is the age of the person  $s$ . If it is less than  $x'$ ,  $\theta(x' - x(s))$  is 1 and otherwise it is zero. Equation (3-63) represents

this statistical process. The age distribution  $f(x')$  is formally the differential of  $N$  (see (3-62)):

$$f(x') = \frac{dN(x')}{dx'} = \sum_s \delta(x' - x(s)) \quad . \quad (3-64)$$

In a small interval  $\Delta x'$ , the population is

$$f(x')\Delta x' = \sum_s \int_{x'}^{x'+\Delta x'} dx \delta(x - x(s)) \quad . \quad (3-65)$$

The definition of the distribution should be based on (3-65). Later when we see summations such as (3-64) we should immediately think of its integral or imagine that the  $\delta$ -function is a sharp peak with finite width.

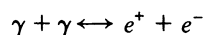
2. Calculate the energy distribution of the free particle
  - (a) in one dimension,
  - (b) in two dimensions,
  - (c) in three dimensions.
3. Use (3-12) to calculate the energy distribution of the state, assuming
  - (a)  $U(\mathbf{r}) = \frac{1}{2} K r^2$
  - (b)  $U(\mathbf{r}) = -Z e^2/r$  .

We can use (b) to estimate the energy of heavy atoms (large  $Z$ ).

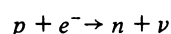
4. Detailed balance comes from the symmetry property of the time direction. This symmetry is a special feature of the equilibrium state. Some states, though apparently steady and unchanging, do not possess this symmetry, and we call them nonequilibrium states. For example, a body with a heat current passing through it cannot be called an equilibrium state, even though the heat current is unchanged in time. But a uniformly moving or rotating body can be regarded as in equilibrium. The reader can think about these situations.

5. Sections 3-2 and 3-3 point out that entropy is intimately related to the concept of a state in quantum mechanics. They also show the importance of conservation laws. The reader may try to derive (3-31) from (3-36) and (3-30).

6. The following reaction occurs inside a star



where  $\gamma$  is a photon and  $e^\pm$  are the positron and the electron respectively. Calculate the population of  $e^+$  and  $e^-$  in equilibrium. In a dense gas of protons, electrons and neutrons the following reaction occurs



where  $\nu$  is the neutrino, which escapes after production. The chemical potential of electron satisfies  $\mu_e \gg mc^2$ , where  $m$  is the mass of the electron. Find the population of  $p$ ,  $e^-$  and  $n$  in equilibrium.

7. Suppose a star explodes at times  $t = 0$ , and this star is a mixed gas of protons and electrons. A detector at distance  $R$  measures the flux of electrons and protons, with  $R \gg$  the radius of the star.

(a) Find the relation between the flux and time. This relation is linked with the distribution of the velocities of the particles.

(b) If the temperature is  $T$  after the explosion, calculate the flux.

8. The ideal boson gas can be analysed by (3-47).

(a) Find the relation between  $\mu$  and  $N/V$ . Notice that when the temperature is lower than a certain critical temperature  $T_c$ ,  $\mu = 0$  and  $f_0$  (the population of the state  $k = 0$ ) is proportional to  $V$ , i.e. there are macroscopically large numbers of particles occupying the lowest state. This phenomenon is usually called Bose-Einstein condensation.

(b) Calculate the critical temperature  $T_c$ .

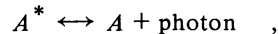
(c) Calculate the relation of  $f_0$  with  $T$ .

(d) Calculate the heat capacity.

(e) Prove that this phenomenon of condensation does not occur in one or two dimensions.

9. The discussion of (3-38) to (3-45) is not limited to fermions. In fact the molecule  $C$  in (3-38) must be a boson (two fermions can combine to form a boson). Attempt to generalise the discussion in Section 3-3 to include bosons.

10. From the reaction



derive (3-52). This result is independent of the condition that  $A$  is a boson.