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| 16. Summary/Notes<br><br><i>This chapter presents a simple derivation of the Maxwell-Boltzmann velocity distribution function, based on the general principle of detailed balance from statistical mechanics, and the concept of summation invariants. The physical meaning of the Maxwell-Boltzmann distribution function is discussed and its properties are analysed. It is shown that the equilibrium distribution function is the most probable distribution consistent with the macroscopic constraints of the system, and it is also the state having maximum entropy. A derivation is given for the equilibrium distribution function in the presence of an external conservative force, and the Boltzmann factor is introduced. Finally, it is presented an analysis of the Saha equation, which specifies the degree of ionization of a gas in thermodynamic equilibrium at a given temperature.</i> |                              |  |   |
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$$n_t = n_i + n_n \dots\dots\dots 44$$

## CHAPTER 7

### THE EQUILIBRIUM STATE

#### 1. THE EQUILIBRIUM STATE DISTRIBUTION FUNCTION

The equilibrium distribution function is the time-independent solution of the Boltzmann equation in the absence of external forces. In the equilibrium state the interactions between the particles do not cause any change in the distribution function with time, and there are no spatial gradients in the particle number density. We deduce, in this section, an expression for the equilibrium distribution function, which is known as the *Maxwell-Boltzmann* or *Maxwellian velocity distribution function*.

For simplicity, we will consider a gas consisting of only one particle species. The extension to a mixture will be indicated in a subsequent section of this chapter. We assume that there are no external forces acting on the system ( $F_{\text{ext}} = 0$ ) and that the particles are uniformly distributed in space. Under these conditions, the distribution function is independent of the position vector  $\underline{r}$  ( $\nabla f = 0$ ) and, since we are looking for a steady state solution of the Boltzmann equation, it is also independent of time ( $\partial f / \partial t = 0$ ). Therefore, it can be denoted by  $f(\underline{v})$ . According to the Boltzmann equation (5.5.27), the equilibrium distribution function satisfies the following condition

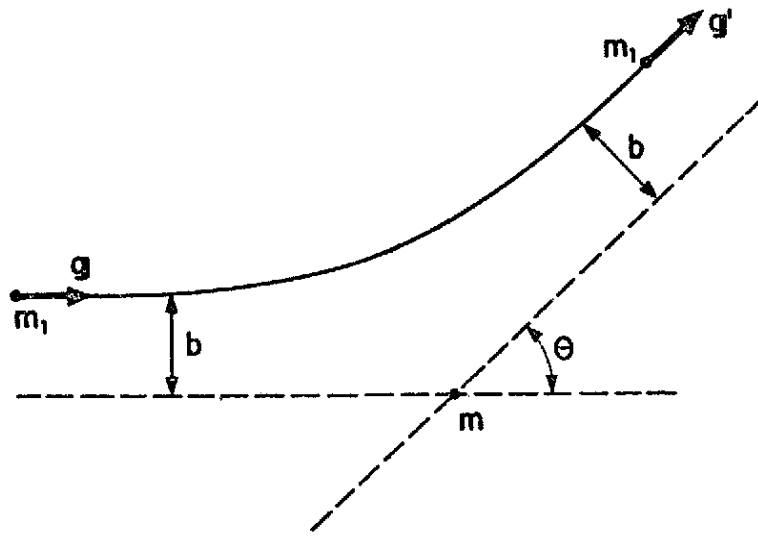
$$\left(\frac{\delta f}{\delta t}\right)_{\text{coll}} = 0 \quad (1.1)$$

Hence, under equilibrium conditions, there are no changes in the distribution function as a result of collisions between the particles. In Chapter 21 we shall derive the expression for the equilibrium distribution function using the Boltzmann collision integral. For the moment, however, in order to simplify matters, it is appropriate to consider a simple derivation based on the *general principle of detailed balance* of statistical mechanics.

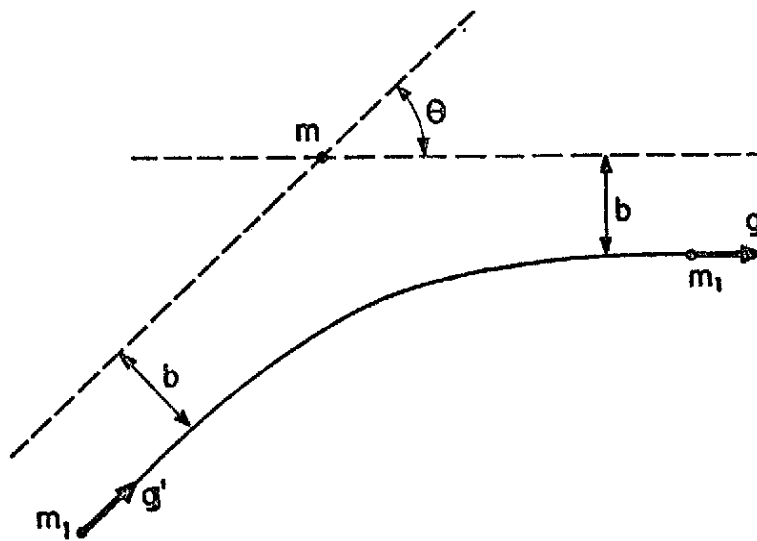
### 1.1 - The general principle of detailed balance and binary collisions

In general this principle asserts that, under equilibrium conditions, the probability of occurrence of any process is equal to the probability of occurrence of the inverse process. Hence, for the case of a system of interacting particles in the state of *equilibrium*, the principle of detailed balance implies that the effect of each type of collision is exactly compensated by the effect of the corresponding inverse collision.

Consider an elastic collision between two particles having velocities  $\underline{v}_1$  and  $\underline{v}$  *before* collision, and  $\underline{v}'_1$  and  $\underline{v}'$  *after* collision. The corresponding inverse collision refers to an elastic collision in which a particle with initial velocity  $\underline{v}'_1$  collides with another particle with velocity  $\underline{v}'$ , the velocities *after* collision being  $\underline{v}_1$  and  $\underline{v}$ , respectively (see Fig. 1).



(a)



(b)

Fig. 1 - (a) Direct collision and (b) inverse collision.

Here  $\underline{g} = \underline{v}_1 - \underline{v}$  and  $\underline{g}' = \underline{v}'_1 - \underline{v}'$ .



Assuming that the velocities of the particles before collision are uncorrelated, the number of binary collisions occurring per unit time in a given volume element  $d^3r$ , about the position  $\underline{r}$  in configuration space, between particles having velocities within the velocity space element  $d^3v$ , about  $\underline{v}$ , and particles with velocities within  $d^3v_1$ , about  $\underline{v}_1$ , in the same configuration space element  $d^3r$  (see Fig. 2), is proportional to the product of the respective number of particles, that is, to  $(f d^3r d^3v) (f_1 d^3r d^3v_1)$ , where  $f_1$  represents  $f(\underline{v}_1)$ .

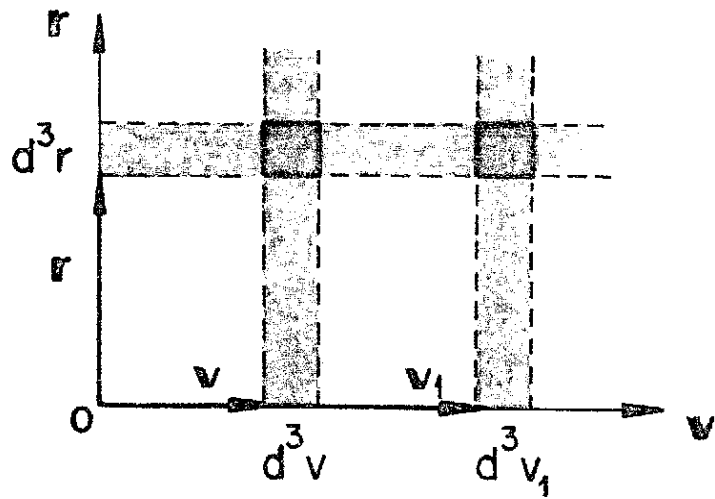


Fig. 2 - Schematic representation of the volume elements  $d^3r d^3v$  and  $d^3r d^3v_1$  in phase space.

In a similar way, assuming the particles to be uncorrelated, the number of corresponding *inverse* binary collisions occurring per unit time in the same volume element  $d^3r$ , about  $\underline{r}$ , in configuration space, between particles having velocities within  $d^3v'$ , about  $\underline{v}'$ , and particles with velocities within  $d^3v'_1$ , about  $\underline{v}'_1$ , is proportional to the product  $(f' d^3r d^3v')$   $(f'_1 d^3r d^3v'_1)$ , where  $f' = f(\underline{v}')$  and  $f'_1 = f(\underline{v}'_1)$ . According to the principle of detailed balance, in the equilibrium state the effect of each direct collision is compensated by the effect of the corresponding inverse collision, so that

$$f' f'_1 d^3v' d^3v'_1 = f f_1 d^3v d^3v_1 \quad (1.2)$$

Since  $d^3v' d^3v'_1 = d^3v d^3v_1$  (see section 2 of Chapter 21), Eq. (1.2) implies that

$$f(\underline{v}) f(\underline{v}_1) = f(\underline{v}') f(\underline{v}'_1) \quad (1.3)$$

The assumption that the velocities of the particles are uncorrelated is known as the *molecular chaos* assumption. It is well justified when the density of the gas is sufficiently small so that the mean free path is larger than the characteristic range of the interparticle forces. Although this is certainly not a general situation for a plasma, the validity of the Maxwell-Boltzmann distribution function is well justified experimentally.

## 1.2 - Summation invariants

It is convenient to introduce at this moment the concept of summation invariants. Consider a collisional interaction between two particles and let  $\chi(\underline{v})$  be a physical quantity (scalar or vector) associated with each particle, which in general may be a function of the particle velocity. If the sum of the quantity  $\chi(\underline{v})$  for the two particles is conserved during the collision process, then  $\chi(\underline{v})$  is called a summation invariant. For a collision between two particles having initial velocities  $\underline{v}$  and  $\underline{v}_1$ , and velocities after collision  $\underline{v}'$  and  $\underline{v}'_1$ , respectively, we have for a summation invariant quantity  $\chi(\underline{v})$ ,

$$\chi(\underline{v}) + \chi(\underline{v}_1) = \chi(\underline{v}') + \chi(\underline{v}'_1) \quad (1.4)$$

From the laws of conservation of mass, momentum and energy, the following quantities are summation invariants in binary elastic collisions:  $\chi = m$ ,  $\underline{\chi} = m\underline{v}$  and  $\chi = mv^2/2$ . Denoting the masses of the two colliding particles by  $m$  and  $m_1$ , we can express the laws of conservation of mass, of momentum and of energy as

$$m + m_1 = m + m_1 \quad (1.5)$$

$$m\underline{v} + m_1\underline{v}_1 = m\underline{v}' + m_1\underline{v}'_1 \quad (1.6)$$

$$\frac{1}{2} mv^2 + \frac{1}{2} m_1 v_1^2 = \frac{1}{2} m(v')^2 + \frac{1}{2} m_1 (v'_1)^2 \quad (1.7)$$

Eq. (1.5) is a trivial one and does not lead to any new information; it corresponds to the fact that a numerical constant is a summation invariant. Eq. (1.6) represents three equations, one for each component of the momentum. The four equations (1.6) and (1.7), together with the equations specifying the impact parameter  $b$  and the angle  $\epsilon$  of the collision plane (obtained through the analysis of the dynamics of binary collisions; see Chapter 20), constitute six equations to be solved for the determination of the six unknown quantities which are the components of the after-collision velocities  $\underline{v}'$  and  $\underline{v}'_1$ , in terms of the initial velocities  $\underline{v}$  and  $\underline{v}_1$ . The binary collision problem is, therefore, uniquely determined by these summation invariants. Any other summation invariant in the collision process gives no additional information and cannot, therefore, be an independent one and may be expressed as a linear combination of the summation invariants  $m$ ,  $m\underline{v}$  and  $(1/2)m\underline{v}^2$ .

### 1.3 - Maxwell - Boltzmann distribution function

We proceed now to derive the equilibrium velocity distribution function starting from Eq. (1.3) and the concept of summation invariants. Taking the natural logarithm of both sides of (1.3) gives

$$\ln f + \ln f_1 = \ln f' + \ln f'_1$$

which shows that  $\ln f$  is a summation invariant in the collision process.

Therefore, it can be written as a linear combination of the summation invariants  $m$ ,  $m\mathbf{v}$ , and  $(1/2)mv^2$ ,

$$\begin{aligned} \ln f &= m(a_0 + \mathbf{a}_1 \cdot \mathbf{v} - \frac{1}{2} a_2 v^2) \\ &= m[a_0 + a_{1x} v_x + a_{1y} v_y + a_{1z} v_z - \\ &\quad - \frac{1}{2} a_2 (v_x^2 + v_y^2 + v_z^2)] \end{aligned} \quad (1.9)$$

where  $a_0$ ,  $\mathbf{a}_1 = a_{1x} \hat{x} + a_{1y} \hat{y} + a_{1z} \hat{z}$  and  $a_2$  are constants. The negative sign in front of  $a_2$  is chosen for convenience in the equations that follow. Completing the squares in the right-hand side of Eq. (1.9) gives

$$\begin{aligned} \ln f &= m \left[ a_0 + \frac{1}{2a_2} (a_{1x}^2 + a_{1y}^2 + a_{1z}^2) \right] - \\ &\quad - \frac{ma_2}{2} \left[ \left( v_x - \frac{a_{1x}}{a_2} \right)^2 + \left( v_y - \frac{a_{1y}}{a_2} \right)^2 + \left( v_z - \frac{a_{1z}}{a_2} \right)^2 \right] \\ &= m \left( a_0 + \frac{a_1^2}{2a_2} \right) - \frac{ma_2}{2} \left( \mathbf{v} - \frac{\mathbf{a}_1}{a_2} \right)^2 \end{aligned} \quad (1.10)$$

Defining new constants by

$$\ln C = m \left( a_0 + \frac{a_1^2}{2a_2} \right) \quad (1.11)$$

$$\underline{v}_0 = \frac{a_1}{a_2} \quad (1.12)$$

we can write Eq. (1.10) in the form

$$f = C \exp \left[ - \frac{1}{2} m a_2 (\underline{v} - \underline{v}_0)^2 \right] \quad (1.13)$$

This expression is known as the Maxwell-Boltzmann, or Maxwellian equilibrium distribution function.

#### 1.4 - Determination of the constant coefficients

The Maxwellian distribution function (1.13) contains five constant coefficients to be determined, namely  $C$ ,  $a_2$ ,  $v_{0x}$ ,  $v_{0y}$ , and  $v_{0z}$ . Note that this is exactly the same number of coefficients in the original equation (1.9). These constants can be expressed in terms of observable physical properties of the system of particles, such as the number density  $n$ , the average velocity  $\underline{u}$  and the kinetic temperature  $T$ .

To relate the observables  $n$ ,  $\underline{u}$  and  $T$ , with the constant coefficients  $C$ ,  $a_2$  and  $\underline{v}_0$ , we proceed as follows. From the definition of the number density we must have

$$n = \int_V f d^3v \quad (1.14)$$

Substituting the Maxwellian distribution function (1.13), results in

$$n = C \int_{\underline{v}} \exp \left[ - \frac{1}{2} m a_2 (\underline{v} - \underline{v}_0)^2 \right] d^3v \quad (1.15)$$

If we use the notation  $A = ma_2/2$  and  $\xi_i = (v_i - v_{0i})$ , with  $i = x, y, z$ , Eq. (1.15) becomes

$$n = C \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \exp \left[ - A (\xi_x^2 + \xi_y^2 + \xi_z^2) \right] d\xi_x d\xi_y d\xi_z \quad (1.16)$$

Performing the integrals over all possible values of  $\xi_x$ ,  $\xi_y$  and  $\xi_z$ , yields

$$n = C \left( \frac{\pi}{A} \right)^{3/2} = C \left( \frac{2\pi}{ma_2} \right)^{3/2} \quad (1.17)$$

From the definition of the average velocity we have

$$\underline{u} = \langle \underline{v} \rangle = \frac{1}{n} \int_{\underline{v}} f \underline{v} d^3v \quad (1.18)$$

and substituting the Maxwellian distribution function (1.13),

$$\underline{u} = \frac{C}{n} \int_{\underline{v}} \underline{v} \exp \left[ -\frac{1}{2} m a_2 (\underline{v} - \underline{v}_0)^2 \right] d^3v \quad (1.19)$$

Using the same notation as in (1.16), we can write

$$\begin{aligned} \underline{u} = & \frac{C}{n} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} (\xi_x \hat{x} + \xi_y \hat{y} + \xi_z \hat{z}) \exp \left[ -A (\xi_x^2 + \xi_y^2 + \xi_z^2) \right] d\xi_x d\xi_y d\xi_z + \\ & + \frac{C}{n} \underline{v}_0 \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \exp \left[ -A (\xi_x^2 + \xi_y^2 + \xi_z^2) \right] d\xi_x d\xi_y d\xi_z \end{aligned} \quad (1.20)$$

The first triple integral in the right-hand side of (1.20) over all possible values of  $\xi_x$ ,  $\xi_y$  and  $\xi_z$  vanishes, since the integrand is an odd function of  $\xi_i$ . According to Eq. (1.16), the second triple integral is equal to  $n/C$ . Thus,

$$\underline{u} = \underline{v}_0 \quad (1.21)$$

which shows that the constant  $\underline{v}_0$  represents the average (flow) velocity of the particles. Recall that the particle velocity  $\underline{v}$  can be written as the sum of the peculiar (random) velocity  $\underline{c}$  and the average velocity  $\underline{u}$ , that is,  $\underline{v} = \underline{c} + \underline{u}$ . If the system has no translational motion as a whole, then  $\underline{v}_0 = \underline{u} = 0$ .



Consider now the thermodynamic definition of the kinetic temperature T,

$$\frac{3}{2} kT = \frac{1}{2} m \langle c^2 \rangle = \frac{m}{2n} \int_{\underline{v}} f c^2 d^3v \quad (1.22)$$

where k is Boltzmann's constant. Substituting the Maxwellian distribution function (1.13), noting that  $\underline{c} = \underline{v} - \underline{u}$  and  $d^3v = d^3c$ , we obtain

$$\frac{3}{2} kT = \frac{mC}{2n} \int_{\underline{c}} c^2 \exp(-Ac^2) d^3c \quad (1.23)$$

Performing the triple integral over all possible values of  $c_x$ ,  $c_y$  and  $c_z$ , gives

$$kT = \frac{C}{na_2} \left( \frac{2\pi}{ma_2} \right)^{3/2} \quad (1.24)$$

We can now solve Eqs. (1.17) and (1.24) for C and  $a_2$ , which gives

$$C = n \left( \frac{m}{2\pi kT} \right)^{3/2} \quad (1.25)$$

$$a_2 = \frac{1}{kT} \quad (1.26)$$

Substituting the results obtained for  $C$ ,  $a_2$  and  $\underline{v}_0$ , into (1.3), and taking  $\underline{c} = \underline{v} - \underline{u}$ , the Maxwellian distribution of random velocities becomes

$$f(\underline{c}) = n \left( \frac{m}{2\pi kT} \right)^{3/2} \exp \left( -mc^2/2kT \right) \quad (1.27)$$

This is the equilibrium distribution function for a system of particles distributed uniformly in space and free from the action of external forces. Note that the number density  $n$  and the temperature  $T$  are independent of the position coordinate  $\underline{r}$  and of the time  $t$ . Once the number density and the temperature of the gas have been established, expression (1.27) represents the only permanent mode for the distribution of the particle velocities in the gas. Whatever may be the velocity distribution function of a gas initially not in equilibrium, it tends to the distribution function (1.27) in the course of time, if the gas is maintained isolated from the action of external forces.

When the system has no translational motion as a whole (if it is maintained inside a container, for example), the average (flow) velocity  $\underline{u}$  is zero and, consequently, we have  $\underline{c} = \underline{v}$  in Eq. (1.27). The equilibrium distribution function depends only on the magnitude of the random velocity  $\underline{c}$ , so that, when a perfectly reflecting surface is immersed in the gas,  $f(\underline{c})$  remains unchanged since the magnitude of the random velocity does not change when the particles are reflected by the surface.

For a plasma in equilibrium, with the various species of particles, such as electrons, ions and neutrals at the same temperature, the random velocities of each species are separately described by a Maxwell-Boltzmann distribution function.

### 1.5 - Local Maxwell-Boltzmann distribution function

In many situations of interest we are dealing with a gas that, although not in equilibrium, is not very far from it. It is then a good approximation to consider that, in the neighborhood of any point in the gas, there is an equilibrium situation described by a *local* Maxwell-Boltzmann distribution function of the form

$$f(\underline{r}, \underline{v}, t) = n(\underline{r}, t) \left[ \frac{m}{2 \pi k T(\underline{r}, t)} \right]^{3/2} \exp \left\{ - \frac{m [\underline{v} - \underline{u}(\underline{r}, t)]^2}{2 k T(\underline{r}, t)} \right\} \quad (1.28)$$

where the number density  $n$ , the temperature  $T$  and the average velocity  $\underline{u}$  are slowly varying functions of the space coordinate  $\underline{r}$  and of the time  $t$ .

## 2. THE MOST PROBABLE DISTRIBUTION

We have seen that the Maxwell-Boltzmann distribution function is the solution of Boltzmann equation representing the equilibrium state of a gas, in the absence of external forces. One of the important conclusions, obtained from the derivation of this distribution function, is that it depends of the cross section for

the particle collisions, as long as they exist. This means that the Maxwell-Boltzmann distribution function is, in a certain way, universal in the description of the equilibrium state, and it should be possible to derive it without explicitly considering the interactions between the particles. A derivation in these terms is in fact presented in statistical mechanics, where it is shown that the Maxwell-Boltzmann distribution function represents the *most probable* distribution function satisfying the macroscopic conditions (constraints) imposed on the system.

In statistical mechanics, to a given macroscopic system there corresponds a very large number of possible microscopic states that lead to the same macroscopic parameters specifying the system, such as number density  $n$ , average velocity  $\underline{u}$  and absolute temperature  $T$ . Each microscopic state is considered to be equiprobable. If we choose, at random, any particular microscopic state for the system, amongst all the possible microscopic states consistent with the macroscopic parameters (such as  $n$ ,  $\underline{u}$ ,  $T$ ), the probability of choosing a Maxwellian distribution is overwhelmingly larger than any other distribution. It is also shown that the entropy is proportional to the probability of having a given distribution. Consequently, the state having maximum entropy is the most probable state consistent with the macroscopic constraints imposed on the system.

The meaning of the Maxwell-Boltzmann distribution function can be further illustrated by the following example. If a dilute gas is prepared in an arbitrary non-equilibrium initial state,

and if there are interactions between the particles so as to allow the gas to pass from the initial state to other states, as time passes the gas will certainly reach the Maxwellian state, since essentially almost all possible microscopic states, consistent with the macroscopic constraints, have a Maxwellian distribution.

The statistical-mechanics derivation of the most probable distribution function provides information only about the equilibrium state, and cannot possibly tell, for example, how long (which depends on the collision cross section) a given distribution function, initially not the equilibrium one, takes to become Maxwellian. The Boltzmann equation, on the other hand, is much more general and provides information also for non-equilibrium situations.

### 3. MIXTURE OF VARIOUS SPECIES OF PARTICLES

For the case of a mixture containing different species of particles, each species having their own number density  $n_\alpha$ , average velocity  $\bar{u}_\alpha$ , and temperature  $T_\alpha$ , we can still perform a calculation to determine the *most probable* distribution subjected to the constraints provided by the set of macroscopic parameters  $n_\alpha$ ,  $\bar{u}_\alpha$ ,  $T_\alpha$ . This requires only that we set  $f_\alpha f_{\alpha 1} = f'_\alpha f'_{\alpha 1}$  for each particle species, but not necessarily  $f_\alpha f_\beta = f'_\alpha f'_{\beta 1}$  ( $\alpha \neq \beta$ ). This condition, therefore, is *not* an equilibrium situation, unless the temperatures and mean velocities of all species are equal. To determine the most probable distribution function for this non-equilibrium gas mixture (*each* species having their *own* number

density, mean velocity and temperature), we independently apply (1.3) for each species in order to maximize the entropy for each species. This also maximizes the entropy for the gas mixture with the specified macroscopic constraints. The problem is completely analogous to the one just solved for a one-component gas and leads, in identical fashion, to

$$f_{\alpha}(v) = n_{\alpha} \left( \frac{m_{\alpha}}{2\pi k T_{\alpha}} \right)^{3/2} \exp \left[ - \frac{m_{\alpha} (\vec{v} - \vec{u}_{\alpha})^2}{2k T_{\alpha}} \right] \quad (3.1)$$

Thus, each species have a Maxwellian distribution of velocities, but with their *own* density, average velocity and temperature. Although this is *not* an equilibrium distribution for the system, since the equilibrium condition  $f'_{\alpha} f'_{\beta_1} = f_{\alpha} f_{\beta_1}$  for all  $\alpha$  and  $\beta$  is not satisfied, it is, nevertheless, the most probable distribution with the specified constraints. Only if the temperatures and average velocities of all species are equal will this be an equilibrium situation. Indeed, if two systems with different species and at different temperatures are brought together, then, as time passes, there will be a transfer of energy through collisions between the two different species, until equilibrium is reached with the two species at the same temperature.

#### 4. PROPERTIES OF THE MAXWELL-BOLTZMANN DISTRIBUTION FUNCTION

Due to the importance of the equilibrium distribution function, we present in this section some of its basic properties.

We consider a gas in thermal equilibrium having no average (flow) velocity,  $\underline{u} = 0$ . If, however, this average velocity is not zero, we suppose that the observer is moving with the average velocity  $\underline{u}$  of the gas; thus, in either case,  $\underline{v} = \underline{c}$ . According to the definition of the distribution function, the number of particles per unit volume, having velocities between  $\underline{v}$  and  $\underline{v} + d\underline{v}$ , that is, between  $(v_x, v_y, v_z)$  and  $(v_x + dv_x, v_y + dv_y, v_z + dv_z)$ , is given by

$$f(\underline{v}) d^3v = n \left( \frac{m}{2\pi kT} \right)^{3/2} \exp(-mv^2/2kT) d^3v \quad (4.1)$$

#### 4.1 - Distribution of a velocity component

The distribution function for one component of the velocity,  $g(v_i)$ , is defined such that  $g(v_i) dv_i$  represents the number of particles per unit volume, with the  $i$ -component of the velocity between  $v_i$  and  $v_i + dv_i$ , irrespective of the values of the other two components of the velocity.

For the  $x$ -component, for example,  $g(v_x) dv_x$  is obtained by integrating  $f(\underline{v})$  over all possible values of the velocity components  $v_y$  and  $v_z$ , that is,

$$g(v_x) dv_x = \int_{v_y} \int_{v_z} f(\underline{v}) dv_x dv_y dv_z \quad (4.2)$$

Substituting the Maxwell-Boltzmann distribution function,

$$g(v_x) dv_x = n \left( \frac{m}{2\pi kT} \right)^{3/2} \exp(-mv_x^2/2kT) dv_x \int_{-\infty}^{+\infty} \exp(-mv_y^2/2kT) dv_y \cdot \int_{-\infty}^{+\infty} \exp(-mv_z^2/2kT) dv_z \quad (4.3)$$

Each of these integrals in (4.3) is equal to  $(2\pi kT/m)^{1/2}$ . Therefore,

$$g(v_x) dv_x = n \left( \frac{m}{2\pi kT} \right)^{1/2} \exp(-mv_x^2/2kT) dv_x \quad (4.4)$$

Obviously, this expression applies to any of the velocity components.

It shows that each of the components,  $v_x$ ,  $v_y$ ,  $v_z$ , has a *Gaussian* distribution, symmetric about the average value  $\langle v_i \rangle = 0$ ,  $i = x, y, z$ .

The distribution function  $g(v_x)$ , given by (4.4), is plotted in Fig. 3.

Note that it is properly normalized so that

$$\int_{-\infty}^{+\infty} g(v_x) dv_x = n \quad (4.5)$$

The fact that the average value  $\langle v_i \rangle$  is zero, is physically evident by symmetry, since each component of the velocity can be equally



positive or negative. Mathematically, we have

$$\begin{aligned} \langle v_i \rangle &= \frac{1}{n} \int_{-\infty}^{+\infty} g(v_i) v_i dv_i \\ &= \left( \frac{m}{2\pi kT} \right)^{1/2} \int_{-\infty}^{+\infty} \exp(-mv_i^2/2kT) v_i dv_i = 0 \end{aligned} \quad (4.6)$$

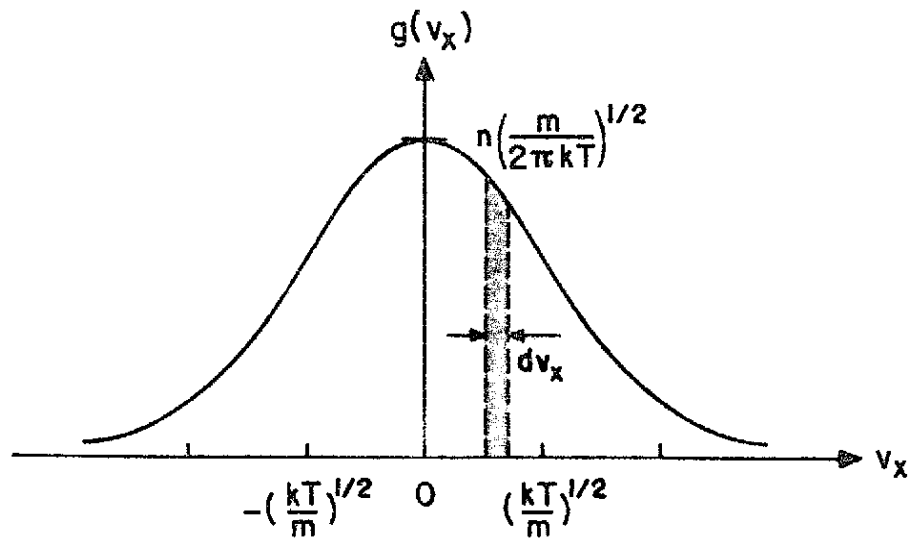


Fig. 3 - The Maxwellian distribution function for a component of the velocity is a Gaussian distribution having zero expectation ( $\langle v_x \rangle = 0$ ) and root-mean-square width  $(\langle v_x^2 \rangle)^{1/2} = (kT/m)^{1/2}$ .

since the integrand is an odd function of  $v_i$ . Consequently, if  $\ell$  represents any odd integer number,

$$\langle v_i^\ell \rangle = 0 \quad ; \quad \ell = 1, 3, 5, \dots \quad (4.7)$$

On the other hand,  $\langle v_i^2 \rangle$  is intrinsically positive and represents the *dispersion*, or *variance* of  $v_i$ ,

$$\langle v_i^2 \rangle = \frac{1}{n} \int_{-\infty}^{+\infty} g(v_i) v_i^2 dv_i = \frac{kT}{m} \quad (4.8)$$

This result is consistent with the theorem of equipartition of energy, according to which

$$\frac{1}{2} m \langle v_i^2 \rangle = \frac{1}{2} kT \quad (4.9)$$

for  $i = x, y, z$ . The *root-mean-square width* of the Gaussian distribution  $g(v_i)$  is, therefore, given by

$$(\langle v_i^2 \rangle)^{1/2} = (kT/m)^{1/2} \quad (4.10)$$

showing that the higher the temperature, the larger will be the width of the distribution function  $g(v_i)$ .

The velocity components behave, individually, like statistically independent quantities. Since  $v^2 = v_x^2 + v_y^2 + v_z^2$ , the

probability that the particle velocity lies between  $\underline{v}$  and  $\underline{v} + d\underline{v}$  is equal to the product of the probabilities that the velocity components lie between  $v_i$  and  $v_i + dv_i$ , for  $i = x, y, z$ , that is

$$\frac{f(\underline{v}) d^3v}{n} = \left[ \frac{g(v_x) dv_x}{n} \right] \left[ \frac{g(v_y) dv_y}{n} \right] \left[ \frac{g(v_z) dv_z}{n} \right] \quad (4.11)$$

#### 4.2 - Distribution of speeds

Since the Maxwell-Boltzmann velocity distribution function is isotropic, it is of interest to define a distribution function of speeds. For this purpose, consider a spherical polar coordinate system in velocity space  $(v, \theta, \phi)$ , as shown in Fig. 4.

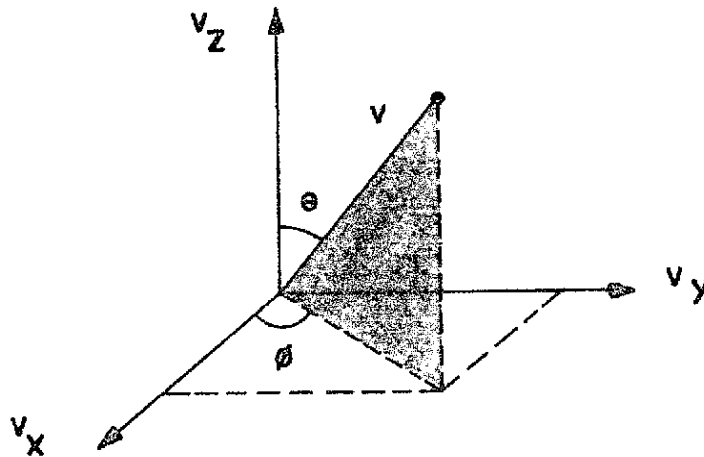


Fig. 4 - Spherical coordinate system  $(v, \theta, \phi)$  in velocity space.

The element of volume  $d^3v$ , in velocity space, between the coordinates  $(v, \theta, \phi)$  and  $(v + dv, \theta + d\theta, \phi + d\phi)$ , is given by

$$d^3v = v^2 \sin \theta \, d\theta \, d\phi \, dv \tag{4.12}$$

The distribution function of speeds,  $F(v)$ , is defined such that  $F(v) \, dv$  is the number of particles per unit volume, having speed  $(v = |\underline{v}|)$  between  $v$  and  $v + dv$ , irrespective of the direction in space of the velocity vector  $\underline{v}$ . Hence, to determine  $F(v)$  we integrate  $f(v)$  over all velocities whose *magnitude* lies between  $v$  and  $v + dv$ , irrespective of  $\theta$  and  $\phi$ , that is, whose velocity vector ends in a spherical shell, in velocity space, of internal radius  $v$  and external radius  $v + dv$ , as shown in Fig. 5. Therefore,

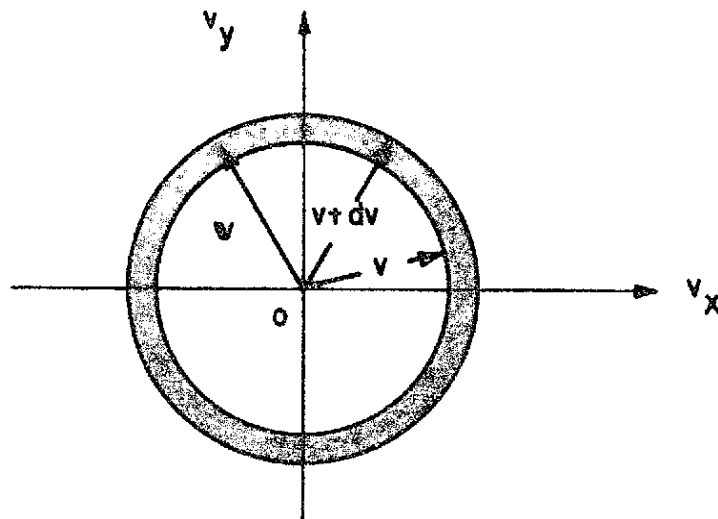


Fig. 5 - Schematic representation, in two dimensions, of a shell in velocity space containing all particles with velocity having magnitude between  $v$  and  $v + dv$ .

$$F(v) dv = \int_{\theta} \int_{\phi} f(v) v^2 \sin \theta d\theta d\phi dv \quad (4.13)$$

Since  $f(v)$  depends only on the magnitude of  $\underline{v}$ , but not on its direction,

$$\begin{aligned} F(v) dv &= f(v) v^2 dv \int_0^{\pi} \sin \theta d\theta \int_0^{2\pi} d\phi \\ &= 4\pi v^2 f(v) dv \end{aligned} \quad (4.14)$$

Note that  $4\pi v^2 dv$  is the volume of the spherical shell in velocity space, shown in Fig. 5. Substituting the Maxwell-Boltzmann distribution function for  $f(v)$ , the distribution of speeds becomes, explicitly,

$$F(v) = 4\pi n \left(\frac{m}{2\pi kT}\right)^{3/2} v^2 \exp(-mv^2/2kT) \quad (4.15)$$

This expression is properly normalized,

$$\int_0^{\infty} F(v) dv = n \quad (4.16)$$

From the expression for  $F(v)$  we see that as  $v$  increases, the exponential factor decreases faster than  $v^2$  increases, resulting in a maximum

in  $F(v)$  for a given value of  $v$  which is called the *most probable speed*. The curve for  $F(v)$  is shown in Fig. 6.

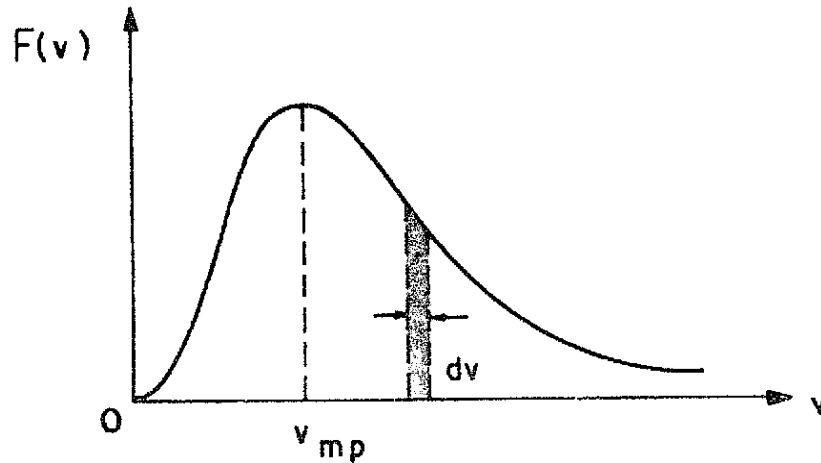


Fig. 6 - Maxwellian distribution of speeds, showing the most probable speed  $v_{mp}$ .

#### 4.3 - Mean values related to the molecular speeds

The *average value* of the speed is given by

$$\langle v \rangle = \frac{1}{n} \int_{\mathbf{v}} f \mathbf{v} d^3\mathbf{v} = \frac{1}{n} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} f \mathbf{v} dv_x dv_y dv_z \quad (4.17)$$

or, equivalently, by

$$\langle v \rangle = \frac{1}{n} \int_0^{\infty} F(v) v dv \quad (4.18)$$

It is intrinsically a positive quantity, since  $v = |\underline{v}|$  is always positive. Using expression (4.15) for  $F(v)$ , we get

$$\begin{aligned} \langle v \rangle &= 4\pi \left( \frac{m}{2\pi kT} \right)^{3/2} \int_0^{\infty} v^3 \exp(-mv^2/2kT) dv \\ &= 4\pi \left( \frac{m}{2\pi kT} \right)^{3/2} \frac{1}{2} \left( \frac{2kT}{m} \right)^2 \end{aligned} \quad (4.19)$$

Therefore,

$$\langle v \rangle = \left( \frac{8}{\pi} \frac{kT}{m} \right)^{1/2} \quad (4.20)$$

Integrals of the type

$$I(j) = \int_0^{\infty} x^j \exp(-\alpha x^2) dx \quad (4.21)$$

where  $j$  represents a positive integer number, occur frequently in the computation of average values using the Maxwellian distribution of speeds. For this reason, we present here for reference the results for some integrals of the type (4.21),

$$I(0) = \frac{1}{2} \sqrt{\pi} \alpha^{-1/2} \quad I(1) = \frac{1}{2} \alpha^{-1}$$

$$\begin{aligned}
 I(2) &= \frac{1}{4} \sqrt{\pi} \alpha^{-3/2} & I(3) &= \frac{1}{2} \alpha^{-2} \\
 I(4) &= \frac{3}{8} \sqrt{\pi} \alpha^{-5/2} & I(5) &= \alpha^{-3} \quad (4.22)
 \end{aligned}$$

The average of the square of the speed is given by

$$\langle v^2 \rangle = \frac{1}{n} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} f v^2 dv_x dv_y dv_z = \frac{4\pi}{n} \int_0^{\infty} f(v) v^4 dv \quad (4.23)$$

Substituting the Maxwellian distribution function for  $f(v)$ ,

$$\langle v^2 \rangle = 4\pi \left( \frac{m}{2\pi kT} \right)^{3/2} \int_0^{\infty} v^4 \exp(-mv^2/2kT) dv \quad (4.24)$$

which gives

$$\langle v^2 \rangle = \frac{3kT}{m} \quad (4.25)$$

This result can also be obtained from Eq. (4.8), noting that

$v^2 = v_x^2 + v_y^2 + v_z^2$  and that  $\langle v_x^2 \rangle = \langle v_y^2 \rangle = \langle v_z^2 \rangle$ . The *root-mean-square speed* is given by

$$v_{\text{rms}} = (\langle v^2 \rangle)^{1/2} = (3kT/m)^{1/2} \quad (4.26)$$



The *most probable speed*,  $v_{mp}$ , corresponds to the velocity for which  $F(v)$  is maximum, and can be obtained by the condition

$$\left[ \frac{d F (v)}{dv} \right]_{v_{mp}} = 0 \quad (4.27)$$

Differentiating Eq. (4.15) with respect to  $v$ , yields

$$\frac{d F (v)}{dv} = 2v \exp (-mv^2/2kT) + v^2 \left( -\frac{mv}{kT} \right) \exp (-mv^2/2kT) \quad (4.28)$$

which, for the condition of maximum expressed in (4.27), gives

$$v_{mp} = (2kT/m)^{1/2} \quad (4.29)$$

Note that the mean speeds  $\langle v \rangle$ ,  $v_{rms}$  and  $v_{mp}$  are all proportional to  $(kT/m)^{1/2}$  and are such that  $v_{mp} < \langle v \rangle < v_{rms}$ . Therefore, they increase with the temperature and, for a given temperature, particles having a larger mass will move with a smaller speed. We have also seen that the average kinetic energy of the random particle motions satisfies the relation

$$\frac{1}{2} m \langle v^2 \rangle = \frac{3}{2} kT \quad (4.30)$$

#### 4.4 - Distribution of thermal kinetic energy

The distribution of thermal kinetic energy  $G(E)$ , where  $E = mv^2/2$ , is defined such that  $G(E) dE$  is the number of particles per unit volume having random kinetic energy between  $E$  and  $E + dE$ . It can be obtained from Eq. (4.15), substituting  $v$  by  $(2E/m)^{1/2}$  and  $dv$  by  $dE / (2mE)^{1/2}$ . Hence,

$$G(E) dE = 4\pi n \left(\frac{m}{2\pi kT}\right)^{3/2} \left(\frac{2E}{m}\right) \exp(-E/kT) \frac{dE}{(2mE)^{1/2}} \quad (4.31)$$

Simplifying this expression, gives

$$G(E) dE = 2n \left[ \frac{E}{(kT)^3} \right]^{1/2} \exp(-E/kT) dE \quad (4.32)$$

The curve for the variation of  $G(E)$  is shown in Fig. 7.

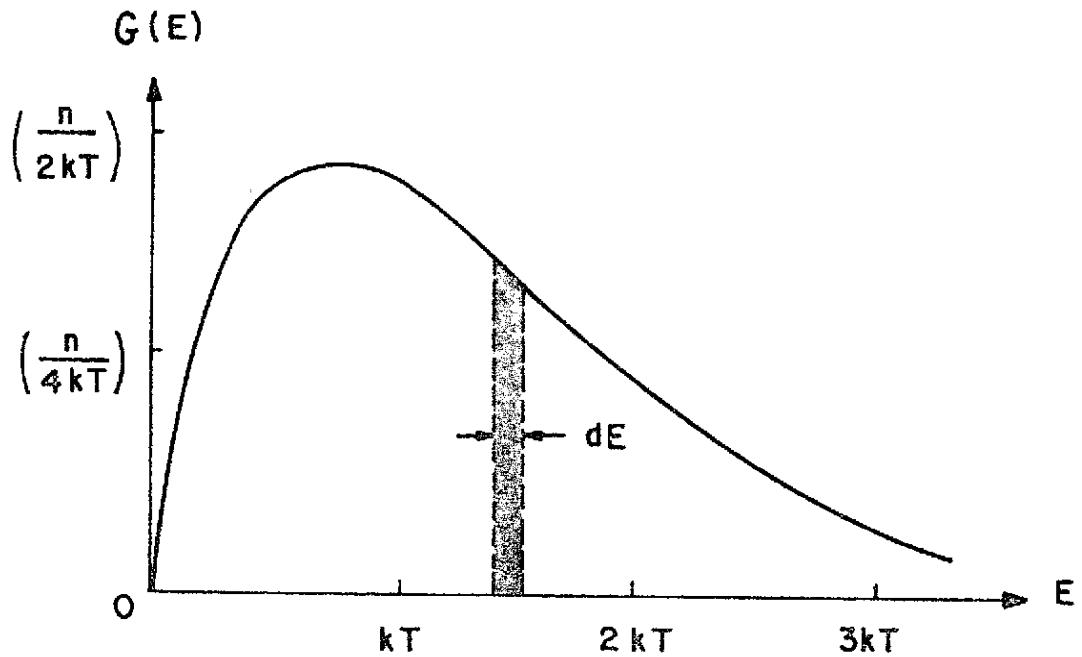


Fig. 7 - The Maxwellian distribution of thermal kinetic energies. The shadowed area represents the number of particles having random kinetic energy between  $E$  and  $E + dE$ .

#### 4.5 - Random particle flux

We have seen in chapter 6 that the particle flux, in a given direction  $\hat{n}$ , is given by

$$\Gamma_n = n \langle v_n \rangle = \int_v f \underline{v} \cdot \hat{n} d^3v \quad (4.33)$$

Let us consider a surface element inside the gas. We are interested in determining the number of particles that reach this surface element

per unit area and time, due to the random particle motions. Eq. (4.33) takes into account particles that reach the surface element, oriented along the direction specified by the unit vector  $\hat{n}$ , coming from all possible directions. Since we are assuming that the average velocity  $\underline{u}$  is zero, the flux given by (4.33) is obviously zero, since  $\langle \underline{c} \rangle = 0$ . In this case, it is of interest to consider only the flux of particles that cross the surface element from the *same side* (such that  $\underline{v} \cdot \hat{n}$  is positive, say), due to their random motions.

Let  $d\underline{S}$  be a surface element situated at the origin of a Cartesian coordinate system  $(x, y, z)$ , and oriented along the  $z$ -axis, that is,  $d\underline{S} = \hat{z}dS$ , as shown in Fig. 8.

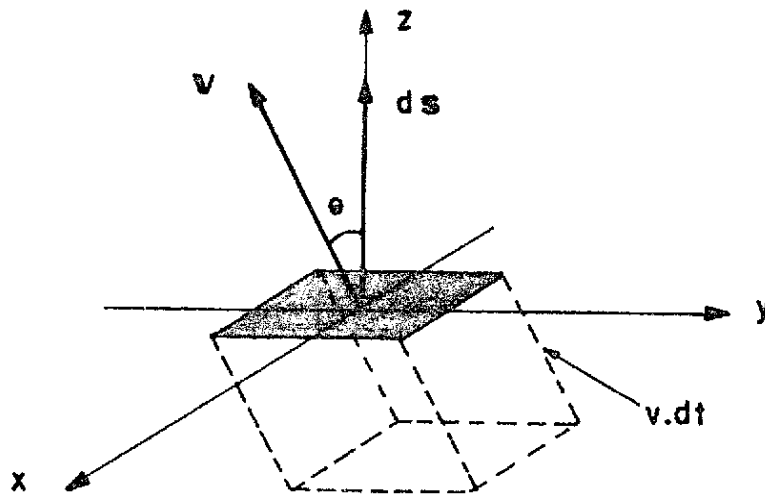


Fig. 8 - Prism of base  $d\underline{S} = \hat{z}dS$  containing the particles having velocity between  $\underline{v}$  and  $\underline{v} + d\underline{v}$  that cross  $dS$  during the time interval  $dt$ .

Consider the particles that cross  $d\underline{S}$  coming from the region  $z < 0$ , having velocities between  $\underline{v}$  and  $\underline{v} + d\underline{v}$ , making an angle  $\theta$  with the  $z$ -axis so that  $\underline{v} \cdot \hat{\underline{z}} = v \cos \theta$ . Expressing  $d^3v$  in terms of spherical coordinates  $(v, \theta, \phi)$

$$d^3v = v^2 \sin \theta \, d\theta \, d\phi \, dv \quad (4.34)$$

the random particle current density, crossing  $d\underline{S}$  from the region  $z < 0$ , is given by

$$\Gamma_z = \int_0^\infty f v^3 \, dv \int_0^{\pi/2} \sin \theta \cos \theta \, d\theta \int_0^{2\pi} d\phi = \pi \int_0^\infty f v^3 \, dv \quad (4.35)$$

Substituting the Maxwellian distribution for  $f$ , we find

$$\Gamma_z = \pi n \left( \frac{m}{2\pi kT} \right)^{3/2} \int_0^\infty \exp(-mv^2/2kT) v^3 \, dv \quad (4.36)$$

and solving the integral, we obtain

$$\Gamma = n \left( \frac{kT}{2\pi m} \right)^{1/2} = \frac{1}{4} n \langle v \rangle \quad (4.37)$$

In this result we have eliminated the index  $z$  from  $\Gamma$ , since the Maxwellian distribution function is isotropic; Eq. (4.37) applies to any direction inside the gas.

It is important to note that the random particle flux is inversely proportional to the square root of the particles mass. In a plasma the current density for the electrons is, therefore, much larger than that for the ions (the ratio of the electron mass to the proton mass, for example, is 1/1836). This difference in the particle flux between electrons and ions plays a very important role in the interaction between a plasma and a material body immersed in it.

#### 4.6 - Kinetic pressure and heat flux

From the definitions of the kinetic pressure dyad

$$\underline{\underline{p}} = \rho \langle \underline{\underline{c}} \underline{\underline{c}} \rangle = m \int \underline{\underline{c}} \underline{\underline{c}} f d^3v \quad (4.38)$$

and the heat flux vector

$$\underline{g} = \frac{1}{2} \rho \langle c^2 \underline{\underline{c}} \rangle = \frac{1}{2} m \int c^2 \underline{\underline{c}} f d^3v \quad (4.39)$$

we obtain, using the Maxwellian distribution function,

$$\begin{aligned} \underline{\underline{p}} &= \rho ( \langle c_x^2 \rangle \underline{\underline{\hat{x}}} \underline{\underline{\hat{x}}} + \langle c_y^2 \rangle \underline{\underline{\hat{y}}} \underline{\underline{\hat{y}}} + \langle c_z^2 \rangle \underline{\underline{\hat{z}}} \underline{\underline{\hat{z}}} ) \\ &= nkT ( \underline{\underline{\hat{x}}} \underline{\underline{\hat{x}}} + \underline{\underline{\hat{y}}} \underline{\underline{\hat{y}}} + \underline{\underline{\hat{z}}} \underline{\underline{\hat{z}}} ) \end{aligned} \quad (4.40)$$

and

$$\underline{q} = 0 \quad (4.41)$$

since the integrals having an odd integrand vanish. The scalar pressure is, therefore,

$$p = nkT \quad (4.42)$$

### 5. EQUILIBRIUM IN THE PRESENCE OF AN EXTERNAL FORCE

A gas under steady state conditions, immersed in a conservative force field, is characterized by a distribution function that differs from the Maxwell-Boltzmann distribution by an exponential factor, known as the *Boltzmann factor*. The conservative force field can be specified in terms of a potential energy  $U(\underline{r})$ , according to

$$\underline{F} = - \underline{\nabla} U(\underline{r}) \quad (5.1)$$

Since the conservative force field is a function only of the position vector  $\underline{r}$ , we expect the steady state solution of the Boltzmann equation for this case to be of the form

$$f(\underline{r}, \underline{v}) = f_0(\underline{v}) F(\underline{r}) \quad (5.2)$$

where  $f_0(v)$  denotes the Maxwell-Boltzmann equilibrium distribution function and  $F(\underline{r})$  is a scalar function of  $\underline{r}$  only, still to be determined. The function  $F(\underline{r})$  can be determined by requiring (5.2) to satisfy the Boltzmann equation under equilibrium conditions in the presence of the conservative field, that is,

$$\underline{v} \cdot \underline{\nabla} \left[ f_0(v) F(\underline{r}) \right] - \left[ \frac{\underline{\nabla} U(\underline{r})}{m} \right] \cdot \underline{\nabla}_v \left[ f_0(v) F(\underline{r}) \right] = 0 \quad (5.3)$$

From the expression for  $f_0(v)$  it can be easily verified that

$$\underline{\nabla}_v f_0(v) = -\frac{mv}{kT} f_0(v) \quad (5.4)$$

Therefore, Eq. (5.3) simplifies to

$$f_0(v) \underline{v} \cdot \left[ \underline{\nabla} F(\underline{r}) + \frac{1}{kT} F(\underline{r}) \underline{\nabla} U(\underline{r}) \right] = 0 \quad (5.5)$$

from which we can write

$$\frac{\underline{\nabla} F(\underline{r})}{F(\underline{r})} = -\frac{1}{kT} \underline{\nabla} U(\underline{r}) \quad (5.6)$$

Since  $dF = \underline{\nabla} F \cdot d\underline{r}$ , Eq. (5.6) may also be written as



$$\frac{dF(\underline{r})}{F(\underline{r})} = -\frac{1}{kT} dU(\underline{r}) \quad (5.7)$$

The solution of this differential equation is

$$F(\underline{r}) = A_0 \exp \left[ -\frac{U(\underline{r})}{kT} \right] \quad (5.8)$$

where  $A_0$  is a constant that can be determined by requiring that

$$\int_{\underline{v}} f(\underline{r}, \underline{v}) d^3v = n(\underline{r}) \quad (5.9)$$

from which we get

$$n(\underline{r}) = A_0 \exp \left[ -\frac{U(\underline{r})}{kT} \right] \int_{\underline{v}} f_0(\underline{v}) d^3v \quad (5.10)$$

Denoting by  $n_0$  the number density in a region where  $U(\underline{r}) = 0$ , under equilibrium conditions, that is,

$$n_0 = \int_{\underline{v}} f_0(\underline{v}) d^3v \quad (5.11)$$

we must choose  $A_0 = 1$ , so that the equilibrium distribution function for this case is (with  $\underline{u} = 0$ )

$$\begin{aligned} f(\underline{r}, v) &= f_0(v) \exp \left[ - \frac{U(\underline{r})}{kT} \right] \\ &= n_0 \left( \frac{m}{2\pi kT} \right)^{3/2} \exp \left\{ - \frac{1}{kT} \left[ \frac{mv^2}{2} + U(\underline{r}) \right] \right\} \end{aligned} \quad (5.12)$$

The number density for a system described by this distribution function is given by

$$n(\underline{r}) = n_0 \exp \left[ - \frac{U(\underline{r})}{kT} \right] \quad (5.13)$$

The factor  $\exp \left[ -U(\underline{r})/kT \right]$ , responsible for the inhomogeneity of the distribution function  $f(\underline{r}, v)$  in (5.12), is known as the *Boltzmann factor*.

An important example is provided by a plasma in the presence of a conservative force due to an electrostatic field

$$\underline{E} = - \underline{\nabla} \phi(\underline{r}) \quad (5.14)$$

where  $\phi(\underline{r})$  is the electrostatic scalar potential. The potential energy, in this case, is

$$U(\underline{r}) = q \phi(\underline{r}) \quad (5.15)$$

The number density for particles of charge  $q$  in equilibrium under the action of an electrostatic field is, therefore,

$$n(\underline{r}) = n_0 \exp \left[ - q\phi(\underline{r})/kT \right] \quad (5.16)$$

This expression will be used in Chapter 11, where we will study the phenomenon of electrostatic shielding in a plasma.

## 6. DEGREE OF IONIZATION IN EQUILIBRIUM - THE SAHA EQUATION

From the methods of statistical mechanics we can determine the degree of ionization in a gas in thermal equilibrium at some temperature  $T$ , without considering the details of the process of ionization. In order to ionize an atom or molecule, it is necessary to add to it a certain amount of energy. This ionization energy is conveniently expressed in *electron volts*, and is normally called the *ionization potential*. Values for the first ionization potential of some atoms are given in Table 1. Note that to provide a mean thermal energy  $kT$  of 1 eV requires a temperature of 11 600 K. Hence, it is apparent that only at very high temperatures the mean kinetic energy  $3kT/2$  of a particle exceeds the ionization energy. However, we will show that a considerable degree of ionization can be achieved even when the mean thermal energy of the particles is far below the ionization energy, since some of the particles, the ones with the largest velocities (in the tail of the Maxwellian

distribution function), have enough energy to produce ionization by collisions. The equilibrium degree of ionization is then determined by a balance between the rate of ionization by collisions and the rate of recombination.

TABLE 1

IONIZATION POTENTIAL ENERGY OF SOME ATOMS

| Element       | Ionization energy U for first electron (eV) |
|---------------|---|
| Helium (He)   | 24.59                                       |
| Argon (A)     | 15.76                                       |
| Nitrogen (N)  | 14.53                                       |
| Oxygen (O)    | 13.62                                       |
| Hydrogen (H)  | 13.60                                       |
| Mercury (Hg)  | 10.44                                       |
| Iron (Fe)     | 7.87  |
| Sodium (Na)   | 5.14  |
| Potassium (K) | 4.34  |
| Cesium (Cs)   | 3.89  |

To calculate the relative numbers of ionized and neutral atoms in a plasma, at a specified temperature, it is necessary to use a particle distribution function similar to that given in (5.13).

However, the physical situation is somewhat different because of the necessary quantum mechanical aspects of the problem.

Denoting by  $n_a$  and  $n_b$  the number density of the particles having energies  $U_a$  and  $U_b$ , respectively, the ratio  $n_a/n_b$  is given, from statistical mechanics, by

$$\frac{n_a}{n_b} = \frac{g_a}{g_b} \exp \left[ - (U_a - U_b)/kT \right] \quad (6.1)$$

where  $g_a$  and  $g_b$  are the statistical weights associated with the energies  $U_a$  and  $U_b$ , that is, the degeneracy factors giving the number of states having the energies  $U_a$  and  $U_b$ , respectively. For the case of a system having only two energy levels,  $U_a$  and  $U_b$ , the fraction ( $\alpha$ ) of all the particles that are in the higher energy state  $U_a$  is given by

$$\alpha = \frac{n_a}{n_a + n_b} = \frac{(n_a/n_b)}{(n_a/n_b) + 1} \quad (6.2)$$

or using Eq. (6.1), with  $U = U_a - U_b$ ,

$$\alpha = \frac{(g_a/g_b) \exp (-U/kT)}{(g_a/g_b) \exp (-U/kT) + 1} \quad (6.3)$$

For the ionization problem, state a is taken as that of the ion-electron pair, state b is that of the neutral atom and  $U = U_a - U_b$  is the ionization energy. The temperature  $T_{1/2}$  for which

$\alpha = 0.5$ , that is, for which fifty per cent of all the atoms are in the ionized state ( $n_a = n_b$ ), can be determined by taking

$$\frac{g_a}{g_b} \exp(-U/kT_{1/2}) = 1 \quad (6.4)$$

which gives

$$T_{1/2} = \frac{U}{k \ln(g_a/g_b)} \quad (6.5)$$

Fig. 9 shows the curve of  $\alpha$  as a function of  $T$ , according to (6.3).

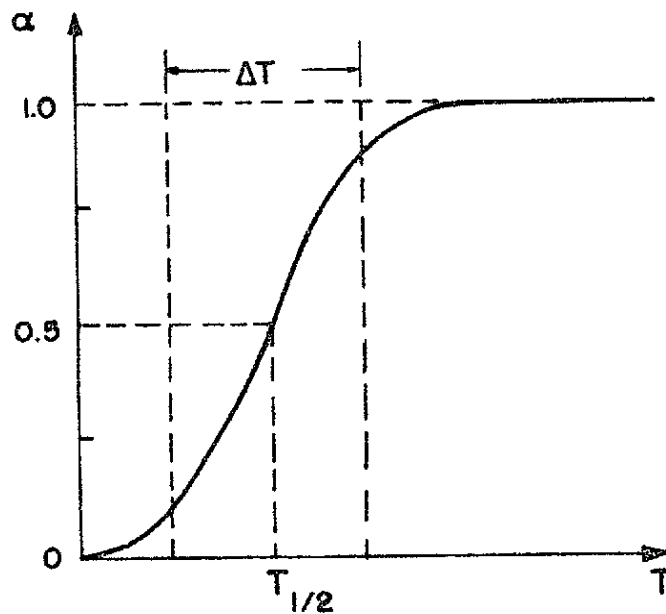


Fig. 9 - The function  $\alpha(T)$ , which gives the fraction of particles in the ionized state as a function of temperature.

The fraction of the particles in the ionized state changes from nearly zero to nearly one over a small temperature range. An *estimate* of this temperature range can be obtained from the temperature difference  $\Delta T$  that would exist between  $\alpha = 0$  and  $\alpha = 1$ , if the curve of  $\alpha(T)$  were a straightline with the slope of the true  $\alpha(T)$  curve at  $T_{1/2}$ . Hence, we take

$$\Delta T = \left[ \frac{d\alpha(T)}{dT} \right]_{T_{1/2}}^{-1} \quad (6.6)$$

From Eq. (6.3) we obtain, assuming  $d(g_a/g_b)/dT \approx 0$ ,

$$\left. \frac{d\alpha(T)}{dT} \right|_{T_{1/2}} = \frac{U \alpha^2}{T^2 (g_a/g_b) \exp(-U/kT)} \Big|_{T_{1/2}} = \frac{U}{4 T_{1/2}^2} \quad (6.7)$$

so that

$$\Delta T = \frac{4T_{1/2}}{\ln(g_a/g_b)} = \frac{4 U}{[\ln(g_a/g_b)]^2} \quad (6.8)$$

From this result we can see that the larger is  $g_a/g_b$  the smaller is  $\Delta T$ .

Since the ionized state is much more degenerate than the neutral state ( $g_a \gg g_b$ ), the curve of  $\alpha(T)$  presents a very steep inclination near  $T_{1/2}$ , with most of the transitions from the neutral state to the ionized state occurring near  $T_{1/2}$ , given by (6.5). Thus,

for  $g_a \gg g_b$  the curve of  $\alpha(T)$  will look approximately like a step function with the ionization occurring near  $T_{1/2}$ .

The degeneracy factors  $g_a$  and  $g_b$  can be obtained from a quantum mechanical calculation. If we neglect the small interaction potential between the ion and the free electron, and also the internal degrees of freedom of all the particles, it turns out that

$$\frac{g_a}{g_b} = \left( \frac{2 \pi m_e kT}{h^2} \right)^{3/2} n_i^{-1} \quad (6.9)$$

where  $h$  is Planck's constant and  $n_i$  the ion number density. For  $T$  in degrees Kelvin and  $n_i$  in  $m^{-3}$ ,

$$\frac{g_a}{g_b} = 2.405 \times 10^{21} T^{3/2} n_i^{-1} \quad (6.10)$$

Using this result in Eq. (6.1), we obtain the following equation

$$\frac{n_i}{n_n} = 2.405 \times 10^{21} T^{3/2} n_i^{-1} \exp(-U/kT) \quad (6.11)$$

which is known as the *Saha equation*. Since  $1 \text{ eV} = kT$  for  $T = 11\,600^\circ\text{K}$ , we can also write the Saha equation as



$$\frac{n_i}{n_n} = 3.00 \times 10^{27} T^{3/2} n_i^{-1} \exp(-U/T) \quad (6.12)$$

with  $T$  in eV and  $n_i$  in  $m^{-3}$ . Thus, when the total number density  $n_t = n_i + n_n$  is sufficiently low, a considerable degree of ionization can be achieved for temperatures that are well below the ionization energy. This is illustrated in Fig. 10, which shows the degree of ionization of hydrogen as a function of temperature, for values of the total number density  $n_t$  of  $10^{16}$ ,  $10^{19}$ ,  $10^{22}$  and  $10^{25} m^{-3}$ .

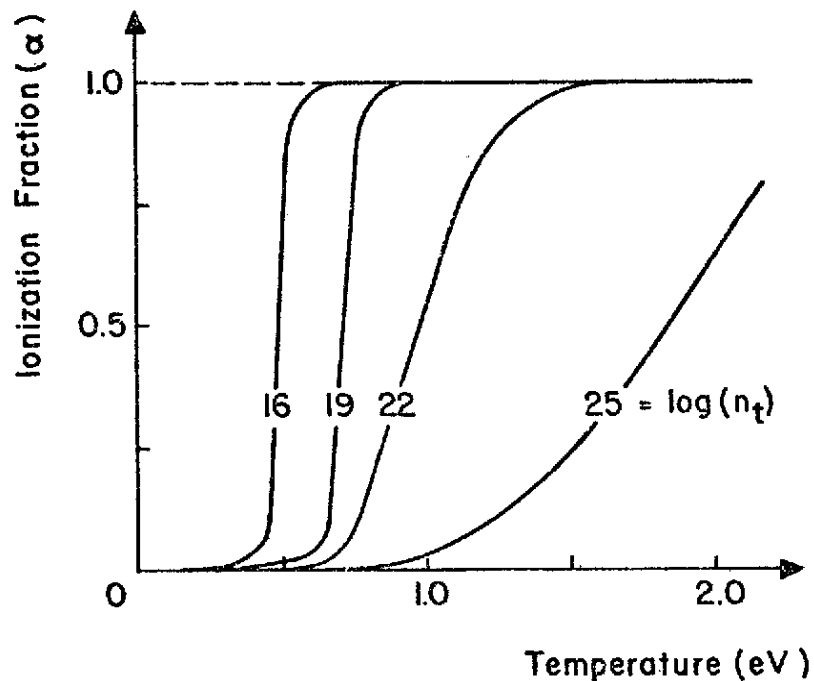


Fig. 10 - Degree of ionization  $\alpha = n_i/(n_i + n_n)$  as a function of temperature for atomic hydrogen ( $U = 13.60$  eV). The various curves refer to different number densities (in  $m^{-3}$ )  $n_t = n_i + n_n$ .

It is clear that, as the number density decreases, the values of  $\Delta T$  and  $T_{1/2}$  decrease significantly, and a significant degree of ionization can be obtained at temperatures far below the ionization energy of atomic hydrogen (13.60 eV). In a gas like cesium vapor, whose ionization energy is only 3.89 eV, a high degree of ionization can be obtained even at relatively low temperatures of the order of  $1000^{\circ}\text{K}$ .

## PROBLEMS

7.1 - A *two-dimensional* gas consisting of only one species and whose particles are restricted to move in a plane (the  $z = 0$  plane), is characterized by a homogeneous, isotropic, two-dimensional Maxwell-Boltzmann distribution function (with  $\underline{u} = 0$ ),

$$f(v) = n_0 \left( \frac{m}{2\pi kT} \right) \exp \left[ - \frac{m(v_x^2 + v_y^2)}{2kT} \right]$$

where  $n_0$  represents the number of particles per unit area.

a) Show that the most probable speed of the particles is

$$v_{mp} = (kT/m)^{1/2} .$$

b) Show that the fraction of the number of particles per unit area, which have speeds greater than the most probable speed is given by  $(1/e)^{1/2}$ , where  $e$  is the base of natural logarithms.

c) Show that the number of particles crossing a unit length per unit time (flux), from one side only, is given by

$$\Gamma = \frac{n_0 \langle v \rangle}{\pi} = n_0 \left( \frac{kT}{2\pi m} \right)^{1/2}$$

d) Show that the kinetic pressure dyad is given by

$$\underline{p} = n_0 kT (\underline{\hat{x}}\underline{\hat{x}} + \underline{\hat{y}}\underline{\hat{y}})$$

7.2 - Consider a gas of particles consisting of only one species, and characterized by the Maxwell-Boltzmann equilibrium distribution function (with  $\underline{u} = 0$ )

$$f(\underline{v}) = n_0 \left( \frac{m}{2\pi kT} \right)^{3/2} \exp \left( - \frac{m\underline{v}^2}{2kT} \right)$$

(a) Show that the total number of particles crossing a unit area per unit time, lying within an element  $d\Omega$  of solid angle, is given by

$$\frac{n_0}{\pi} \left( \frac{kT}{2\pi m} \right)^{1/2} \cos \theta d\Omega$$

where  $\theta$  denotes the angle between the solid angle and the direction of the normal to the area considered.

(b) Show that the *fraction* of the particles that cross a unit area perpendicular to the x-axis per unit time, from the same side, having the velocity components in the range

$d^3v = dv_x dv_y dv_z$ , about  $\underline{v}$ , is given by

$$\frac{1}{2\pi} \left( \frac{m}{kT} \right)^2 v_x \exp \left( - \frac{m\underline{v}^2}{2kT} \right) d^3v$$

(c) Deduce the value of the thermal energy flux triad  $\underline{Q}$  for the Maxwellian gas.

7.3 - The distribution of thermal kinetic energies  $E$ , for a gas in the Maxwellian state, is given by

$$G(E) = 2n \left[ \frac{E}{\pi(kT)^3} \right]^{1/2} \exp \left( - \frac{E}{kT} \right)$$

Calculate the most probable energy and show that the velocity of the particles, which have this energy, is equal to  $(kT/m)^{1/2}$ .

7.4 - The entropy of a system can be expressed in terms of the distribution function as

$$S = -k \int \int_{r, v} f \ln f \, d^3v \, d^3r$$

Prove that, for a Maxwellian distribution function, the entropy satisfies the following thermodynamic relations

$$\left( \frac{\partial S}{\partial E} \right)_{V, N} = \frac{1}{T}$$

$$\left( \frac{\partial S}{\partial V} \right)_{E, N} = \frac{p}{T}$$

where  $N$  is the total number of particles in the system,  $V$  is the total volume, and  $E = 3NkT/2$  is the total energy.

7.5 - Derive an expression for the Doppler intensity profile (thermal broadening) of a spectral line emitted near the central frequency  $\nu_0$ , assuming that the emitting atoms have a Maxwellian velocity distribution. Ignore all other factors that contribute to the shape of the line.

*Hints:* (1) The change in frequency due to the Doppler effect associated with the relative (nonrelativistic) motion of the emitting atom, with respect to the direction of observation (x-direction, e.g.), is given by

$$\nu - \nu_0 = -\nu_0 \frac{v_x}{c}$$

where  $c$  denotes the velocity of light. (2) The observed intensity in the frequency range between  $\nu$  and  $\nu + d\nu$ , that is,  $I(\nu) d\nu$ , is proportional to the number of emitting atoms per unit volume, which have velocities along the direction of observation (x-direction) between  $v_x$  and  $v_x + dv_x$ .

7.6 - Consider a gas mixture containing  $n_e$  electrons and  $n_i$  oxygen ions per unit volume, all in thermal equilibrium at temperature  $T$  and having no drift velocity.

(a) Resolve the motion of the particle species into the motion in space of the *center of mass*, plus the *relative motion* of one species with respect to the other, but with the reduced mass. Calculate the Jacobian,  $J$ , of this transformation of velocities, and show that  $|J| = 1$ .

(b) Show that the velocities of the center of mass have a Maxwellian distribution, and that the *relative* velocities also have a Maxwellian distribution, but with the reduced mass.

(c) What must be the magnitude of  $T$  such that 20% of the electrons have a *relative* kinetic energy greater than 2 eV?

The following integral will be useful:

$$\int_{x_0}^{\infty} x^2 \exp(-\alpha x^2) dx = \frac{x_0 \exp(-\alpha x_0^2)}{2\alpha} + \frac{\sqrt{\pi}}{4} \alpha^{-3/2} \operatorname{erfc}(\alpha^{1/2} x_0)$$

where  $\operatorname{erfc}(\alpha^{1/2} x_0)$  denotes the *complementary error function*.

- 7.7 - A gas of  $O_2$  molecules is in the equilibrium state, with number density  $n$  and absolute temperature  $T$ . Calculate the average value of the reciprocal of the particle velocity, that is,  $\langle 1/v \rangle$ .
- 7.8 - A plasma is in equilibrium under the action of an external electrostatic field  $\underline{E}$  and a gravitational field  $\underline{g}$ . Consider that the plasma as a whole is moving with constant velocity  $\underline{u}_0$ , with respect to the observer's frame of reference. Write down the distribution function for the species of type  $\alpha$  for this plasma.
- 7.9 - Consider the particles in the Earth's atmosphere under equilibrium conditions in the presence of the Earth's gravitational field. Assume a horizontally stratified atmosphere with constant temperature  $T$  and consider a constant value  $g$  for the acceleration due to gravity. Derive an expression for the number density  $n(z)$  as a function of height  $z$ , for the particles of mass  $m$ , in terms of the number density  $n(z_0)$  at a base level  $z_0$ , and of the scale height  $H = kT/mg$ . How is this expression for  $n(z)$  modified, when both  $T$  and  $g$  vary with height?



- 7.10 - The temperature of a plasma, in thermal equilibrium with a neutral gas, can be determined experimentally by measuring the electron density  $n_e$  with a microwave transmission experiment, and the neutrals number density in a particular excited state through the rate of transitions to a lower state. Determine the temperature of a plasma, with only one type of ions, whose electron number density is  $10^{20} \text{ m}^{-3}$ , and which is in equilibrium with a state of ionization potential 2 eV whose population is  $10^{15} \text{ m}^{-3}$ .
- 7.11 - Consider two large chambers which communicate with each other only through a small aperture of area  $A$  in a very thin wall, as indicated in Fig. P 7.1. The chambers contain an ideal gas at a *very low pressure*, such that the particles mean free path is much larger than the dimensions of  $A$ , and are at temperatures  $T_1$  and  $T_2$ . Determine the ratio  $p_1/p_2$  of the pressures in the two chambers assuming that, under equilibrium conditions, the flux of particles through the aperture  $A$  from one chamber must equal that from the other. What would be the result in the case of *normal conditions of pressure*? Give a physical explanation for the two different results.

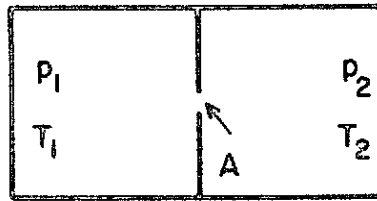


Fig.P7.1

7.12 - Show that the average thermal energy per particle, for a gas in thermodynamic equilibrium, is equal to  $1.292 \times 10^{-4}$  eV/ K .

7.13 - Use the laws of conservation of momentum and energy in a collision, to show that the Maxwell-Boltzmann distribution function

$$f(\underline{v}) = n \left[ \frac{m}{2\pi kT} \right]^{3/2} \exp \left[ -\frac{m(\underline{v} - \underline{u})^2}{2kT} \right]$$

satisfies the following equation of detailed balance

$$f' f'_1 = f f_1$$