An Introduction to Plasma Physics and its Space Applications, Volume 1 Fundamentals and elementary processes

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Chapter 3

Basic kinetic theory of neutral gases

The word *kinetic* comes from the ancient Greek $\kappa\nu\eta\tau\delta\zeta$ which means 'of or relating to motion', thus a kinetic description considers the effects of motion of particles in the physical description of a neutral gas or plasma. The kinetic theory connects the molecular and microscopic properties to macroscopic physical quantities evaluated as averages over a large number of particles. This statistical description of neutral gases in thermodynamic equilibrium is discussed in this chapter and these concepts will be used later to introduce the basic physical properties of plasmas.

3.1 The probabilistic description of gases

The characteristic mean free path λ_c for the dominant collisional process introduced in chapter 1 gives us a first length scale for the physical description of neutral gases and plasmas. We might think there are few particles with which an atom or molecule can collide along the distance between two successive atomic or molecular encounters. On the contrary, as shown by the example calculation in box 3.1, the number of particles into a box volume λ_c^3 is always huge, even for low gas pressures. This is due to the smallness of the characteristic sizes of the atoms or molecules compared to the typical distances that particles travel.

Instead of tracking the huge number of individual interacting particles, the physical description of these systems requires the statistical approach of kinetic theory, which treats gases and plasmas under equilibrium and non-equilibrium conditions. Classical kinetic theory deals essentially with the connection between the motions and interactions of particles on a microscopic scale and the macroscopic physical properties of the system. As we shall see, magnitudes such as the local gas pressure or temperature result from statistical averages calculated on a huge number of particles. In addition, the specific properties of collisional processes between atoms or molecules determine macroscopic transport properties as viscosity or thermal conductivity.

Box 3.1. Calculation of the number of particles

Using the expression for the gas atom density of note 2.1 for the argon pressure of $p = 10^{-3}$ mbar at 0 °C we have $n_a \simeq 4.4 \times 10^{13}$ atoms by cubic centimeter. The corresponding mean free path for elastic collisions between argon atoms (see table 2.1) is $\lambda_c = 6.4$ cm. We can estimate the number of particles contained in a box of side λ_c ,

 $N_a = n_a \times \lambda_c^3 = (4.38 \times 10^{13}) \times (2.62 \times 10^2) \simeq 1.2 \times 10^{16}$ particles

Reducing the pressure to $p = 10^{-6}$ mbar we have, $n_a \simeq 4.4 \times 10^{10}$ cm⁻³ and the mean free path increases up to $\lambda_c = 640$ cm, now we obtain,

$$N_a = n_a \times \lambda_c^3 = (4.38 \times 10^{10}) \times (2.62 \times 10^8) \simeq 1.2 \times 10^{19}$$
 particles

Next, we will introduce the simplest kinetic description of the equilibrium thermodynamic state, where the atoms are considered as points of mass m that move in space. We will essentially consider its translational movement, not the molecular rotation or vibrational motions.

3.2 The Maxwell–Boltzmann distribution

The kinetic description of the time-independent equilibrium state of an isolated gas makes use of the Maxwell–Boltzmann (MB) velocity distribution function. Here we will justify this expression using simple arguments and later by a more rigorous treatment.

The conditions for an isolated neutral gas to be in thermodynamic equilibrium are restrictive, since there must be simultaneous mechanical, thermal and chemical equilibrium. The first requires the balance of forces between the system and its environment. Thermal equilibrium implies the gas has a uniform temperature that is equal to that of its surroundings. Finally, a system in chemical equilibrium does not spontaneously experience internal changes, such as chemical reactions or diffusive mass transfer.

The kinetic description of a neutral gas should reflect these general properties and in the equilibrium state of a gas of molecules with mass m at temperature T the macroscopic properties, such as the particle density n_o are uniform and constant over time. The cornerstone of kinetic theory is the *velocity distribution function* $f(\mathbf{v})$, that statistically describes the spectrum of molecular velocities; some particles move fast, whereas others will be practically at rest.

The equilibrium probability of finding one molecule with the x velocity component of the velocity between v_x and $v_x + dv_x$ is $dP = f(v_x) dv_x$ and the corresponding number dn of particles is $dn=n_o f(v_x) dv_x$, both are independent of time and the position \mathbf{r} .

Since there is not a preferred direction for molecular motion, the gas particles move randomly and the three components (v_x, v_y, v_z) may be treated independently. The total probability of finding one particle with velocity in the range v and v + dv is¹,

$$dP = f(\mathbf{v}) d^3 \mathbf{v} = (f(v_x) dv_x) \times (f(v_y) dv_y) \times (f(v_z) dv_z)$$
$$= f(v_x) f(v_y) f(v_z) dv_x dv_y dv_z$$

Energy is conserved in the state of macroscopic equilibrium and thus $dP = f(\mathbf{v}) d\mathbf{v}$ is invariant under time reversal. That is, the probability distribution function is independent of the direction $f(\mathbf{v}) = f(-\mathbf{v})$ of the velocity of particles because the stationary equilibrium state of the gas is irrespective of whether motion of molecules goes forward or backward along any direction in the gas volume. The function $f(\mathbf{v}) \equiv f(v^2)$ where $\mathbf{v} \cdot \mathbf{v} = v^2 = v_x^2 + v_y^2 + v_z^2$ respects this temporal symmetry,

$$f(\mathbf{v}) = f\left(v_x^2 + v_y^2 + v_z^2\right) = f\left(v_x^2\right) f\left(v_y^2\right) f\left(v_z^2\right)$$

The only function that satisfies such a relationship² is a power of the speed components and we can write,

$$f(v_x) = A e^{-v_x^2/B}$$
(3.1)

and similar expressions for v_y and v_z . The minus sign in equation (3.1) keeps the decreasing probability $f(v_x) > 0$ bounded as $v_x^2 > 0$ grows, whereas B > 0 has units of the square of a velocity to hold the ratio v_x^2/B dimensionless. Hence we may introduce the ratio,

$$\frac{v_x^2}{B} = \left(m \ v_x^2/2\right) / (k_B T)$$
(3.2)

between the *kinetic energy* $m v_x^2/2$ and the *thermal energy* $E_{th} \sim k_B T$ of the gas. The constant A in equation (3.1) is determined by normalizing the function $f(v_x)$ to the unity,

$$\int_{-\infty}^{\infty} f(v_x) \, dv_x = 1 \tag{3.3}$$

that gives $A = (2 \pi k_B T/m)^{1/2}$, we obtain in one dimension,

$$f_{mb}(v_x) = \left(\frac{m}{2 \pi k_b T}\right)^{1/2} e^{-m v_x^2/2 k_B T}$$
(3.4)

and similar expressions for $f(v_v)$ and $f(v_z)$.

Finally, the speeds of the gas molecules of mass m at temperature T are distributed according to the Maxwell–Boltzmann probability density function,

¹ In the following we will use indistinctly $dv = d^3v = dv_x dv_y dv_z$ and also in other integrals involving dr, etc. ² f(a, b, c) = f(a)f(b)f(c).

$$f_{mb}(\mathbf{v}) = \left(\frac{m}{2\pi k_B T}\right)^{3/2} \exp\left(-\frac{m v^2}{2k_B T}\right)$$
(3.5)

The probability dP of finding one molecule with velocity v and v + dv is $dP = f_{mb}(v) dv$ and $dn = n_o dP$ represents the number density of such particles. The probability distribution (3.5) is normalized to the unity by considering all possible values of the velocity components (v_x, v_y, v_z) and,

$$\int_{-\infty}^{+\infty} f_{mb}(\mathbf{v}) \, d^3 \mathbf{v} = \int_{-\infty}^{+\infty} f_{mb}(\mathbf{v}_x) f_{mb}(\mathbf{v}_y) f_{mb}(\mathbf{v}_z) \, d\mathbf{v}_x \, d\mathbf{v}_y \, d\mathbf{v}_z = 1$$

As we can see, the function of $f_{mb}(v)$ is independent of r and time, reflecting the characteristics of the thermodynamic equilibrium state where the macroscopic properties are steady and uniform.

The Maxwell–Boltzmann velocity distribution function $dn = n_o f_{mb}(\mathbf{v}) d\mathbf{v}$ gives the number density of particles with velocities between \mathbf{v} and $\mathbf{v} + d\mathbf{v}$. Equivalently³, the density of particles within the volume dv^3 is centered in the velocity \mathbf{v} .

The probability of finding *one* particle is given by the *probability distribution* function $dP = f_{bm}(\mathbf{v}) d\mathbf{v}$ and in one dimension $f_{mb}(v_x)$ is represented in figure 3.1 for argon at temperatures of 300, 600, 1000 and 1300 K (equivalent to 0.026, 0.052, 0.086 and 0.112 eV) and the same graph can be drawn for $f_{mb}(v_y)$ and $f_{mb}(v_z)$. The function $f_{mb}(v_x)$ has a maximum for $v_x = 0$ and decreases rapidly with the speed. When the temperature increases the distribution becomes wider and the height of its maximum is reduced to preserve the integral (3.3) equal to unity.

Equation (3.4) has an important property; it only depends on v_x^2 and is thus symmetrical with respect to the vertical dotted line of figure 3.1. The probability of finding a particle with a certain positive or negative velocity is exactly equal; at any point in the gas the average number of particles with $v_x > 0$ is exactly the same as those with $v_x < 0$ and the same can be said for v_y and v_z .



Figure 3.1. The one dimensional velocity distribution function (3.4) for argon at different temperatures k_BT .

³We will use indistinctly the mathematical notations dv^3 and dv and $dv^3 = dv$.

Since $f_{mb}(\mathbf{v}) = f_{mb}(\mathbf{v}^2)$ we can easily transform the Maxwell–Boltzmann *velocity* distribution (3.5) into a *kinetic energy* distribution function. We can express the probability $dP = f_{mb}(\mathbf{v}) d\mathbf{v}$ in a more convenient way using spherical coordinates in equation (3.5) for the particle velocity and,

$$d^3v = v^2 \sin\theta \ d\theta \ d\phi \ dv$$

where θ and ϕ are the polar and azimuthal angles, respectively. Then,

$$dP = f_{mb}(\mathbf{v}) \, d\mathbf{v} = \left(\frac{m}{2\pi k_B T}\right)^{3/2} \exp\left(-\frac{m \, v^2}{2 \, k_B T}\right) v^2 \sin\theta \, d\theta \, d\phi \, dv$$

and the integration over θ and ϕ gives dP = f(v) dv where,

$$f_{mb}(v) = \left(\frac{m}{2\pi k_B T}\right)^{3/2} \exp\left(-\frac{m v^2}{2 k_B T}\right) (4\pi v^2)$$
(3.6)

The kinetic energy $E = mv^2/2$ transforms for $dP = f_{mb}(v) dv$ into $dP = g_{mb}(E) dE$ with,

$$g_{mb}(E) = \frac{2}{\sqrt{\pi}} \frac{\sqrt{E}}{(k_B T)^{3/2}} e^{-E/k_B T}$$
(3.7)

This Maxwell–Boltzmann energy distribution is equivalent to $f_{mb}(v)$ and $g_{mb}(E) dE$ and expresses the probability of finding a particle with kinetic energy within the range of E and E + dE since,

$$\int_0^\infty g_{mb}(E) dE = 1 \tag{3.8}$$

The function $g_{mb}(E)$ accounts for the three components of the speed and is represented in figure 3.2, it becomes wider for higher gas temperatures such as for $f_{mb}(v_x)$ in figure 3.1. The height of the maxima also decreases with T to hold the normalization integral (3.8) unchanged.



Figure 3.2. The energy distribution function (3.7) for different gas temperatures.

The probability distribution $g_{mb}(E)$ becomes wider and the maximum decreases with T to preserve the normalization (3.8) constant. This broadening of $f_{mb}(v_x)$ and $g_{mb}(E)$ in figures 3.1 and 3.2 shows the increasing number of energetic particles in the high energy tail of the Maxwell–Boltzmann distribution as the gas temperature grows.

The most probable velocity is the thermal speed,

$$v_{th} = \sqrt{\frac{2 k_B T}{m}} \tag{3.9}$$

mentioned above and corresponds to the maximum of the distribution function f(v) and that can also be calculated setting $(df_{mb}/dv)_{v_{th}} = 0$ in equation (3.6). The thermal velocity can be used to rewrite the Maxwell–Boltzmann velocity distribution (3.5) as,

$$f_{mb}(\mathbf{v}) = \left(\frac{1}{\pi^{3/2} v_{th}^3}\right) \exp\left(-v^2/v_{th}^2\right)$$

The probability distribution $g_{mb}(E)$ in figure 3.2 decreases rapidly for values $E > E_m$ over the energy $E_m > 0$ of the maximum and this *most probable energy* is $E_m = k_B T/2$ evaluating setting in equation (3.7),

$$\left(\frac{dG_{mb}}{dE}\right)_{E_m} = 0$$

3.3 Averaging over distributions

The kinetic theory relates the macroscopic physical properties of the thermodynamic equilibrium state of a neutral gas as the average of a physical quantity over a large number of molecules using the probability distribution function. Specifically, the Maxwell–Boltzmann distribution functions $f_{mb}(\mathbf{v})$ or $g_{mb}(E)$ can be employed to calculate a macroscopic property $H(\mathbf{v})$ of the system as the averages⁴,

$$\langle H(\mathbf{v}) \rangle = \int_{-\infty}^{+\infty} H(\mathbf{v}) f_{mb}(\mathbf{v}) d^3 \mathbf{v} \quad \text{or also,}$$

$$\langle H(E) \rangle = \int_{0}^{\infty} H(E) g_{mb}(E) dE \qquad (3.10)$$

and here $dP = f_{mb}(v) dv$ is the probability density and the integral of H(v) dP is the average of a physical magnitude. For example,

⁴These concepts will be generalized later.

$$\langle n \rangle = n_o \int_{-\infty}^{+\infty} f_{mb}(\mathbf{v}) d^3 \mathbf{v} = n_o$$
 and,
 $\langle n \rangle = n_o \int_{0}^{\infty} g_{mb}(E) dE = n_o$

is the spatially uniform number of particles n_o per volume unit in the thermodynamic equilibrium state. A further integration gives,

$$N_{a} = \int_{-\infty}^{+\infty} n_{o} d^{3}r = n_{o} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} f_{mb}(\mathbf{v}) d^{3}v d^{3}r$$

the total number of particles N.

Using equation (3.10) the probability distributions (3.5) and (3.7) relate the equilibrium gas temperature with the average kinetic energy $e_i = \langle m v^2/2 \rangle$ per particle

$$e_i = \langle m v^2/2 \rangle = \int_{-\infty}^{+\infty} f_{mb}(v) \left(\frac{mv^2}{2}\right) d^3v = \frac{3}{2} k_B T$$
 (3.11)

where $\langle m v_x^2/2 \rangle = k_B T/2$ is the equal contribution to e_i of each (v_x, v_y, v_z) component of the velocity. Equivalently,

$$e_i = \int_0^\infty E g_{mb}(E) dE = \frac{3}{2} k_B T$$

and $U_i = n_o e_i$ is the internal energy by volume unit of this ideal gas.

The root mean square speed (rms) defined as $v_R = \sqrt{\langle v^2 \rangle}$ is also related with the mean kinetic energy,

$$v_R^2 = \langle v^2 \rangle = \int_{-\infty}^{+\infty} v^2 f_{mb}(v) d^3 v$$

= $\int_{0}^{+\infty} f_{bm}(v) v^2 (4\pi v^2) dv = \left(\frac{3 k_B T}{m}\right)$ (3.12)

so that, $e_i = m v_R^2/2$. Additionally, the *mean thermal speed* $\bar{v} = \langle |v| \rangle = \langle v \rangle$ can be calculated using the probability distribution (3.6) as,

$$\bar{\mathbf{v}} = \langle \mathbf{v} \rangle = \int_{-\infty}^{+\infty} \mathbf{v} f_{mb}(\mathbf{v}) d^3 \mathbf{v}$$
$$= \int_{0}^{+\infty} f(\mathbf{v}) \mathbf{v} (4\pi \mathbf{v}^2) d\mathbf{v} = \left(\frac{8 k_B T}{\pi m}\right)^{1/2}$$
(3.13)

The energy $E_m = k_B T/2$ corresponding to the maximum of $g_{mb}(E)$ in figure 3.2 is below the kinetic energies $m \bar{v}^2/2$ and $m v_R^2/2$ for these velocities. The numerical expression for the thermal speed is calculated in the following box 3.2 as a function of the gas temperature T and the atomic number Z.

In the general case the drift velocities that characterize the macroscopic motion of gas molecules can be also defined from the averages (3.10). However, in the

Box 3.2. Average speeds

The relation between the temperatures is Kelvin and eV is $T [K] = 11\ 600 \times T [eV]$, the molecular mass is $m = Z \times M_{amu}$ where $M_{amu} = 1.66 \times 10^{-27}$ kg is the mass atom unit. For the mean thermal speed (3.13),

$$\bar{v}^{2} = \left(\frac{8 k_{B}T}{\pi m}\right) = \frac{8 \times (1.38 \times 10^{-23}) \times (1.6 \times 10^{4} \times T \text{ [eV]})}{3.14 \times (1.66 \times 10^{-27} \times Z)}$$
$$= 2.48 \times 10^{8} \frac{T \text{ [eV]}}{Z}$$

this gives,

$$\bar{v} = 1.57 \times 10^4 \sqrt{\frac{T \text{ [eV]}}{Z}} \text{ m s}^{-1}$$

and for the thermal speed (3.9) $v_{th} = \bar{v} \times (\sqrt{\pi}/2)$ we also have,

$$v_{th} = 1.39 \times 10^4 \sqrt{\frac{T \,[\text{eV}]}{Z}} \,\mathrm{m \ s^{-1}}$$

For argon gas at T = 300 K (0.026 eV) we obtain $\bar{v} = 399.5$ m s⁻¹ and $v_{th} = 353.7$ m s⁻¹.

thermodynamic equilibrium state of a gas described by the Maxwell–Boltzmann distribution there is no macroscopic transport of mass, kinetic energy or momentum.

For a fixed gas temperature, the average kinetic energy per particle $\langle m v^2/2 \rangle$ is positive because the gas molecules are in permanent motion. Nevertheless, if we calculate the average $\langle v_x \rangle$ of $v_x dP = v_x f_{mb}(v) dv$ along the direction X,

$$\langle v_x \rangle = \int_{-\infty}^{+\infty} v_x f_{mb}(\mathbf{v}) d^3 \mathbf{v} = \int_{-\infty}^{+\infty} v_x f_{mb}(v_x) dv_x = 0$$

because $v_x f_{mb}(v_x)$ is an odd function. In other words, figure 3.1 shows the probabilities of finding a molecule with speeds $v_x > 0$ and $v_x < 0$ are equal and thus the average over all possible particle speeds v_x is zero, and we also have,

$$\langle v_x \rangle = \langle v_x \rangle = 0$$

as was assumed in the derivation of the Maxwell-Boltzmann distribution.

Furthermore, because the X-axis points along an arbitrary direction, we conclude that the average speed of gas molecules along *any* straight line drawn into the gas volume is null. This property means there is no privileged direction for the motion of particles in the state of thermodynamic equilibrium of a gas.

Using the velocity distribution (3.4) we can calculate the average velocity $\overline{v_x} > 0$ of particles *with positive speeds* integrating only for $v_x > 0$,



Figure 3.3. The random flux of particles with $v_x > 0$ through the (Y, Z) plane.

$$\overline{v_x} = \int_0^\infty v_x \, dP = \int_0^\infty v_x f(v_x) \, dv_x = \left(\frac{k_B T}{2 \pi m}\right)^{1/2}$$

This new characteristic velocity $\overline{v_x}$ defines *the random flux of gas particles*⁵ $\Gamma_x = n_o \overline{v_x}$ crossing an infinite plane (Y, Z) perpendicular to the X-axis. This situation is illustrated figure 3.3 where gas particles move randomly but only those with $v_x > 0$ (blue arrows) contribute to the speed $\overline{v_x}$ and then to the flux Γ_x of particles with $v_x > 0$ crossing the plane (Y, Z) represented by the vertical dotted line.

Moreover, using the average,

$$\langle |v_x| \rangle = \int_{-\infty}^{+\infty} |v_x| f(\mathbf{v}) d^3 \mathbf{v} = 2 \int_{0}^{+\infty} v_x f(\mathbf{v}) d^3 \mathbf{v} = \left(\frac{2k_B T}{\pi m}\right)^{1/2} = 2 \overline{v_x}$$

we obtain for the flux Γ_x

$$\Gamma_x = n_o \ \overline{v_x} = \frac{1}{2} \ n \ \langle |v_x| \rangle = \frac{1}{4} \ n_o \ \overline{v}$$

where the factor 1/2 accounts for the two particle motions considered in the average $\langle |v_x| \rangle$. Again, the direction of the *X*-axis is arbitrary and we can generalize the vector $\Gamma = n_o \overline{v_n} \mathbf{n}$ as the random flux of gas particles along the direction indicated by the unit vector \mathbf{n} .

This principle has several applications, the following example in box 3.3 makes use of this random flow to calculate the *effusion* leak of molecules. The isothermal pressure drop inside the container can be also employed to determine the molecular mass of a gas, as shown in box 3.4.

These principles and the distribution functions (3.5) and (3.7) can also be used to describe the equilibrium of non-chemically reactive gases composed of different molecules. Molecular collisions transfer energy between both gaseous species and the equilibrium state of the system has a common temperature T, although the

⁵ The number of gas molecules by unit of time and surface area.

Box 3.3. Molecular effusion

Consider the box of volume V of figure 3.4 which contains a gas at equilibrium with a small hole connected to a vacuum. The diameter $d = 2 R \leq \lambda_c$ of this hole is smaller or comparable with mean free path λ_c of gas molecules inside. This flux of molecules cannot be treated as a continuum and it is not governed by fluid transport equations.



Figure 3.4. Effusion.

The particles have a density n_o inside the box and after passing through the hole do not return. There is no molecules with speeds $v_x < 0$ at the orifice and integrating the velocity distribution (3.5),

$$\langle v \rangle = \int_{-\infty}^{+\infty} dv_z \int_{-\infty}^{+\infty} dv_y \int_{0}^{+\infty} v_x f_{mb}(\mathbf{v}) dv_x = \left(\frac{k_B T}{2 \pi m}\right)^{1/2}$$

The flux $\Gamma = n_o \langle v \rangle = n_o \bar{v}/4$ represents the number of molecules exiting per unit time per unit area through the hole. The average $\langle n_o m v \rangle$ gives the mass flux density $n_o m \bar{v}_x = \rho \bar{v}/2$ where $\rho = m n_o$ is the gas density in the box.

Using $\Gamma = n_o \bar{v}_x$ we can estimate the number of molecules leaking through the surface of area A. For argon (Z = 40) at temperature T = 300 K and we have,

$$\Gamma = n_o \times \frac{\bar{v}}{4} = (2.42 \times 10^{16} \times p \text{ [mbar]}) \times \left(\frac{(4.0 \times 10^4)}{4}\right)$$
$$= 2.42 \times 10^{20} \times p \text{ [mbar]}$$

particles per second and per square centimeter. For a circular hole of 1 mm in diameter (r = 0.05 cm) the number of lost particles by second is,

$$\frac{dN}{dt} = A \times \Gamma = (\pi \times 2.5 \times 10^{-3}) \times (2.42 \times 10^{20} \times p \text{ [mbar]})$$
$$= 1.9 \times 10^{17} \times p \text{ [mbar]}$$

This represents a huge number of particles even for pressures inside the box as low as 10^{-6} mbar.

characteristic velocities (3.9) or (3.13) will be different for each type of particle according to its molecular mass.

3.4 Rate constant and collision frequencies

The collision frequencies for a single particle ν_c (2.3) and total ν_{ab} (2.4) have been introduced in section 2.2 assuming that all colliding particles have the same relative

Box 3.4. Gas leak rate

The number of molecules lost by time unit leaking from the box in figure 3.4 is,

$$\frac{dN}{dt} = A \times \Gamma = A \times n_o \times \bar{v}_x = A \times \frac{p}{k_B T} \times \left(\frac{k_B T}{2 \pi m}\right)^{1/2} = \frac{A \times p}{(2\pi m k_B T)^{1/2}}$$

where $A = \pi R^2$ is the area of the hole and p the pressure inside the box. Assuming the drop of pressure inside is isothermal,

$$\frac{dp}{dt} = -\frac{d}{dt} \left(\frac{Nk_B T}{V} \right) = \frac{k_B T}{V} \times \frac{dN}{dt} < 0$$

where the negative sign accounts for the decrease in p as molecules leak. We obtain the following differential equation for the pressure drop,

$$\frac{dp}{dt} = A \frac{p}{V} \left(\frac{k_B T}{2 \pi m} \right)^{1/2} = A \bar{v}_x \text{ pand}, \ p(t) = p_o e^{-t/\tau_o}$$

where $p_o = n_o k_B T$ and $\tau_o = V \bar{v}_x / A$ is a characteristic time. Plotting $\ln p(t)$ inside the box against *t* the slope $1/\tau_o$ permits us to determine the molecular mass *m* as long as the temperature *T* in the box remains constant. In the case where we have a solid sample inside the container the measurement of $\ln p_o$ yields the vapor pressure of this substance.

speed. Both concepts can be generalized for encounters between atoms or molecules with a generic velocity distribution f(v) such as (3.7) to consider the effects of thermal motion.

Two particle species *a* and *b* have the *effective interaction surface* $\sigma_{ab} = \pi (r_a + r_b)^2$ introduced in section 2.2. Here we consider a number of *target* particles⁶ per unit volume $dn_b = n_{ob} f_b(\mathbf{u}_b) d\mathbf{u}_b$ with velocities between \mathbf{u}_b and $\mathbf{u}_b + d\mathbf{u}_b$ moving with relative speed $|\mathbf{v}_a - \mathbf{u}_b|$ with respect to a single *a* projectile particle with velocity \mathbf{v}_a . During the time interval δt the *a* particle sweeps a cylinder of length $\delta t \times |\mathbf{v}_a - \mathbf{u}_b|$ and cross sectional area ν_{ab} , as shown in figure 3.5.

The number of collision events of the *a* projectile $\delta \nu_a(\mathbf{v}_a) \times \delta t$ equals the number of *b* targets contained inside the cylinder of figure 3.5. This quantity is given by the product of its volume $\sigma_{ab} \times |\mathbf{v}_a - \mathbf{u}_b| \, \delta t$ by dn_b ,

$$\delta \nu_a(\mathbf{v}_a) \times \delta t = (\sigma_{ab} \times |\mathbf{v}_a - \mathbf{u}_b| \times \delta t) \times (n_{ob} f_b(\mathbf{u}_b) d\mathbf{u}_b)$$

The integration over all possible velocities u_b of target particles gives the number of collisions by a single projectile a per unit of time with the background of b particles,

⁶ For simplicity we will write $du_b = d^3u_b = du_{bx} du_{by} du_{bz}$ and equivalently $du_a = d^3u_a$. The integrals are extended over all possible values $-\infty < u_{ax} < +\infty$ of the speed components (u_{ax}, u_{ay}, u_{az}) .



Figure 3.5. Scheme of molecular collisions.

$$\langle \nu_a(\mathbf{v}_a) \rangle = n_{ob} \int_{-\infty}^{+\infty} \sigma_{ab} |\mathbf{v}_a - \mathbf{u}_b| f_b(\mathbf{u}_b) d\mathbf{u}_b$$
 (3.14)

This expression generalizes equation (2.3) by considering the velocity distribution $f_b(\mathbf{u}_b)$ of target particles colliding with a single projectile molecule.

However, the incident particles do not always have a fixed speed v_a and the effects of its velocity distribution must be considered. The equation (2.4) for the *total* collision frequency v_{ab} between a and b species can be also extended to account for the velocity spread of projectile a molecules.

Now, the quantity of incoming particles is $dn_a = n_{oa} f_a(\mathbf{u}_a) d\mathbf{u}_a$ with velocities in the range $(\mathbf{u}_a, \mathbf{u}_a + d\mathbf{u}_a)$ moving with relative speed $|\mathbf{u}_a - \mathbf{u}_b|$ with respect to the target particles. The number of collision events between both species in the unit of time is,

$$\delta \nu_{ab} = \langle \nu_a(\boldsymbol{u}_a) \rangle \times \left(n_{oa} \times f_a(\boldsymbol{u}_a) \, d\boldsymbol{u}_a \right)$$

and the integration over all possible velocities u_a of projectile molecules gives,

$$\langle \nu_{ab} \rangle = n_{oa} n_{ob} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \sigma_{ab} |\boldsymbol{u}_{a} - \boldsymbol{u}_{b}| f_{a}(\boldsymbol{u}_{a}) f_{b}(\boldsymbol{u}_{b}) d\boldsymbol{u}_{a} d\boldsymbol{u}_{b}$$
(3.15)

This expression generalizes the equation (2.4) and accounts for the velocity distributions of both target and projectile particles.

So far the *interaction surface* $\sigma_{ab} = \pi (r_a + r_b)^2$ in equation (3.15) only depends on the radii (r_a, r_b) of colliding particles and can be understood as the *effective length of interatomic forces* (see figure 2.3). We will generalize this concept in chapters 5 and 6 where this *effective interaction surface* will be denominated *total cross section* $\sigma_T(|u_a - u_b|)$ which usually is an experimentally determined magnitude and depends on the relative velocity $|u_a - u_b|$ of colliding particles.

At this point the above formula (3.15) can be generalized simply as,

$$\langle \boldsymbol{\nu}_{ab} \rangle = n_{oa} \, n_{ob} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \sigma_T(|\boldsymbol{u}_a - \boldsymbol{u}_b|) \, |\boldsymbol{u}_a - \boldsymbol{u}_b| f_a(\boldsymbol{u}_a) f_b(\boldsymbol{u}_b) \, d\boldsymbol{u}_a \, d\boldsymbol{u}_b \qquad (3.16)$$

or equivalently $\langle \nu_{ab} \rangle = n_{oa} n_{ob} \langle K_{ab} \rangle$ where,

$$\langle K_{ab} \rangle = \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \sigma_T(|\boldsymbol{u}_a - \boldsymbol{u}_b|) |\boldsymbol{u}_a - \boldsymbol{u}_b| f_a(\boldsymbol{u}_a) f_b(\boldsymbol{u}_b) d\boldsymbol{u}_a d\boldsymbol{u}_b$$
(3.17)

is the *rate constant* or *reaction rate* of the collisional process. Equations (3.16) and (3.17) generalize equations (2.3) and (2.4) accounting for the velocity distribution functions $f_a(\mathbf{u}_a)$ and $f_b(\mathbf{u}_b)$ of both particle species.

Equation (2.4) for ν_{ab} is recovered from equation (3.16) in the thermodynamic equilibrium state where $f_a(\mathbf{u}_a)$ and $f_b(\mathbf{u}_b)$ are Maxwell–Boltzmann distributions (3.5). For constant total cross section $\sigma_T(|\mathbf{u}_a - \mathbf{u}_b|) \simeq \sigma_{ab}$ in the limit of low target particle velocities $|\mathbf{u}_a - \mathbf{u}_b| \simeq u_b$ we have,

$$\langle \boldsymbol{\nu}_{ab} \rangle = n_{oa} \ n_{ob} \ \sigma_{ab} \times \left(\int_{-\infty}^{+\infty} f_{mb}(\boldsymbol{u}_a) \ d\boldsymbol{u}_a \right) \times \left(\int_{-\infty}^{+\infty} u_b f_{mb}(\boldsymbol{u}_b) \ d\boldsymbol{u}_b \right)$$
$$= \sigma_{ab} \ n_{oa} \ n_{ob} \ \bar{\boldsymbol{v}}_b$$

the first integral is the unity, the second is the *mean thermal speed* of equation (3.13) for projectile particles. This low target particle speed approximation implicitly assumes that $m_a \gg m_b$ so that $\bar{v}_a \ll \bar{v}_b$ because the temperatures of species in $f_{mb}(\boldsymbol{u}_b)$ and $f_{mb}(\boldsymbol{u}_b)$ are equal in the thermodynamic equilibrium.

The above approximation is no longer valid when particles have comparable masses and, using equation (3.5) the rate constant (3.17) in the thermal equilibrium is,

$$\langle K_{ab} \rangle (T) = \sigma_{ab} \frac{(m_a \ m_b)^{3/2}}{(2\pi k_B T)^3} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} |\mathbf{v}_a - \mathbf{v}_b| e^{-m_a \mathbf{v}_a^2/2k_B T} e^{-m_b \mathbf{v}_b^2/2k_B T} d\mathbf{v}_a \ d\mathbf{v}_a$$

The kinetic energy can be expressed in terms of the relative $V_r = v_a - v_b$ and the center of mass $V_{CM} = (m_a v_a + m_b v_b)/(m_a + m_b)$ velocities as,

$$E_k = \frac{m_a v_a^2}{2} + \frac{m_b v_b^2}{2} = \frac{M_{ab}}{2} V_{CM}^2 + \frac{\mu_{ab}}{2} V_r^2$$

where $\mu_{ab} = m_a m_b / (m_a + m_b)$ is the reduced mass $M_{ab} = m_a + m_b$ and $dv_a dv_b = dV_{CM} dV_r$. Therefore,

$$\langle K_{ab} \rangle(T) = \sigma_{ab} \frac{(m_a \ m_b)^{3/2}}{(2\pi k_B T)^3} \left[\int_{-\infty}^{+\infty} e^{-M_{ab} V_{CM}^2 / 2k_B T} dV_{CM} \right]$$
$$\times \left[\int_{-\infty}^{+\infty} V_r e^{-\mu_{ab} V_r^2 / 2k_B T} dV_r \right]$$

with the first integral,

$$\int_{0}^{2\pi} d\theta \int_{0}^{\pi} \sin \varphi \, d\varphi \, \int_{0}^{\infty} V_{CM}^{2} e^{-M_{ab}V_{CM}^{2}/2k_{B}T} dV_{CM} = \left(\frac{2\pi k_{B}T}{M_{ab}}\right)^{3/2}$$

The second integral involving the relative velocity becomes,

$$4\pi \int_{o}^{\infty} V_{r}^{3} e^{-\mu_{ab} V_{r}^{2}/2k_{B}T} dV_{r} = 8\pi \left(\frac{k_{B}T}{\mu_{ab}}\right)^{2}$$

and finally,

$$\langle K_{ab} \rangle (T) = \sigma_{ab} \frac{(m_a \ m_b)^{3/2}}{(2\pi k_B T)^3} \left[\left(\frac{2\pi k_B T}{M_{ab}} \right)^{3/2} \right] \\ \times \left[8\pi \left(\frac{k_B T}{\mu_{ab}} \right)^2 \right] = \sigma_{ab} \left(\frac{8k_B T}{\mu_{ab}} \right)^{1/2}$$

In this case, the reaction rate constant only depends on the gas temperature and,

$$\left(\frac{8k_BT}{\pi \ \mu_{ab}}\right)^{1/2} = \left(\frac{8k_BT}{\pi \ m_a} + \frac{8k_BT}{\pi \ m_b}\right)^{1/2} = (\bar{v}_a + \bar{v}_b)^{1/2}$$

In the limit where $m_a \gg m_b$ we have $\mu_{ab} \simeq m_b$ and we recover ν_{ab} as in equation (2.4). When both molecules are alike $m_a \simeq m_b$ we have,

$$\langle K_{ab} \rangle (T) = \sqrt{2} \ \bar{v}_a$$
 and therefore $\langle \nu_{ab} \rangle = n_{oa} \ n_{ob} \ \sigma_{ab} \ \sqrt{2} \ \bar{v}_a$

Therefore, the consideration of *thermal effects for both molecular species* introduces a factor $\sqrt{2}$ with respect to ν_{ab} in the phenomenological expression (2.4).

So far we have considered a constant total cross section $\sigma_T(|v_a - v_b|) \simeq \sigma_{ab}$ in equation (3.17) which implicitly models the molecular encounter similarly to the elastic collision of two spherical billiard balls⁷. The interaction takes place only when particles are in contact and this situation is not always physically realistic. The long-range nature of intermolecular forces decreases with a power of the interatomic distance and cross sections are functions of the relative velocity of colliding particles in the general case.

3.5 The neutral gas in a force field

The Maxwell–Boltzmann probability distributions $f_{mb}(\mathbf{v})$ and $g_{mb}(E)$ do not consider the gas under external forces that break the spatial symmetry of the thermodynamic equilibrium state. The energy of a molecule is $E = mv^2/2 + V(\mathbf{r})$ when the force $\mathbf{F}(\mathbf{r}) = -\nabla V$ can be derived from the scalar potential $V(\mathbf{r})$ and this introduces in equations (3.5) and (3.7) the *Boltzmann factor* $e^{-V(\mathbf{r})/k_B T}$ and,

$$n(E) dE = n_o \frac{2}{\sqrt{\pi}} \frac{\sqrt{E}}{(k_B T)^{3/2}} \exp\left(-\frac{E + V(\mathbf{r})}{k_B T}\right)$$

is the number of molecules by unit volume with energy between E and E + dE, a similar expression can be derived for equation (3.5). The integration over the kinetic energy E leads to,

$$n(\mathbf{r}) = n_o e^{-V(\mathbf{r})/k_B T}$$

and in this case the molecules are not uniformly distributed in space. For the Earth, gravitational field $n(h) = n_o \exp(-m g_o h/k_B T)$ where g_o is the standard acceleration

 $^{^{7}}$ The kinematics of binary encounters and the elastic collisions between two hard spheres are discussed in appendix A.

and $n(0) = n_o$ is the particle density at the ground level (h = 0) decreasing with the height *h*. However, the temperature of the system is uniform and most macroscopic properties of thermodynamic equilibrium still hold.

In the laboratory scale this effect is negligible and the distribution of particles can be considered uniform, but it is important when modeling gases on terrestrial or planetary scales.

3.6 Equipartition of energy

The *equipartition energy theorem* states that each degree of freedom having a quadratic term in velocity or coordinates in the expression of the energy of the system contributes to the average thermal energy with a factor $k_BT/2$ in the thermodynamic equilibrium. An important conclusion is that the average energy of all degrees of freedom of the system *only depends on the temperature of the system*.

For example, for a monoatomic gas $E = m (v_x^2 + v_y^2 + v_z^2)/2$ and using the velocity distribution function (3.5) we calculated the average energy per particle (3.11),

$$\begin{split} \langle E \rangle &= \int_{-\infty}^{+\infty} \left(\frac{m v_x^2}{2} \right) f_{mb}(v_x) \, dv_x + \int_{-\infty}^{+\infty} \left(\frac{m v_y^2}{2} \right) f_{mb}(v_y) \, dv_y \\ &+ \int_{-\infty}^{+\infty} \left(\frac{m v_z^2}{2} \right) f_{mb}(v_z) \, dv_z \end{split}$$

The three integrals are equal and,

$$\langle E \rangle = \frac{k_B T}{2} + \frac{k_B T}{2} + \frac{k_B T}{2} = \frac{3}{2} k_B T$$

the thermal energy is equally distributed in the state of equilibrium between the three possible translational speeds for molecular motion according to energy equipartition theorem,

$$\left\langle \frac{m}{2} v_x^2 \right\rangle = \left\langle \frac{m}{2} v_y^2 \right\rangle = \left\langle \frac{m}{2} v_z^2 \right\rangle = \frac{k_B T}{2}$$

In polyatomic gases, thermal energy is also shared by vibrational and/or rotational degrees of freedom that also have a quadratic dependence on the interatomic distance q or the angular velocity ω because, respectively, $E = \kappa q^2/2$ and $E = I \omega^2/2$, where I is the moment of inertia of the molecule.

We will not demonstrate here this powerful concept of classical statistical mechanics that will be illustrated by means of an example. As in section 3.5 we consider the force $F_z = -\kappa z$ acting over the mass *m* that is immersed in a gas. We are only interested in the motion along the direction *Z* where the harmonic oscillator moves, because by symmetry $\langle x \rangle = \langle y \rangle = 0$ as the gas molecules hit it on average equally along both *X* and *Y* directions.

The kinetic energy is $m v_z^2/2$ and its potential energy $\kappa z^2/2$ contributes with a quadratic term to the total energy at any instant,

$$E = \frac{m v_z^2}{2} + \frac{\kappa z^2}{2}$$

The molecular collisions keep the mass in thermal equilibrium with the gas which acts as a *thermal bath* at temperature T. Using equation (3.5) the velocity distribution becomes,

$$f(z, v_z) = Ae^{-E/k_BT} = A \exp\left(-\frac{m v_z^2}{2k_B T}\right) \exp\left(-\frac{\kappa z^2}{2 k_B T}\right)$$

The constant A is determined by the normalization,

$$A \int_{-\infty}^{+\infty} e^{-(m v_z^2/2k_B T)} dv_z \int_{-\infty}^{+\infty} e^{-(\kappa z^2/2k_B T)} dz = 1$$

which gives,

$$A = \left(\frac{m}{2\pi k_B T}\right)^{1/2} \left(\frac{\kappa}{2\pi k_B T}\right)^{1/2}$$

Finally, the distribution function has two arguments,

$$f(z, v_z) = \left(\frac{m}{2\pi k_B T}\right)^{1/2} \left(\frac{\kappa}{2\pi k_B T}\right)^{1/2} \exp\left(-\frac{m v_z^2}{2k_B T}\right) \exp\left(-\frac{\kappa z^2}{2 k_B T}\right)$$

which depend on the particle speed v_z and the coordinate z. The distribution $f(z, v_z)$ can be seen as the natural extension of the equilibrium Maxwell–Boltzmann distribution $f_{mb}(v)$ to a non-uniform system. The force F_z breaks the equilibrium along Z and therefore, the probability of finding m with speed within the range $(v_z, v_z + dv_z)$ also depends on this spatial coordinate. The kinetic theory makes use of more general distribution functions f(r, v, t) that apply to non-equilibrium systems.

The average energy along the Z direction is given by,

$$\langle E \rangle = \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} E f(v_z) \, dv_z \, dz$$

= $A \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \left(\frac{m v_z^2}{2} + \frac{\kappa z^2}{2} \right) f(v_z) \, dv_z \, dz$

and then,

$$\langle E \rangle = A \int_{-\infty}^{+\infty} \left(\frac{m \ v_z^2}{2} \right) e^{-(m \ v_z^2/2k_B T)} dv_z \int_{-\infty}^{+\infty} e^{-(\kappa \ z^2/2k_B T)} dz$$

$$+ A \int_{-\infty}^{+\infty} e^{-(m \ v_z^2/2k_B T)} dv_z \int_{-\infty}^{+\infty} \left(\frac{\kappa \ z^2}{2} \right) e^{-(\kappa \ z^2/2k_B T)} dz$$

$$(3.18)$$

The first term is the equation (3.11) in one dimension, the kinetic energy weighted with Maxwell–Boltzmann distribution $f_{mb}(v_z)$ and represents the average kinetic

energy of the oscillator. The second term is the average potential energy along all possible values of z. We finally obtain,

$$\langle E \rangle = \left\langle \frac{m v_z^2}{2} \right\rangle + \left\langle \frac{\kappa z^2}{2} \right\rangle = \frac{k_B T}{2} + \frac{k_B T}{2} = k_B T$$

As we can, see this result for the harmonic oscillator is a special case of the general equipartition of energy theorem.

3.7 Commentaries and further reading

So far we have not considered the rotational and vibrational motions of molecules that, by the principle of equipartition also share part of the energy. More general distributions can be introduced to account for these additional degrees of freedom. The fundamental concepts discussed in this chapter can be found in a number of references. The complete discussion of equilibrium kinetic theory is in chapter 2 of [1] and the equipartition theorem is rigorously demonstrated in section 6.4 in reference [2]. Chapters 3 and 8 of the book [3] contain further information on the reaction rate in connection to molecular collisions between charged particles. The monograph [4] contains a through approach to these subjects in connection to plasma collision phenomena.

References

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