

CHAPTER 2

The Non-Equilibrium Equations and the Relaxation of the Internal Degrees of Freedom

2.1 Introduction

In the next Section the Boltzmann equation, i.e. the equation to which the non-equilibrium distribution function of the molecules must satisfy, is considered. Rather than develop a derivation of such an equation, which can be found in many books [2, 3, 6], we have preferred to consider some rigorous properties of its solution. Next, we have introduced the equation of Wang Chang and Uhlenbeck, i.e. the equations to which the distribution function of each internal quantum state of the molecules must satisfy. Then, by assuming the hypothesis of an “*extreme dilution*” of the molecules in an isothermal bath, the system of Master equations is derived. Such equations are then applied to the vibrational and rotational relaxation of molecules.

2.2 The Boltzmann Transport Equation

We shall complete the elements of the kinetic theory of gases discussed in the preceding chapter by considering the Boltzmann transport equation. This equation is applicable to binary collisions between molecules deprived of internal degrees of freedom when the average time $\langle \tau \rangle$ between two collisions [see Eq. (1.9.5)] is much greater than the duration of the collision τ_c [see the next Eq. (2.4.2)]. This is equivalent to saying that the collisions are well-defined space-time events, or that there is no overlap between the two successive collisions involving a given molecule. For a gas in a non-equilibrium condition, we now introduce the distribution function defined as [1]

$$f(\mathbf{r}, \mathbf{v}, t) d^3r d^3v, \quad (2.2.1)$$

so that it gives the number of molecules that, at the time t , have positions lying within the volume element d^3r about \mathbf{r} and the velocities lying within the

volume element d^3v of velocity-space about \mathbf{v} . The general equation satisfied by the function $f(\mathbf{r}, \mathbf{v}, t)$ is written [2,3]

$$\left(\frac{\partial}{\partial t} + \mathbf{v} \cdot \Delta_{\mathbf{r}} + \frac{\mathbf{F}}{m} \cdot \Delta_{\mathbf{v}}\right) f(\mathbf{r}, \mathbf{v}, t) = \left(\frac{\partial f}{\partial t}\right)_{coll}. \quad (2.2.2)$$

In this equation the first two terms on the left-hand side (l.h.s.) member represent the local time variation and the convective variation of the function f respectively. The third term gives the rate of variation of f due to the external force \mathbf{F} acting on the molecules of mass m . Finally, the right hand side (r.h.s.) member of Eq. (2.2.2) gives the rate of variation of f due to the collisions. The calculation of this term involves the detailed analysis of the binary collisions and the explicit form of the Eq. (2.2.2) for $\mathbf{F}=0$ is written [4]

$$\left(\frac{\partial}{\partial t} + \mathbf{v}_1 \cdot \nabla_{\mathbf{r}}\right) f_i(\mathbf{r}, \mathbf{v}_1, t) = \iint (f'_2 f'_1 - f_2 f_1) g_{12} \cdot I(g_{12}, \theta, \varphi) d^2\Omega d^3v_2, \quad (2.2.3)$$

where $I(g, \theta, \varphi)$ is the “*differential cross section*” in the centre of the mass frame of the colliding molecules, and θ, φ are the angles specifying the direction of the vector $\mathbf{g}'_{12} = (\mathbf{v}'_2 - \mathbf{v}'_1)$ in a spherical polar coordinates system whose polar axis is established by the direction of the vector $\mathbf{g}_{12} = (\mathbf{v}_1 - \mathbf{v}_2)$. Here \mathbf{v}_1 and \mathbf{v}_2 (\mathbf{v}'_1 and \mathbf{v}'_2) are the velocities of the molecules before (*after*) the collision. Hence, we have

$$f_i = f(\mathbf{r}, \mathbf{v}_i, t), \quad f'_i = f(\mathbf{r}, \mathbf{v}'_i, t), \quad (i = 1, 2)$$

and $d^2\Omega = \sin\theta d\theta d\varphi$.

Some rigorous properties of the Boltzmann equation follow from the fact that in any molecular collision there are some conserved dynamical quantities, $\chi(\mathbf{v})$ being one of these quantities associated to a molecule of velocity \mathbf{v} such that for every collision $(\mathbf{v}_1, \mathbf{v}_2) \rightarrow (\mathbf{v}'_1, \mathbf{v}'_2)$ we have

$$\chi(\mathbf{v}_1) + \chi(\mathbf{v}_2) = \chi(\mathbf{v}'_1) + \chi(\mathbf{v}'_2).$$

Hence we can assume $\chi(v)$ to be an “*invariant of binary collisions*”. The following theorem can be demonstrated [5]:

$$\int \chi(\mathbf{v}) \left(\frac{\partial f}{\partial t}\right)_{coll} d^3v = 0. \quad (2.2.4)$$

It must be remembered that the conservation equation for a collisional invariant $\chi(v)$ can be obtained by multiplying both the members of Eq. (2.2.2) by $\chi(\mathbf{v})$ and then by integrating over \mathbf{v} . The collision term then vanishes by virtue

of Eq. (2.2.4). By this procedure, setting successively $\chi = m$, $\chi = mv_i$, $i = (1, 2, 3)$, $\chi = (1/2)m(v - \langle v \rangle)^2$, we obtain the equation not only for the conservation of mass but also for the components of the momentum, and the thermal energy. A very important method for obtaining an approximate solution of the Boltzmann equation is the “*method of moments*”. This will be described in detail in Chap. 9. Then, it can be demonstrated that, when the distribution function does not depend on r and t and $\mathbf{F} = 0$, the solution of Eq. (2.2.2) coincides with the Maxwell distribution [Eq. (1.8.3)] [6]. In non-equilibrium situations, in order to obtain the time dependent distribution function, it is necessary to solve Eq. (2.2.2) with the assigned initial conditions. In view of future developments we report the expression in spherical coordinates (r, θ, φ) of Eq. (2.2.2). For a stationary flow ($\partial f / \partial t = 0$), and in absence of external force ($\mathbf{F} = 0$), we have [7]

$$v_r \frac{\partial f}{\partial r} + \frac{v_\varphi}{r \sin \theta} \frac{\partial f}{\partial \varphi} + \frac{v_\theta}{r} \frac{\partial f}{\partial \theta} + \frac{v_\varphi^2 + v_\theta^2}{r} \frac{\partial f}{\partial v_r} +$$

$$- \left(\frac{v_\varphi v_\theta}{r} \cotan \theta + \frac{v_r v_\varphi}{r} \right) \frac{\partial f}{\partial v_\varphi} + \left(\frac{v_\varphi^2}{r} \cotan \theta - \frac{v_r v_\theta}{r} \right) \frac{\partial f}{\partial v_\theta} = \left(\frac{\partial f}{\partial t} \right)_{coll}. \quad (2.2.5)$$

2.3 The Wang Chang–Uhlenbeck and the Master Equations

The Boltzmann transport equation can be generalised in order to treat the evolution of the internal (i.e. *vibrational and rotational*) states of the molecules [8,9]. While the translations can be treated classically, the internal motions must be quantized. For each quantum state i (the index i can indicate the whole set of quantum numbers necessary to specify the internal state of the molecule), it is necessary to introduce its own distribution function $f_i(\mathbf{r}, \mathbf{v}, t)$, and this must satisfy its own Boltzmann equation. The generalised (*semiclassical*) form of such an equation (Wang Chang–Uhlenbeck) is written [8,9,10]

$$\left(\frac{\partial}{\partial t} + \mathbf{v}_i \cdot \nabla_{\mathbf{r}} \right) f_i = \sum_{j,k,l} \iint (f'_k f'_l - f_i f_j) g_{ij} I_{ij}^{kl}(g_{ij}, \theta, \varphi) d^2 \Omega d^3 v_j. \quad (2.3.1)$$

In this case, the binary anelastic collisions change not only the velocities of the two collisional partners but also their internal quantum states according to the scheme

$$[(\mathbf{v}_i, i), (\mathbf{v}_j, j)] \rightarrow [(\mathbf{v}'_k, k), (\mathbf{v}'_l, l)],$$

where \mathbf{v}_α is the velocity of the molecule in the internal state α and the apex is introduced to indicate the quantities after the collision. By indicating as E_α the internal energy of the molecule in the state α ($\alpha = i, j, k, l$), the energetic balance in the anelastic collision is written

$$(E_k + E_l) - (E_i + E_j) = -\Delta E_{kin}, \quad (2.3.2)$$

or the variation of the kinetic energy of the couple of molecules is equal and opposite to the variation of their internal energy. Moreover, in Eq. (2.3.1), g_{ij} is the relative velocity of the molecules entering in collision ($\mathbf{g}_{ij} = \mathbf{v}_i - \mathbf{v}_j$) and $I_{ij}^{kl}(\mathbf{g}, \theta, \varphi)$ is the differential cross-section of the above-considered process. This is a function of the relative velocity g_{ij} and of the angles θ, φ individuating the solid angle $d\Omega$ inside which the molecules in the state j are diffused.

For future developments it is useful to specialise Eq (2.3.1) for the case of anelastic collisions between molecules M endowed of internal states counter-signed by a single quantum number i and “atoms” A (or *inert molecules*, i.e. *those that are not undergoing variations of their internal state*). The atoms A can only exchange their kinetic energy with the molecules M . We shall suppose that the “active” molecules M are “*extremely diluted*” in the gas of “atoms” A (*hypothesis of the extreme dilution*). The scheme of the collisions is now the following: $[(\mathbf{v}_i, i), \mathbf{v}] \rightarrow [(\mathbf{v}_k, k), \mathbf{v}']$, and the energetic balance becomes

$$(E_k - E_i) = -\Delta E_{kin}, \quad (2.3.3)$$

with the same meaning of ΔE_{kin} .

The consequence of the hypothesis of the “*extreme dilution*” (or the “*infinite thermal bath*”) is that the energetic exchanges between M and A do not influence the temperature of the gaseous mixture. Hence, the relaxation of the internal energy of the active molecules M can be considered as “*isotherm*”. The distribution of the velocity \mathbf{v}_a of the inert molecules of the thermal bath will be assumed as Maxwellian characterised by a constant translational temperature T_A and a density n_A , that is

$$f_A(\mathbf{v}_A, T_A) = n_A (m_A / 2\pi k_B T_A)^{3/2} e^{-\frac{m_A v_A^2}{2k_B T_A}}.$$

Because of the previous hypothesis we can write

$$n = \sum_i n_i = \sum_i \int f_i d^3v \ll \int f_A(v_A, T_A) d^3v_A = n_A,$$

where n_i is the density of the molecules in the state i , and n the total density of the molecules M . Assuming the space homogeneity of the gas ($\nabla_r f_i = 0$), Eq. (2.3.1) becomes [$f'_i = f_i = f_A$]

$$\frac{\partial f_i}{\partial t} = \sum_k \iint (f'_k f_A - f_i f_A) g I_i^k(g, \theta, \varphi) d^2\Omega d^3v_A, \quad (2.3.4)$$

($i=0,1,2,\dots$).

After multiplication of both the members of Eq. (2.3.4) by d^3v_i and integration, we obtain

$$\frac{\partial}{\partial t} \int f_i d^3v_i = \sum_k \left[\iiint f'_k f_A g I_i^k d^2\Omega d^3v_A d^3v_i - \iiint f_i f_A g I_i^k d^2\Omega d^3v_A d^3v_i \right].$$

Let us now pose in the first integral of the r.h.s. member of the previous equation the following [11]:

$$I_i^k = I_k^i, \quad d^3v_A d^3v_i = d^3v_A d^3v'_k.$$

By integration over the scattering angles θ and φ , we obtain the “integral cross-section” σ_α^β (cm²) expressed by

$$\sigma_\alpha^\beta = \int I_\alpha^\beta d^2\Omega = \iint I_\alpha^\beta \sin\theta d\theta d\varphi.$$

With the previous results we can write

$$\frac{\partial n_i}{\partial t} = \sum_k \left[\iint f'_k f_A g \sigma_k^i d^3v'_k d^3v_A - \iint f_i f_A g \sigma_i^k d^3v_i d^3v_A \right]. \quad (2.3.5)$$

Then we introduce the average values $K_\alpha^\beta = \langle\langle g \sigma_\alpha^\beta \rangle\rangle$ defined by

$$K_i^k = \frac{\iint f_i f_A (g \sigma_i^k) d^3v_i d^3v_A}{\iint f_i f_A d^3v_i d^3v_A} = \frac{\iint f_i f_A (g \sigma_i^k) d^3v_i d^3v_A}{n_i n_A},$$

$$K_k^i = \frac{\iint f'_k f_A (g \sigma_k^i) d^3v_k d^3v_A}{\iint f_k f_A d^3v_k d^3v_A} = \frac{\iint f'_k f_A (g \sigma_k^i) d^3v_k d^3v_A}{n_k n_A}, \quad (2.3.6)$$

The quantity K_α^β (cm³ sec⁻¹), representing the numbers of transitions $\alpha \rightarrow \beta$ per second and per unit densities of molecules M and A , is an average value of

the product $g\sigma_{\alpha}^{\beta}$ weighted over the velocity distributions. Such a quantity is called “rate constant” for the process $\alpha \rightarrow \beta$, and it is generally a function of the temperature T_A of the thermal bath. By substituting the Eq. (2.3.6) in the Eq. (2.3.5) we obtain ($i=0,1,2,\dots$)

$$\frac{\partial n_i}{\partial t} = n_A \sum_k (K_k^i n_k - K_i^k n_i) \quad (\text{cm}^{-3} \text{sec}^{-1}). \quad (2.3.7)$$

The system of first order differential Eqs. (2.3.7) is known as “the system of rate equations” or “Master equations”. It will have constant coefficients if, during the time evolutions of the populations n_i , the bath temperature T_A remains constant. This is realised in the case of the “extreme dilution”. Moreover, the solution of the system (2.3.7) must satisfy the assigned initial conditions $n_i(0)$ ($i=0,1,2,\dots$). In addition it is useful to observe that, even if the number N_l of the involved energy levels of the molecule is not very large, because the system (2.3.7) contains N_l equations each with N_{l-1} terms, we see that it is necessary to know $N_l(N_{l-1})/2$ independent constant K_{α}^{β} . Frequently, it is necessary to include an adequate number of levels but this causes the solution of the system (2.3.7) to become very complicated.

2.4 Energy Transfer During Collisions

The topics we shall develop in the next Secs. are limited to the following situations:

- i) Gas of molecules M diluted in a monatomic gas A , for instance He or Ar in large excess. These mixtures are frequently used by many molecular beams spectroscopists, because they allow then to obtain a more effective cooling of the molecular gas that is being studied;
- ii) Gas pure of molecule M .

The most important energy transfers that can happen between the degrees of freedom during the collisions $M-A$ and $M-M$ are the following:

- i) Between one of the vibration modes of the molecule M and the translations of M or A ($V-T$ processes);
- ii) Between one of the rotational modes of the molecule M and the translations of M or A ($R-T$ process);
- iii) Between one of the vibrational modes of the molecule M and an identical or different mode of another molecule M ($V-V$ process). In the case of biatomic

molecules M these kinds of transfer processes are possible between the same and unique vibrational mode. Therefore these processes are “*resonant*”.

The V - V processes that can happen between two distinct molecules are referred to as “*intermolecular V-V processes*”. Processes V - V between two distinct vibrational motions of the same molecule are also possible and are referred to as “*intramolecular V-V processes*”. The processes V - V can be “*resonant*” or “*non-resonant*”. In the last case the energy difference is supplied or absorbed by the translatory degrees of freedom. In the case of a highly diluted mixture of molecule M in A , the processes V - V are very rare and can be neglected. The energetic balances of the above-mentioned processes are:

i) *Processes V-T and R-T:*

The balance is expressed by the Eq. (2.3.3) that we can rewrite as

$$E_k^{(a)} - E_i^{(a)} = -\Delta E_{kin},$$

$E_k^{(a)}$ and $E_i^{(a)}$ being the energies of two levels of the vibrational or rotational mode (a).

ii) *Processes V-V:*

In this case we have

$$(E_k^{(a)} - E_i^{(a)}) + (E_l^{(b)} - E_j^{(b)}) = -\Delta E_{kin},$$

where $E_k^{(a)}$ and $E_i^{(a)}$ the energies of two levels of the mode (a) of a molecule are and $E_l^{(b)}$ and $E_j^{(b)}$ the energies of two levels of the mode (b) of the other molecule. This is true for intermolecular V - V transfer. As regards intramolecular transfer, the modes (a) and (b) are two distinct vibrational modes of the same molecule. Multiquanta transitions are also possible but less probable, hence we can have $k \neq i \pm 1$, $l \neq j \pm 1$. For resonant V - V transfers in the last equation we have $\Delta E_{kin} = 0$. Moreover, it is well known that the resonant transfers are faster than the non-resonant ones, and that the latter, for which $\Delta E / hc \leq 50 \text{ cm}^{-1}$, it can be assumed to be resonant [12]. It is clear that the V - V transfers happen with greater probability than the processes V - T .

In classical mechanics, the action variables of a system performing a non-degenerate periodic motion remain constant when the system undergoes a modification, which develops slowly. The variation of the forces applied to the system must be very small during time τ which is much greater than $1/\nu$, ν being one of the independent frequencies of the motion (*Adiabatic theorem*) [13]. In quantum mechanics the probability of finding the system in its eigenstates does not change in time if the perturbation $V(t)$ has a small variation during a time

interval of the order of $T_{ik} = 1/\nu_{ik} = h/(E_k - E_i)$ [14]. Therefore, during an adiabatic variation of the perturbation no transitions between the quantum states of the system can happen. If the perturbation $V(t)$ is small and the time interval τ in which it is applied is suitably long, the adiabaticity condition can be stated by saying that the parameter ξ , given by

$$\xi = \tau / [h / (E_k - E_i)] = \tau / T_{ik}, \quad (2.4.1)$$

must be much greater than the unity. Differently, if the perturbation is applied "impulsively" so that $\xi < 1$, the probability of transition between the states becomes appreciable. In the case of a collision between molecules, the time interval during which the perturbation is applied is characterised by the ratio: "effective action range R of the intermolecular force" / "relative velocity g of the colliding molecules" [15], that is

$$\tau = \tau_{coll} = R / g. \quad (2.4.2)$$

Since the intense short range forces are the more effective in inducing transitions, the repulsive part of the intermolecular potential [i.e. the term $\varepsilon(r_m / r)^{12}$ of Eq. (1.3.1)] is an important one, while the attractive long range term, can, in a first approximation, be neglected. Therefore, we shall assume $R = r_m$ [see Fig. 1.3.2] in Eq. (2.4.2). Hence, Eq. (2.4.1) becomes

$$\xi = \frac{\frac{r_m}{\langle g \rangle}}{\left(\frac{h}{E_k - E_i} \right)} \cong \frac{r_m}{\langle g \rangle} \frac{E_k - E_i}{h} = \sqrt{\frac{\pi\mu}{8K_B}} \frac{r_m}{\sqrt{T}} \nu_{ik}, \quad (2.4.3)$$

with the assumption $\langle g \rangle = (8K_B T / \pi\mu)^{1/2}$ [see Eq. (1.9.7)].

By Eq. (2.4.3) we can observe that with the increase of the temperature of the gas the collisions become more effective in inducing transitions between quantum states. Indeed $\xi \propto (T)^{-1/2}$.

We shall now try to estimate the parameter ξ for collisions with the energy transfers V - T and R - T . In the first case, as the energy difference between two adjacent vibrational states (i.e. with quantum numbers ν and $\nu + 1$) of an harmonic oscillator is $h\nu$, we have

$$\xi = \frac{r_m}{\langle g \rangle} \nu. \quad (2.4.4)$$

Now, $r_m \cong 3 \cdot 10^{-8}$ cm, and at room temperature it is $\langle g \rangle \approx 10^4$ cm/sec, hence, $\tau_{coll} = 3 \cdot 10^{-12}$ sec. Since $\nu = 10^{13}$ sec $^{-1}$, Eq. (2.4.4) gives $\xi \approx 30$. We see

that the ξ value is at least one order of magnitude greater than the unity and the exchange V - T is rather improbable at moderate temperature. Let us now consider the exchange R - T . For molecules assimilable to rigid rotors of the linear or spherically symmetric polyatomic type, the rotational energy is given by (see Appendix A.2)

$$E_j = BJ(J+1). \quad (2.4.5)$$

The energy differences between the rotational states of quantum number J and $J+1$ is therefore

$$E_{j+1} - E_j = 2B(J+1). \quad (2.4.6)$$

Now, it is useful to observe that, dissimilar to the case of harmonic vibrations where $E_{v+1} - E_v = \text{const.}$, in the case of the rotations, the energy difference $E_{j+1} - E_j$ increases with the increasing quantum number j . For rotations the parameter ξ of Eq. (2.4.1) becomes

$$\xi = \frac{r_m}{\langle g \rangle} \frac{E_{j+1} - E_j}{h} = \frac{r_m}{\langle g \rangle} \frac{2B(J+1)}{h}. \quad (2.4.7)$$

Now, the frequency of the quanta producing rotational transitions is of the order of $10^9 \div 10^{12} \text{ sec}^{-1}$, and as we have $\tau_{\text{coll}} = 3 \cdot 10^{-12} \text{ sec}$, the result is $\xi = 3 \cdot 10^{-3} \div 3 \cdot 10^{-1}$. This result satisfies the condition $\xi \ll 1$ for an effective energy transfer and it has been observed that the transfers R - T happen almost at each collision for the majority of the polyatomic molecules. Only hydrogen and the hydrides show exceptions. In other words we can say that the rotational degrees of freedom rapidly equilibrates with the translational ones.

There is another difference between the relaxations of vibrations and rotations. Because anharmonicity is usually present, the energy separation of two neighbouring vibrational levels is not constant but decreases with the increasing quantum number v . Therefore, the transfer to translations of the vibrational quanta is favoured for the upper level. The inverse situation happens for the dissipation of rotational quanta. In such a case, as shown by Eq. (2.4.7), the adiabaticity parameter ξ increases with the increasing rotational quantum number J . Hence, the transfer of rotational energy quanta to the translations are more probable at the low J values. At this point we note that, in this case the upper rotational levels can become overpopulated with respect to a Boltzmann distribution.

2.5 The Vibrational Energy Relaxation

Holding the same hypotheses that allowed us to obtain the Eq. (2.3.7), we now consider a mixture of molecules M and A which are initially in thermal equilibrium at the temperature T_A . As a consequence of a transient perturbation, the internal state of the “active” molecules M is modified. At the end of the perturbation, that we shall assume as time $t = 0$, the distribution of the molecules over the different states (*vibrational or rotational*) will be defined by the set of state densities $n_i(0)$ ($i=0,1,2,\dots$). Here, $n_i(0)$ is the density of molecules in the state i at the time $t = 0$ and the distribution over the internal states of M will differ from the maxwellian at the temperature T_A . For increasing time, the density $n_i(t)$ will relax to the final value $n_i(\infty)$ coincident with the densities in thermal equilibrium with the bath at the temperature T_A . If E_i is the energy of the i th level and $n_i(t)$ the density of molecules at that level at the time t , the increase of internal energy of the molecules M at the same moment will be

$$E(t) = \sum_{i=0}^{\infty} n_i(t) E_i \text{ (erg / cm}^3\text{)}. \quad (2.5.1)$$

In particular, at the end of the perturbation the increment of the internal energy density is

$$E(0) = \sum_{i=0}^{\infty} n_i(0) E_i, \quad (2.5.2)$$

while the final equilibrium value is given by

$$E_{eq} = E(t \rightarrow \infty) = \sum n_i(\infty) E_i. \quad (2.5.3)$$

The Eq. (2.5.1) shows that, in order to calculate the time law of the relaxation of the internal energy $E(t)$, it is necessary to solve the system of Eqs. (2.3.7), by determining the function $n_i(t)$ that satisfies the given initial conditions $n_i(0)$.

Now in particular let us consider the relaxation V - T . In order to simplify and solve the equations system (2.3.7), we assume that the molecules M have only one vibrational mode, and that this mode can be assimilated to a “*quantized harmonic oscillator*”. These two hypotheses allow us not only to introduce important simplifications but also to obtain a solution. In fact:

- i) By neglecting the zero level energy $h\nu/2$, that cannot be transferred, the energy of the i th level is given by $E_i = ih\nu$, and therefore the energy levels are equidistant, (i.e. $E_{i+1} - E_i = h\nu = \text{const.}$ for any i);

- ii) Only the transitions between adjacent levels are allowed; hence, the transition probability $K_i^k \neq 0$ is valid only if $k = i \pm 1$;
- iii) The transition probability between the two states is proportional to the quantum number of the upper level. Thus, $K_i^{i-1} / K_i^0 = i / 1 = i$, and $K_{i+1}^i / K_i^{i-1} = (i+1) / i$. From these equations it follows that we have

$$K_{i+1}^i = [(i+1) / i] i K_i^0 = (i+1) K_i^0 \quad (2.5.4)$$

Similarly we found

$$K_i^{i+1} = (i+1) K_0^1, \quad (2.5.5)$$

- iv) By applying Eq. (2.3.7) to the ground level, in the condition of thermal equilibrium we have

$$(\partial n_0 / \partial t)_\infty = -K_0^1 n_0(\infty) + K_1^0 n_1(\infty) = 0.$$

Hence we have

$$K_0^1 = K_1^0 [n_1(\infty) / n_0(\infty)] = K_1^0 e^{-\theta_v / T_A}, \quad (2.5.6)$$

having utilised the following relation [see Eq. (1.5.5)]

$$\frac{n_1(\infty)}{n_0(\infty)} = \frac{g_1}{g_0} e^{-\frac{\theta_v}{T_A}} \quad \text{where } [\theta_v = (E_1 - E_0) / K_B]$$

and $g_1 = g_0 = 1$, because the levels are not degenerate.

If we now refer to the above hypothesis i), the time derivative of the internal energy can be written

$$\frac{\partial E}{\partial t} = \sum_i E_i \frac{\partial n_i}{\partial t} = h\nu \sum_i i \frac{\partial n_i}{\partial t}, \quad (2.5.7)$$

where the terms $i(\partial n_i / \partial t)$ can be obtained from Eq. (2.3.7). Here we find (see Appendix B.1) that the energy density $E(t)$ satisfies the following first order linear differential equation (*Landau-Teller equation*) [16]:

$$\partial E / \partial t = -(\tau)^{-1} (E - E_{eq}), \quad (2.5.8)$$

in which τ is the (constant) “*V-T relaxation time*” given by

$$\tau = \tau_{VT} = [n_A K_1^0 (1 - e^{-\theta_v / T_A})]^{-1} \quad (\text{sec}), \quad (2.5.9)$$

and

$$E_{eq} = E(\infty) = n \frac{h\nu e^{-\theta_v / T_A}}{e^{-\theta_v / T_A} - 1}, \quad (\text{erg/cm}^3) \quad (2.5.10)$$

is the value of the vibrational energy density of the harmonic oscillator system in equilibrium at the temperature T_A .

The differential equation (2.5.8) admits the general solution ($\tau = const.$)

$$E(t) = [E(0) - E(\infty)]e^{-t/\tau} + E(\infty). \quad (2.5.11)$$

With further reference to a system of harmonic oscillators plunged in an infinite thermal bath at the temperature T_A , be P_1^0 the probability that, as it results from a collision $M-A$, a transition $i=1 \rightarrow k=0$ can happen. Therefore, $N_1^0 = 1/P_1^0$ is the average number of collisions necessary to produce such a transition. With reference to the definition of rate constants [Eqs. (2.3.6)], we have for the number of transition $i \rightarrow 0$ in the unity time

$$K_1^0 n_A = P_1^0 Z_{MA} = Z_{MA} / N_1^0 \text{ (sec}^{-1}\text{)}, \quad (2.5.12)$$

where Z_{MA} is the frequency of the collisions undergone by a molecule M with the inert molecules A . This frequency is expressed by the Eq. (1.9.11), that is

$$Z_{MA} = n_A [(d_M + d_A) / 2]^2 \sqrt{8K_B T_A / \mu_{MA}}.$$

It should be noted that, for the assumed above hypothesis, the frequency of the collision $M-M$ is negligible. If we refer to Eq. (2.5.12), the Eq. (2.5.9) can be rewritten

$$\tau = [P_1^0 Z_{MA} (1 - e^{-\theta/T_A})]^{-1}. \quad (2.5.13)$$

Finally, we observe that the Eq. (2.5.12) can be generalised as follows:

$$K_\alpha^\beta = Z'_{MA} P_\alpha^\beta, \quad (2.5.14)$$

where

$$Z'_{MA} = (Z_{MA} / n_A) = [(d_M + d_A) / 2]^2 \sqrt{8K_B T_A / \mu_{MA}}.$$

From Eqs. (2.5.14), (2.5.4) and (2.5.5) it then follows that

$$P_{i+1}^i = (i+1)P_1^0, \quad P_i^{i+1} = (i+1)P_0^1 = (i+1)P_1^0 e^{-\theta_v/T_A}.$$

Therefore, once P_1^0 is known, all the probabilities P_α^β are known. Taking account of Eq. (2.5.14), the Eq. (2.3.7) can be rewritten

$$\frac{\partial n_i}{\partial t} = Z'_{MA} n_A \sum_k (P_k^i n_k - P_i^k n_i). \quad (2.5.15)$$

Now we need to calculate the probability P_1^0 of the decay from the state $k=1$ to the state $i=0$. To this end we will discuss the elementary treatment developed by Landau e Teller [16]. These authors developed a classical theory of the transfer V - T assuming a collinear collision between two biatomic molecules, one of which (M) is assumed to vibrate, while the other (A) is assumed to be rigid. The calculus of the probability P_1^0 is developed by assuming: i) The intermolecular potential is reduced to its repulsive part which is then approximated by an exponential law, that is: $V(r) = Ae^{-r/r_m} = Ae^{-\alpha r}$, r being the intermolecular separation, and $r_m = 1/\alpha$ being the characteristic range of the intermolecular forces. This law substitute the term $\varepsilon = (r_m/r)^{12}$ of the Lennard–Jones potential [see Eq. (1.3.1)]; ii) The transition probability is an exponential function of the adiabaticity parameter ξ [see Eq. (2.4.4)], that is, $P_1^0 = P^* Ae^{-\tau/T} = P^* Ae^{-v r_m/v}$. Here, P^* is a “steric factor” depending on the relative orientation of the colliding molecules, iii) The velocity distribution of the molecules is assumed to be an uni-dimensional Maxwell distribution, that is

$$dn = n \frac{\mu}{K_B T} e^{-\frac{\mu v^2}{2K_B T}} v dv.$$

The effective value of P_1^0 is then obtained by averaging over this velocity distribution. That is by calculating the integral:

$$P_1^0 = \int P^* A e^{-v r_m/v} dn.$$

The calculation leads to the following results:

$$P_1^0 = const. \left[\left(\frac{4\pi^2 v^2}{\alpha^2} \right) \frac{\mu}{K_B T} \right]^{1/6} e^{-\frac{3}{2} \left[\left(\frac{4\pi^2 v^2}{\alpha^2} \right) \frac{\mu}{K_B T} \right]^{1/3}}. \quad (2.5.16)$$

In the previous equation μ is the reduced mass of the colliding molecules. Eq. (2.5.16) shows that $P_1^0 \propto T^{-1/6} \exp(T^{-1/3})$. By calculating the logarithm of both members of this equation, and by observing that the exponential term is dominant on the term $T^{-1/6}$, we have

$$\ln P_1^0 = \ln \left[\frac{1}{\tau Z_{MA} (1 - e^{-\theta/l})} \right] = \ln(1/N_1^0) = A - BT^{-1/3}.$$

This kind of dependence of τ on the temperature (Landau–Teller plot) is shown in many gases in a wide range of temperatures.

In the case of vibrational relaxation of harmonic oscillators in an infinite thermal bath and subject to a generic initial distribution more evolved methods have

been developed to solve the Eq. (2.3.7). The more interesting are the “*method of the generating function*” [17], and “*the method of moments*” [18]. The obtained solutions show that:

- i) If the initial distribution of the active molecules on the vibrational levels is Boltzmannian at the temperature $T(t=0)$, this will relax through a continuous sequence of Boltzmann distribution characterised by a vibrational temperature which is decreasing and comprised between the initial $T(0)$ and the final $T(\infty) = T_A$ temperatures. This behaviour is known as “*canonic invariance*”. It is possible to define a “*vibrational temperature*” $T_V(t)$ at any time during the relaxation process. For the vibrational energy, the Eq. (2.5.8) with τ_{VT} given by Eq. (2.5.9) is still valid.
- ii) If the initial distribution is “*non-Boltzmannian*”, this will relax approaching more and more closely the Boltzmann distribution corresponding to the equilibrium temperature T_A . In this case it is not possible to precisely define a vibrational temperature during the relaxation process. However, the vibrational energy $E(t)$ still follows the Eq. (2.5.8) with a unique constant τ . This fact shows that the relaxation law depends only on the vibrational energy added by the perturbation to the molecules, and it does not depend on its initial distribution on the vibrational levels.

Therefore, the validity of the law expressed by Eq. (2.5.8) for $E(t)$ is a more important circumstance than the existence of a vibrational temperature. Finally, we need to observe that, in the previous specified hypotheses, the existence of a “*unique*” relaxation time appears surprising. Really, this is not due to the fact that all of the transition of the harmonic oscillator has the same probability or the same relaxation times, but rather to the fact that they match together so as to obtain a unique value of τ_{VT} . The relaxation time τ_{VT} appears as a measure of the time in which the vibrational energy is retained inside the molecule. We shall now attempt to generalise the above results. We will preserve all previous hypotheses with exception to the “*extreme dilution*”. Hence, we will now consider a mixture of molecules M and A containing a small, although finite, percentage of molecules M

$$\eta = n / (n + n_A).$$

As regards the appreciable values of η , it is no longer possible to neglect the effect of the collisions M - M on the relaxation V - T . Moreover, the relaxation of the molecules M can be assumed to be “*quasi-isotherm*” since the energy delivered by the molecules M to the translations of the molecules M and A is negligi-

ble. With the above limitation the temperature of the gaseous mixture undergoes only a small variation so that the values of the rate constant K_{α}^{β} of Eq. (2.3.7) can be assumed to be unvaried during the relaxation. Since we have assimilated the vibration of the molecules M to harmonic hoscillators, all of the V - V energy transfer is “*resonant*”. Be now $(P_{10}^{01})_{M-M}^{V-V}$ the probability that in a collision between two M molecules, the first one is disexcited from the vibrational level 1 to level 0, while the second, initially in the level 0, is excited to level 1. The calculations developed for this probability [19] show that this is

$$(P_{10}^{01})_{M-M}^{V-V} \gg (P_1^0)_{M-A, M-M}^{V-T}$$

In other words, the probability of a resonant exchange V - V is much greater than the probability of the relaxation V - T $1 \rightarrow 0$. Therefore, the “*vibrational equilibration time*” $(\tau_{10}^{01})_{M-M}^{V-V}$ will be much shorter than the relaxation time $(\tau_1^0)_{M-A, M-M}^{V-T}$. Hence, it follows that, whatever the initial distribution $n_i(0)$ ($i=0,1,2,\dots$) of the molecules on its vibrational states is, the relaxation process will develop as follows. At the beginning, the resonant V - V processes redistribute the vibrational quanta so as to produce a Boltzmann distribution. In this “*thermalization phase*” the excited vibrational mode behaves as decoupled from the translations. The exchange of vibrational quanta with the translations occurs successively. During this V - T relaxation, the effective V - V resonant exchange keeps a Boltzmann distribution at the vibrational levels characterised by a time decreasing vibrational temperature. The V - T relaxation processes of the molecules M due to the collisions M - A and M - M have probabilities $(P_1^0)_{M-A}^{V-T}$ and $(P_1^0)_{M-M}^{V-T}$ respectively. It is evident that the disexcitation probability of a molecule in a collision M - A is greater than the corresponding probability in a collision M - M , because of the greater relative velocity of the molecules and consequently of the reduced adiabaticity of the collision. It can be shown [20] that the vibrational energy relaxation is again described by the Eq. (2.5.8) with a unique relaxation time given by

$$\frac{1}{\tau_{MIX}^{V-T}} = \frac{\eta}{\tau_{M-M}^{V-T}} + \frac{1-\eta}{\tau_{M-A}^{V-T}},$$

where

$$\frac{1}{\tau_{M-A}^{V-T}} = Z_i (P_1^0)_{M-A}^{V-T} (1 - e^{-\theta_v/T}),$$

and

$$\frac{1}{\tau_{M-M}^{V-T}} = Z_i (P_1^0)_{M-M}^{V-T} (1 - e^{-\theta_v/T}),$$

with

$$Z_i = Z_{MA} + Z_{MM}.$$

If η ($0 < \eta < 1$) has an appreciable value the relaxation is “*non-isothermal*”, and the rate constants K_α^β are functions of the bath temperature. It can be shown [21] that, in this case, the equation holds

$$\frac{\partial E^V}{\partial t} = \left[\frac{1}{\tau_{MIX}(t)} \right]^{V-T} [E^V(\infty) - E^V(t)],$$

where τ_{MIX} is now a function of the time. Therefore, the solution of this equation is no longer expressed by Eq. (2.5.11). This result also holds for a pure gas of molecules M ($\eta = 1$) [22]. From the previous considerations it is clear that the Landau–Teller Eq. (2.5.8) still holds for the cases $\eta \gg 0, 0 < \eta < 1, \eta = 1$, but the relaxation time takes some different expressions. All of the above considerations hold for molecules M assimilable to harmonic oscillators. We shall now consider “*anharmonic oscillators*” (*diatomic*) molecules in an infinite thermal bath. The intermolecular potential is assumed to be a Morse potential [23], that is

$$V(r) = D_e [1 - e^{-\alpha(r-r_e)}]^2,$$

where D_e is the energy for which the molecule M dissociates, and r_e is the equilibrium separation between the two atoms constituting the molecule. For the energetic levels the solution of the Schrodinger equation gives [24]

$$E_i = h\nu_0(i - X_e i^2),$$

where $h\nu_0 = E_1 - E_0$ and X_e is the “*anharmonic constant*” which has a value ranging between 10^{-3} and 10^{-2} for many diatomic molecules. Now for the rate constant we have [24]

$$K_1^0 = Z'_{MA} P_1^0 \frac{(1 - 2X_e)^2}{1 - 3X_e},$$

which is very close to the value of K_1^0 for the harmonic oscillator.

However, at this point we need to calculate P_α^β for an anharmonic oscillator. For this sort of oscillator strict selection rules do not exist in the sense that transition between “*any*” two levels are possible. However, the analysis of the problem shows that $P_K^j \propto X_e^{|K-j|-1}$ so that most of the transitions happen for $\Delta K \leq 2$ but the transitions with $\Delta K = \pm 1$ are strongly preferred with respect to those with $\Delta K = \pm 2$. It must be observed that some interesting relaxation processes are often limited to the lower vibrational levels, and although in this case the anhar-

monicity may be neglected, the latter cannot be neglected when it is necessary to take account of the higher levels.

The Master equation (2.3.7) or (2.5.15) for a system of Morse oscillator has already been written, however, an analytical solution has not yet been found [25]. Frequently, it is necessary to resort to numerical solutions. It is found that there is a slight difference between the calculated levels populations and the populations of a system of harmonic oscillators. The deviations are of the order of X_e for an initial Boltzmann distribution of the anharmonic oscillators. Therefore, the relaxation of such a distribution can be accurately described by the relaxation of a harmonic oscillator system. Let us now consider the vibrational relaxation of polyatomic molecules. In this case several vibrational modes contribute to the internal energy of the molecule and can independently relax. However, a vast majority of molecules exist that show a “*unique*” relaxation process involving the whole vibrational energy of the molecule. This is due to the fast V - V intramolecular exchange which always maintains in equilibrium the distribution of the vibrational energy among the active vibrational modes. The total vibrational energy then relaxes through the V - T transfer of a single mode. This is the mode of lower energy which, having the smaller adiabaticity parameter ξ , exhibits the fastest V - T decay.

2.6 The Rotational Energy Relaxation

In Sec. 2.3 we have deduced the Master equation from the Wang Chang-Uhlembeck equation (2.3.1). It is useful to remark that the Eq. (2.3.1) was obtained from the following hypothesis: i) The conservation of the angular momentum in the binary collisions is not accounted for; ii) That in the moments before and after the collision the molecules have well defined internal states. Now, the energy indetermination δE of a state is bound to its mean life δt by the “*indetermination principle*”. Hence, we have $\delta E \geq \hbar / \delta t$. In the case we are discussing this is $\delta t = (P'_{J+1} Z_C)^{-1}$, P'_{J+1} being the probability that, in the course of one collision the molecule in the rotational state $(J+1)$ decays to the state J , and Z_C (sec^{-1}) is the average collisional frequency. If the energy difference between two adjacent states ΔE is less or of the order of δE , the internal quantum states are not well defined, and the spectrum of the internal energy can be assumed to be continuous. A similar circumstance cannot be verified in the case of the vibrations where $\Delta E \gg \delta E$, but it can happen for the rotations of heavy molecules

endowed with a large moment of inertia I when the density n is high. In fact, we have $\delta E \geq \hbar P_{j+1}^j Z_C = \hbar P_{j+1}^j (\pi d^2) \langle g \rangle n$, and for molecules assimilable to spherical rotators we obtain $\Delta E = E_{j+1} - E_j = 2B(j+1) = \hbar^2(j+1)/I$. In the previous equation we have used the Eqs. (1.9.4) and (2.4.6). Now, we have $P_{j+1}^j \cong 1$ for small J values, and moreover P_{j+1}^j decreases when J increases, which follows from Eq. (2.4.7) [$\xi \propto (J+1)$]. If I and n assume high values, we can have $\Delta E < \delta E$. In this case the rotation can be classically treated as made for the translations. For the following work we shall assume $\Delta E > \delta E$ and the validity of semiclassical Eq. (2.3.1). By assuming the validity of the general considerations expressed in Sec. 2.5, we shall now consider the relaxation R - T . In particular the internal energy E of Eqs. (2.5.2;3) now becomes the rotational energy. For molecules M assimilable to rigid rotors the rotational energy is $E_J = BJ(J+1) = K_B \cdot \theta_R \cdot J(J+1)$, J being the “rotational quantum number”. This expression of E is applicable to biatomic and linear polyatomic molecules (see Appendix A.3). Keeping the hypothesis of the infinite thermal bath, the Master equation now becomes

$$\frac{\partial n_J}{\partial t} = \sum_{J'} n_A (K_{J'}^J n_{J'} - K_J^{J'} n_J), \quad (2.6.1)$$

where

$$K_J^{J'} = \frac{1}{n_J n_A} \int f_J f_A \sigma_J^{J'}(g) d^3 v_J d^3 v_A, \quad (2.6.2)$$

with

$$\sigma_J^{J'}(g) = \int I_J^{J'}(g, \theta, \varphi) d\Omega, \quad (2.6.3)$$

with the meanings of the symbols quite analogous to those used in Eq. (2.3.6). In particular

$$n_J = \int f_J d^3 v_J, \quad f_J$$

being the velocity distribution function of the molecules in the state characterised by the rotational quantum number J . For the relaxation R - T , the cross section $\sigma_J^{J'}$ is usually assumed to be dependent on the energy difference or “gap” ($E_{J'} - E_J$), according to one of the following laws [26]:

$$\sigma_J^{J'} \propto e^{-(E_{J'} - E_J)} \text{ (Exponential gap law)} \quad (2.6.4)$$

$$\sigma_J^{J'} \propto (E_{J'} - E_J)^{-\alpha} \text{ (Power law).}$$

From both such laws, it follows that the small energy transfers are more probable than the large ones and, therefore, the lower rotational states relax more rapidly than the higher ones. This is in accordance with the considerations mentioned in Sec. 2.4. In order to test the possibility of writing an equation similar to Eq. (2.5.8), for the relaxation of the rotational energy, we have to point out the following differences of rigid rotor from harmonic oscillator: i) The energy difference between the adjacent rotational states is not constant, but is a function of j [see Eq. (2.4.6)]; ii) There are no selection rules limiting the transitions to adjacent states, but the transition between states with J and $J' \neq J \pm 1$ are allowed; iii) There are no recurrent relationship between the rate constant which are similar to the relationship (2.5.4;5). This situation allows us to foresee that an equation similar to Eq. (2.5.4) for the relaxation of rotational energy will be very difficult to obtain. Further complications can be introduced by the exchanges R - R that may play an important role. Therefore, even if the initial distribution over the rotational states is Boltzmannian, it will relax without preserving the “canonical invariance”, and it will not be possible to define a “rotational temperature”. The necessary conditions so that the canonical invariance in a relaxation process exists have been established by H.C. Andersen et al. [29]. Some researchers [27, 28], in analogy with the Eq. (1.4.2) involving the translations, have introduced a rotational temperature T_R through the following equation:

$$T_R = \frac{1}{K_B} \sum_J \frac{n_J}{n} E_J = \sum_J \frac{n_J}{n} \theta_R J(J+1), \quad (2.6.5)$$

with $n = \sum_J n_J$. The temperature defined in such a way appears as an index of the “total” rotational energy contained in the molecule, independently from how it is distributed on the rotational states. Although, strictly speaking, Eq. (2.5.8) cannot be used to describe the relaxation process of the rotational energy, nevertheless, it has often been used for an approximated description of such a process.

By taking account of the proportionality of the temperature T_R and the total rotational energy according to Eq. (2.6.5), we can write

$$\frac{dT_R}{dt} = -\frac{1}{\tau_R} [T_R(0) - T_A], \quad (2.6.6)$$

where T_A is the (*translational*) temperature of the thermal bath and τ_R the “rotational relaxation time”. Several authors used different definitions of τ_R (see for instance Ref. [30]). A meaningful physical quantity which gives an estima-

tion of the rapidity of the transfer R - T (or V - T) is the “rotational (or vibrational) collision number” expressed by

$$N_i = \tau_i / \langle \tau \rangle, \quad (2.6.7)$$

($i=R, V$), where $\langle \tau \rangle$ is the average time between two successive collisions given by

$$\langle \tau \rangle = \left[\pi \left(\frac{d_M + d_A}{2} \right)^2 \cdot \sqrt{(8K_B T / \pi \mu_{12})} n_A \right]^{-1}.$$

However, N_i does not contain any information on the state to state transfer rates, and yet it is a useful data on the R - T or V - T global relaxation rates. In the case of the molecular beams, the internal degrees of freedom of the active molecules are initially in thermal equilibrium with the translations of the atoms (or molecules) of the bath. Then, because of the expansion in the vacuum to supersonic speed, the thermal bath is cooled through a sequence of quasi-equilibrium states corresponding to decreasing translational temperature. All the degrees of freedom of the active molecules attempt to maintain the equilibrium with the bath. However, the vibrations and rotations relax with slower rates. In order to treat the problem it is necessary to couple the equation of the fluid mechanics with the equation describing the relaxation of the internal energy. To conclude the subject of the rotational relaxation we shall report the expression of the collision number N_R obtained by a purely classical analysis. It is found to be [30]

$$N_R = \frac{N_R^\infty}{1 + (\pi^{3/2} / 2)(T^* / T)^{1/2} + (\pi^2 / 4 + \pi)(T^* / T)},$$

where

$$N_R^\infty = \frac{1}{16} \left(\frac{\alpha d}{\varepsilon} \right)^2, \quad T^* = \frac{\varepsilon}{K_B}.$$

This calculation considers the case of two biatomic homonuclear molecules AB and CD . The intermolecular potential function used is the following:

$$U = A \left[e^{-\alpha r_{AC}} + e^{-\alpha r_{AD}} + e^{-\alpha r_{BC}} + e^{-\alpha r_{BD}} \right] - B e^{-\alpha r / 2},$$

in which r is the distance between the centre of mass of the two molecules, while A, B, C, D indicate the repulsion centres and the corresponding r their separations. Moreover, d indicates the nuclear separation and ε the depth of the minimum of the potential U . For an in depth study of the above-considered matter, a close reading of the references [12, 17, 24, 30] is highly recommended.