Chapter 13
Non-equilibrium Plasmas

In laboratory and astrophysical plasmas, the conditions of excitation of the atoms are determined not only by their interaction with the electromagnetic field, but also by collisional processes between the atoms and the particles of the plasma. In this chapter we show how it is possible to describe this type of processes and what is their impact on atomic populations.

13.1 The Kinetic Temperature of the Electrons

We have seen in Chap. 10 that at thermodynamic equilibrium the electrons of an electrically neutral plasma have a velocity distribution described by a Gaussian function (the so-called Maxwellian distribution of velocities). The condition of thermodynamic equilibrium is, however, an idealized condition that, in practice, can be realized only with a certain degree of approximation. Both astrophysical and laboratory plasmas that are commonly observed for spectroscopic applications must—just for the fact that they are observable—emit radiation towards the external environment, which necessarily implies a situation of non-equilibrium, at least for their more exterior layers. In such situations, the concept of temperature loses its meaning, as do all the laws of thermodynamic equilibrium. For example, the distribution of the populations of an atomic species between the different states of ionisation and excitation cannot be determined anymore by the Saha-Boltzmann law but must be determined by solving the statistical equilibrium equations. In principle it is therefore to be expected that under non-equilibrium conditions the distribution of the velocities of the electrons differs from the Maxwellian distribution.

However, there is a wide range of physical conditions in which, despite an overall non-equilibrium, the velocity distribution of the electrons is effectively Maxwellian. This is due to the fact that the collisional processes, which cause the redistribution of kinetic energy between the various electrons and therefore tend to establish a condition of equilibrium, are much more effective than the processes that are opposed to the establishment of the condition of equilibrium.

The processes of the first type are the elastic electron-electron collisions (and also the elastic electron-atom collisions that are, however, less effective). The processes of the second type are the inelastic electron-atom collisions, in which an electron transfers part of its kinetic energy which is converted into internal energy (excitation or ionisation) of the atomic system, or the superelastic electron-atom collisions in which the inverse processes occur (the electron gains kinetic energy due to de-excitation or recombination of the atom). Without pretending to give a rigorous proof of this fact, we simply develop some order of magnitude considerations to show that, in general, the mean free times between two successive processes of the first type are much shorter than the mean free times of the processes of the second type. This justifies, albeit not quite rigorously, that the velocity distribution of the electrons can be considered as Maxwellian to within a good approximation.

Denoting by N_e the electron density and by σ_E the cross section for elastic electron-electron collisions, the mean free time between two elastic collisions τ_E is given by

$$\tau_E \simeq \frac{1}{N_e \sigma_E v},$$

where v is the typical velocity of the electrons. Similarly, denoting by N_a the density of the atoms and by σ_A the cross section for inelastic (or superelastic) electron-atom collisions, the mean free time between two collisions of this type is given by

$$\tau_A \simeq \frac{1}{N_a \sigma_A v}.$$

From the two previous equations we obtain

$$\frac{\tau_E}{\tau_A} \simeq \frac{N_a \sigma_A}{N_e \sigma_E}.$$

The cross section σ_E can be estimated in the following way. Suppose that an electron having kinetic energy ϵ approaches another electron at rest. We can assume that the two electrons collide only if the incident electron will have a distance from the other electron less than a critical value b_c given by the equation

$$\frac{e_0^2}{b_c} = \epsilon.$$

In this case, in fact, the energy due to the Coulomb repulsion becomes comparable to the kinetic energy and we have an appreciable exchange of energy between the two particles. Solving for b_c and averaging over the energy of the particles we get

$$\sigma_E \simeq b_c^2 \simeq \frac{e_0^4}{\langle \epsilon^2 \rangle} \simeq \frac{e_0^4}{\langle \epsilon \rangle^2}.$$

Now we introduce the parameter T_e, the kinetic temperature of the electrons (or electron temperature), with the relation

$$\langle \epsilon \rangle \simeq k_B T_e.$$

By substitution we obtain, as an order of magnitude,

$$\sigma_E \simeq \frac{e_0^4}{k_B^2 T_e^2} \simeq 2.8 \times 10^{-6} T_e^{-2} \text{ cm}^2,$$

with T_e in K. If we consider for example a temperature range typical of stellar atmospheres (4×10^3 K $< T_e < 2 \times 10^4$ K), the cross section σ_E varies between 10^{-13} and 10^{-14} cm^2. The actual calculation of the cross section σ_A is more complex and has to be performed by means of a quantum-mechanical approach. The result is that, for the same temperature range, the value of σ_A is approximately of the order of 10^{-21} or 10^{-22} cm^2. We therefore obtain, as an order of magnitude

$$\frac{\tau_E}{\tau_A} \simeq 10^{-8} \frac{N_a}{N_e},$$

and even in the presence of a weakly ionised plasma with $N_e/N_a = 10^{-4}$, we still obtain a value of the order of 10^{-4} for this ratio.

We can conclude that an electron undergoes a large number of elastic collisions before suffering an inelastic (or superelastic) one, so that such collision will not be able to alter appreciably the Maxwellian distribution of velocity. The above considerations lead us to the conclusion that at a given point of a typical stellar atmosphere we can uniquely define a parameter T_e (kinetic temperature of the electrons) that characterizes the velocity distribution of the electrons. This parameter maintains a well defined operational definition, unlike the thermodynamic temperature T that completely loses its significance in non-equilibrium conditions.

13.2 Electron-Atom Collisions

Consider the collision between an electron having kinetic energy ϵ and an atom of a given atomic species. If the atom is, before the collision, in the energy level $|u_b\rangle$, it could be excited by the collision with the electron to the level $|u_a\rangle$ of higher energy.[1] For this process to occur, it is necessary that the relation $\epsilon \geq (\epsilon_a - \epsilon_b)$ is satisfied. After the collision, the electron is found to have a kinetic energy ϵ' given by

$$\epsilon' = \epsilon - (\epsilon_a - \epsilon_b).$$

Obviously, the inverse process can also occur, i.e. the collision is followed by the de-excitation of the atomic level $|u_a\rangle$ to the level $|u_b\rangle$. In this case, the energy of the colliding electron is given, after the collision, by

$$\epsilon' = \epsilon + (\epsilon_a - \epsilon_b).$$

The processes of the first type are called inelastic electron-atom collisions, while those of the second type are called superelastic electron-atom collisions (although some authors prefer to speak of collisions of the first and of the second kind, respectively).

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[1] As in Chap. 11, we use here the index a to denote the upper level and the index b to denote the lower level.
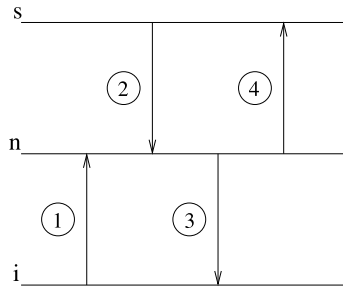
Fig. 13.1 Schematic representation of the collisional processes that contribute to the statistical equilibrium equations of a given level (the intermediate level in the figure). (1) Inelastic collisions from lower levels; (2) superelastic collisions from higher levels; (3) superelastic collisions to lower levels; (4) inelastic collisions to higher levels

The effect of the collisions on the atomic populations can be conveniently described by means of statistical equilibrium equations similar to those which we introduced in Chap. 11 for the interaction of an atom with the radiation field. For the population of a given level n, denoting by the index i the lower levels (i.e. those with lower energy) and by the index s the upper levels (i.e. those having higher energy), the equation describing the evolution of the system, if there are only collisions, is written in the form

$$\frac{dN_n}{dt} = \sum_i N_i C_{in}^{(A)} + \sum_s N_s C_{sn}^{(S)} - \sum_i N_n C_{ni}^{(S)} - \sum_s N_n C_{ns}^{(A)}. \qquad (13.1)$$

The four terms appearing in this equation are shown in the diagram of Fig. 13.1. The quantities $C_{ba}^{(A)}$ and $C_{ab}^{(S)}$ appearing in this equation are called collisional rates. They are due, respectively, to inelastic and superelastic collisions. These quantities are obviously proportional to the density of the colliding particles. They also depend on the velocity distribution of the particles and on atomic properties related to the wavefunctions of the two levels between which the transition occurs. For electronic collisions, the rate for inelastic collisions from level b to level a can be expressed by means of the cross section

$$C_{ba}^{(A)} = N_e \int_{v_0}^{\infty} \sigma_{ba}(v) f(v) v \, dv,$$

where N_e is the electron density, $f(v)$ is the velocity distribution of the electrons, and $\sigma_{ba}(v)$ is the cross section for collisional excitation relative to the velocity v. The limit of integration v_0 is the threshold velocity, i.e. the minimum electron velocity for the electron to be able to excite the atom from level b to level a. It is given by

$$\frac{1}{2}mv_0^2 = \epsilon_a - \epsilon_b.$$

Similarly, the rate for superelastic collisions is given by

$$C_{ab}^{(S)} = N_e \int_0^\infty \sigma_{ab}(v) f(v) v \, dv,$$

where $\sigma_{ab}(v)$ is the cross-section for collisional de-excitation.

13.3 The Einstein-Milne Relations

When the velocity distribution of the colliding electrons is Maxwellian, it can be proved, by means of thermodynamic considerations, that the two collisional rates introduced in the previous section are simply related. These thermodynamic considerations, due to Milne, are very similar to those previously developed by Einstein to determine the relations between the coefficients involved in the statistical equilibrium equations for the interaction between atoms and radiation (Einstein coefficients, see Sect. 11.7). For this reason, these relations are called Milne or Einstein-Milne relations.

Consider an atom consisting of only two levels, a and b, subject to collisions by a plasma of electrons with density N_e. If the system is in thermodynamic equilibrium at the temperature T, we can invoke the so-called principle of detailed balance to assert that the number of collisional transitions (due to the electrons) that occur between level a and level b are exactly balanced by the number of collisional transitions (also due to the electrons) that occur between level b and level a. In other words, at thermodynamic equilibrium conditions, a perfect balance must hold for any process that contributes to populate or de-populate the atomic levels regardless of the number and of the characteristics of the physical processes that are simultaneously in operation (radiative processes, collisional processes still with electrons, but among other pairs of levels, collisional processes with other atomic species, etc.). Otherwise, in fact, it would be possible to construct an ideal machine, working in cycle, which could produce work at the expense of a single source, which would contradict the second law of thermodynamics. If we denote then by $\tilde{N}_a$ and $\tilde{N}_b$ the populations of the levels a and b in thermodynamic equilibrium, we must have, writing the evolution equation for the population of level a,

$$0 = \frac{dN_a}{dt} = \tilde{N}_b C_{ba}^{(A)} - \tilde{N}_a C_{ab}^{(S)}.$$

Solving this equation and using the Boltzmann equation to express the ratio $\tilde{N}_b/\tilde{N}_a$ (Eq. (10.6)), we obtain, in thermodynamic equilibrium at the temperature T,

$$\frac{C_{ab}^{(S)}}{C_{ba}^{(A)}} = \frac{\tilde{N}_b}{\tilde{N}_a} = \frac{g_b}{g_a} e^{(\epsilon_a - \epsilon_b)/(k_B T)}.$$

On the other hand, the two collisional rates depend only on atomic factors and on the velocity distribution of the electrons. The result that we have obtained thus continues to be valid even outside thermodynamic equilibrium, as long as the velocity

distribution of the electrons is Maxwellian. If we are under these conditions, far less restrictive than the thermodynamic equilibrium, and if we denote by T_e the kinetic temperature of the electrons, we obtain the Einstein-Milne relation

$$\frac{C_{ab}^{(S)}}{C_{ba}^{(A)}} = \frac{g_b}{g_a} e^{(\epsilon_a - \epsilon_b)/(k_B T_e)}. \tag{13.2}$$

13.4 The Two-Level Atom in Non-equilibrium Conditions

Consider a two-level atom that interacts with a radiation field having, at the frequency ν corresponding to the transition, the mean intensity J_ν. Let the atom be subject to collisions with a population of electrons having kinetic temperature T_e. Taking into account both collisional processes (Eq. (13.1)) and radiative processes (Eq. (11.29)), the statistical equilibrium equation for the population of the upper level is

$$\frac{dN_a}{dt} = -N_a \big(A_{ab} + B_{ab} J_\nu + C_{ab}^{(S)} \big) + N_b \big(B_{ba} J_\nu + C_{ba}^{(A)} \big).$$

In stationary conditions, solving the equation we obtain

$$\frac{N_b}{N_a} = \frac{A_{ab} + B_{ab} J_\nu + C_{ab}^{(S)}}{B_{ba} J_\nu + C_{ba}^{(A)}}.$$

We now substitute this result into the expression for the source function given by Eq. (11.36). Taking into account the relations between the Einstein coefficients (Eqs. (11.27) and (11.28)) and the Einstein-Milne relations between the collisional rates (Eq. (13.2)), with some algebra we obtain

$$S_\nu = \frac{J_\nu + \varepsilon B_\nu(T_e)}{1 + \varepsilon}, \tag{13.3}$$

where B_ν is the Planck function and where we have introduced the quantity ε defined by

$$\varepsilon = \frac{C_{ab}^{(S)}(1 - e^{-h\nu/(k_B T_e)})}{A_{ab}}.$$

Apart from a correction factor of the order of unity, ε represents the ratio between the number of de-excitations of the upper level due to superelastic collisions and the number of de-excitations due to spontaneous emission. The general expression that we have found for S_ν allows us to write, inverting Eq. (11.36), the ratio of the populations N_b/N_a in the form

$$\frac{N_b}{N_a} = \frac{g_b}{g_a} \left(\frac{2h\nu^3}{c^2 S_\nu} + 1 \right).$$

If we introduce $\bar{n}_\nu = J_\nu c^2/(2h\nu^3)$ as the average number of photons per mode at frequency ν, and $\bar{n}_\nu(T_e) = B_\nu(T_e)/(2h\nu^3)$ as the average number of photons per

mode relative, at the same frequency, to the blackbody radiation of temperature T_e, we obtain

$$\frac{N_b}{N_a} = \frac{g_b}{g_a}\left(\frac{1+\varepsilon}{\bar{n}_v + \varepsilon\bar{n}_v(T_e)} + 1\right). \tag{13.4}$$

The above expressions (Eqs. (13.3) and (13.4)) assume a special form in three limiting cases of particular importance.

(a) The first case is when $\varepsilon \gg 1$. Substituting in the expressions for the source function and for the ratio between the populations we get

$$S_v = B_v(T_e), \qquad \frac{N_b}{N_a} = \frac{g_b}{g_a}e^{h v/(k_B T_e)}.$$

In this case the collisions are extremely effective and are able to thermalise the atomic populations at the kinetic temperature. For the ratio of populations we obtain the Boltzmann equation (Eq. (10.6)), while for the source function we obtain the Planck function, both relative to the temperature T_e. This limiting case is known as local thermodynamic equilibrium (LTE).

(b) The second case is when $\varepsilon \ll 1$ and, at the same time, $\varepsilon B_v(T_e) \ll J_v$. Substituting in the same equations we get

$$S_v = J_v, \qquad \frac{N_b}{N_a} = \frac{g_b}{g_a}\left(\frac{1}{\bar{n}_v} + 1\right).$$

This time the collisions have a completely negligible role and the source function is just the average over the solid angle of the incoming radiation. The atom simply behaves as a scattering centre of the radiation. For the atomic populations, defining a suitable "radiation temperature" T_r through the equation

$$\bar{n}_v = \frac{1}{e^{h v/(k_B T_r)} - 1},$$

we obtain

$$\frac{N_b}{N_a} = \frac{g_b}{g_a}e^{h v/(k_B T_r)},$$

which shows that the atomic populations are in equilibrium with the radiation temperature. The parameter T_r that we have so defined is however a completely *ad hoc* parameter. Indeed, for an arbitrary radiation field, there is a different T_r value for each frequency.

(c) Finally, the third case is when the inequalities $\varepsilon \ll 1$ and $\varepsilon B_v(T_e) \gg J_v$ hold. Again substituting we obtain

$$S_v = \varepsilon B_v(T_e), \qquad \frac{N_b}{N_a} = \frac{g_b}{g_a}\left(\frac{1}{\varepsilon\bar{n}_v(T_e)} + 1\right).$$

This is an intermediate case in which, although the collisions are not very effective in de-populating the upper level, the kinetic temperature is so high and the radiation field is so diluted that actually the collisions (and not the radiative processes) are populating the upper level.

The three cases that we have schematically described here are suitable to describe, in a qualitative way, the conditions of excitation of an atom which is located, respectively, in the photosphere, in the chromosphere and in the solar corona. For laboratory plasmas, the most common physical situations are those described by case (a) (plasma with high densities, as discharge lamps) or by case (b) (plasmas of low densities, for experiments of optical pumping with lasers).