Transport of electronic energy in thermal plasmas

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Reactive and internal thermal conductivities for equilibrium Hydrogen plasma have been calculated by the Chapman-Enskog method. The equilibrium composition of the plasma is determined by taking consistently into account the number of allowed atomic electronic excited states (EES) as determined by the average interparticle distance. The coefficients depend on the inclusion of realistic cross sections for the interactions with EES. In particular, the interplay between the two coefficients that describe the transport of electronic and ionization energy is analyzed.

1. Introduction

The transport of vibrational and rotational internal energy is an important mechanism for increasing the thermal conductivity of diatomic and polyatomic molecules. Different theories have been proposed, the most simple being represented by the Eucken theory [1]. In this case the rotational and vibrational contributions to the thermal conductivity can be obtained by the following equation:

$$\lambda_{Rot+Vib} = \eta \cdot \left(c_{V,Rot} + c_{V,Vib} \right) \qquad (1)$$

More precisely the Chapman-Enskog method gives for a simple gas [2]:

$$\lambda_{Rot+Vib} = \rho \mathcal{D} \cdot \left(c_{V,Rot} + c_{V,Vib} \right) \qquad (2)$$

which coincides with eq. (1) in the following approximation for the interaction potential:

$$\frac{\rho \mathcal{D}}{\eta} = 1 \qquad (3)$$

Equation (2) is the result of different approximations:

- Boltzmann distribution over internal states;
- Independence of internal states and molecular velocity;
- Inelastic collisions are negligible;
- Cross sections do not depend on the internal state.

Improvement of this simple theory has been obtained by including the effect of inelastic collisions [3, 4] as well as the effect of non-equilibrium vibro-rotational distribution functions [5]. These studies basically confirm the Eucken approach.

On the contrary the transport of electronic energy due to the diffusion of electronically excited states is usually neglected on the believe that the electronic energy is very small and the diffusion cross sections of electronically excited states are very high. On the basis of these arguments Devoto concluded many years ago that the transport of electronic energy could be neglected in LTE plasmas [6]. Devoto used the simple Eucken expression, eq. (2) that is reported here, specialized for the electronic degrees of freedom:

$$\lambda = \lambda_{tr} + \lambda_E = \frac{5}{2} \eta c_V \left\{ 1 - \left(1 - \frac{2}{5} \frac{\rho \mathcal{D}}{\eta} \right) \frac{c_{V,E}}{c_V} \right\} \qquad (4)$$

An estimation of the term $\frac{\rho \mathcal{D}}{\eta}$ gives a value of about 0.5 while $c_{V,E} \frac{m}{k}$ was estimated to lie in the interval $1.34 \cdot 10^{-4} - 4.7 \cdot 10^{-2}$ in the temperature range 8000-15000K, considering the effect of only the first electronic state of atomic hydrogen. This simple estimation does not consider that in thermal plasmas, depending on the pressure and on the temperature, the adimensional internal specific heat can reach values up to 10-100 so that the second term in eq. (4) can be more important than the translational contribution. Of course this dramatic increase of internal specific heat is due to the excitation of electronically excited states belonging to very high principal quantum numbers so that also the rough estimation of the factor $\frac{\rho \mathcal{D}}{\eta}$ performed by Devoto should be improved. These kinds of considerations have never been taken into account so that the contribution of the electronic degrees of freedom to the thermal conductivity has been completely overlooked.

In addition, one cannot forget that the excitation of electronic states occurs in the same temperature range as the ionization process. The transport of ionization energy is therefore a strictly correlated phenomenon to which we now turn. For atomic plasmas it can be calculated through the equation [7]:

$$\lambda_r = p \frac{\Delta H^2}{k^2 T^3} \frac{N_e N_H}{(N_e + N_H)^2} \mathcal{D}_H^{H^+}$$ (5)

In turn the reaction enthalpy is given by:

$$\Delta H = \frac{5}{2} kT + I - E_{\text{int}}$$ (6)

where I is the ionization potential eventually corrected by its lowering due to the microfields, 5/2kT is the translational enthalpy and E_{int} is the internal electronic energy of atomic hydrogen. This simple equation tells us that the internal energy decreases the transport of ionization energy so that we arrive to the paradox that the electronic excitation can decrease the diffusive transport in thermal plasmas.

Another paradox was found many years ago [8] and confirmed more recently [9] that the transport of ionization energy in atomic LTE plasmas is almost independent of the presence of electronically excited states which with their enormous charge transfer cross sections should decrease the corresponding contribution. The reactive thermal conductivity at atmospheric pressure is left unchanged when taking into account and neglecting the dependence of electronically excited cross sections on the principal quantum number. This strange behavior was ascribed to some compensation effects present in the determinantal equation describing the reactive thermal conductivity.

2. Theoretical approach

Internal and reactive thermal conductivities of equilibrium hydrogen plasma have been calculated in the framework of the Chapman-Enskog method [2]. In order to properly account for the presence of electronic excited states (EES), each electronic excited state of the Hydrogen atom, H(n), n being the principal quantum number, is considered as a separate species. The composition is obtained under a global equilibrium assumption:

i. the concentration of the species present (H, H$^+$, e) is obtained by solving the Saha equation;

ii. the concentration of EES satisfies a Boltzmann distribution.

The maximum number of EES is determined by the confined atom (CA) model:

$$a_0 n_{\max}^2 < N^{-1/3}$$ (7)

where a_0 is the Bohr radius, $n_{\max}$ the maximum allowed principal quantum number and N the particle density. The number of EES actually used in calculations, however, never exceeds 12 due to the lack of collision integral data for Hydrogen atoms with larger principal quantum number. This restriction only affects calculations at p = 1 atm where $n_{\max} = 12$ is used throughout.

Calculations are carried out to the second nonvanishing approximation in Sonine polynomials. The collision integrals for the relevant interactions among H(n), H$^+$ and electrons are the same used in our previous works [9, 10]. They present a strong dependence on the principal quantum number especially for collision integrals diffusion-type of H(n)-H$^+$ collisions. A sample of results is reported in fig. 1 where we show the dependence on the temperature of the collision integrals H(n)-H$^+$ for selected values of the principal quantum number comparing them with the Coulomb collision integrals for the H$^+$-H$^+$ interaction. We can see that the reported H(n)-H$^+$ diffusion-type collision integrals at high temperature are many orders of magnitude higher than the corresponding H$^+$-H$^+$ values.
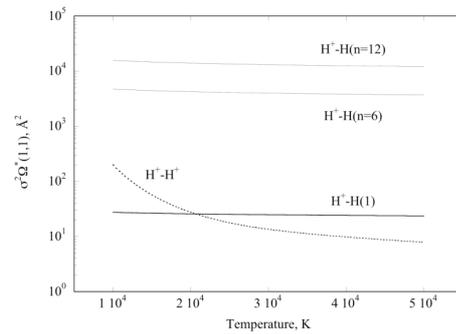

Figure 1. Temperature dependence of diffusion-type collision integrals for H(n)-H$^+$ interactions for selected values of the principal quantum number n and for the H$^+$-H$^+$ interaction.

The convective heat flux describes the transport of enthalpy due to diffusion. It is defined by:

$$\mathbf{q} = \sum_i N_i h_i \mathbf{V}_i = -\left(\lambda_r + \lambda_{\text{int}}\right) \cdot \nabla T \qquad (8)$$

where h_i is the enthalpy carried by i-type particles, $\mathbf{V}_i$ the diffusion velocity and $\lambda_r, \lambda_{\text{int}}$ are the reactive and internal thermal conductivity, respectively.

It is further assumed that [11]:

  i. thermal diffusion is negligible;
  ii. total pressure is uniform;
  iii. there are not non-electromagnetic forces acting on the plasma;
  iv. the plasma is quasi neutral;
  v. the plasma is in thermal and chemical equilibrium;
  vi. the total current density equals zero (i.e. the ambipolar diffusion regime has been established, as in all actual experiments).

Under these assumptions, the diffusion velocities are written [10]:

$$\mathbf{V}_i = -\sum_j \frac{N}{N_j} D_j^i \mathbf{d}_j \qquad (9)$$

where:

$$\mathbf{d}_i = \nabla\left(\frac{N_i}{N}\right) - \frac{N_i}{N}\frac{e_i \mathbf{E}'}{kT} \qquad (10)$$

and $\mathbf{E}'$ is the ambipolar electric field.

In particular, in eq. (9) the atomic terms read:

$$\sum_{n=1}^{n_{\max}} \frac{N}{N_{H(n)}} \mathbf{D}_{H(n)}^i \mathbf{d}_{H(n)} =$$
$$= \frac{N}{N_H}\mathbf{D}_H^i \mathbf{d}_H + \sum_{n=1}^{n_{\max}} \mathbf{D}_{H(n)}^i \frac{E_n - \langle E \rangle}{kT^2}\nabla T \qquad (11)$$

$\langle E \rangle$ being the average Hydrogen atom electronic energy.

The gradients of the species concentrations are then expressed in terms of the equilibrium constant and the ambipolar electric field in terms of the gradient of the temperature [10].

Now, the second term on the R.H.S. of eq. (11) does not vanish also in the case that no chemical reaction occurs and it is therefore recognized as the term producing the internal thermal conductivity. If

equal cross sections are considered for all EES it is given by:

$$\sum_{n=1}^{n_{\max}} \mathbf{D}_{H(n)}^i \frac{E_n - \langle E \rangle}{kT^2} = \qquad (12)$$
$$= \begin{cases} 0 \quad ; \quad i = H^+, e \\ \left(\mathbf{D}_i^i - \mathbf{D}_i^j\right)\dfrac{E_n - \langle E \rangle}{kT^2} \quad ; \quad \begin{array}{l} i = H(n); n = 1,\dots,n_{\max} \\ j = H(m); m \neq n \end{array} \end{cases}$$

that gives for the internal thermal conductivity:

$$\lambda_{\text{int}} = \left(\mathbf{D}_H^H - \frac{N_H}{N_{H(n)}}\mathbf{D}_{H(n)}^{H(m)}\right)\cdot \qquad (13)$$
$$\cdot\frac{N_H\left(\langle E^2 \rangle - \langle E \rangle^2\right)}{kT^2} \quad ; \quad \begin{cases} n = 1,\dots n_{\max} \\ m \neq n \end{cases}$$

The reactive thermal conductivity, instead, in the "usual" case, i.e. when equal cross sections are considered for all EES, reproduce the results of the simplified Butler-Brokaw expression, eq. (5).

3. Results

The assumption of equal cross sections for all EES being no longer valid, the question arises what the effect will be on the transport of electronic and ionization energy. In a previous work [9] both contributions were mixed together and the overall effect was barely noticeable. We wish to show that, indeed, the effect of EES is by no means negligible and that it produces in the two coefficients modifications of opposite sign that compensate in the thermal equilibrium case. This realization is useful in that, if the equilibrium condition is relaxed (it is often the case for low-temperature discharge plasmas) we can expect large influence of EES on transport of electronic and ionization energy.

Figure 2 shows the reactive thermal conductivity of equilibrium hydrogen plasma at different pressures. The two sets of curves refer to "usual" and "abnormal" values. We note that:

  i. the reactive thermal conductivity decreases with increasing pressure. This happens because at higher pressure, ionization shifts to higher temperatures where atom internal energy is higher (and therefore reaction enthalpy lower);
  ii. although the EES cross sections are larger than the ground state ones, the abnormal coefficient can be larger than the usual one. This points to the fact that the reactive thermal conductivity is a complicated combination of multicomponent diffusion coefficients;

iii. the coefficient is not dramatically dependent on EES cross sections even at high pressure, when the population of EES is significant.

Overall, however, the curves follow the behavior predicted by eq. (5) and peak when the reaction enthalpy is at a maximum.
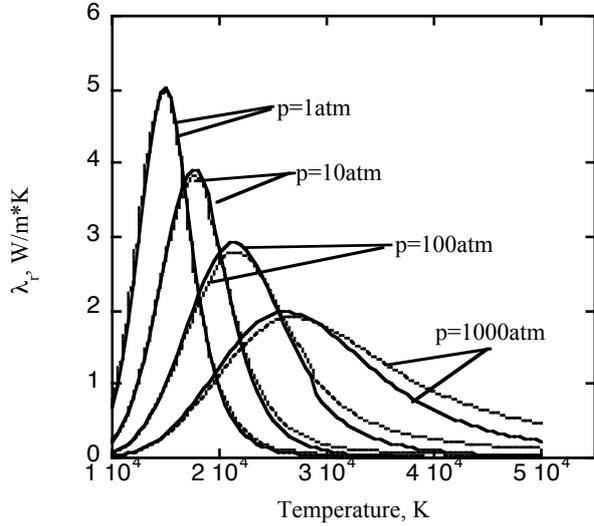

Figure 2. Reactive thermal conductivity of equilibrium hydrogen plasma at different pressures. (Solid line: abnormal; dashed line: usual).

A detailed analysis shows that the main contribution comes from the proton diffusion that brings with it its ionization energy. In this term the EES enter through the diffusion coefficient $D_H^{H^+}$ which is an average of the diffusion coefficients of the proton towards the atom states, weighted with their populations [10]. Therefore, high lying states contribute little to the final result.

The internal thermal conductivity behaves quite differently. It can be written as:

$$\lambda_{\text{int}} = \sum_i N_i h_i \cdot \left(\sum_{n=1}^{n_{\max}} D_{H(n)}^i \frac{E_n - \langle E \rangle}{kT^2} \right) \qquad (14)$$

Figure 3 shows the internal thermal conductivity of equilibrium hydrogen plasma at different pressures.

It increases with increasing pressure as the population of EES increases and it becomes of comparable value as the reactive term at high pressure. Also, the effect of EES has an opposite sign as compared to the previous case: it reduces the coefficient below the usual value at low temperatures and above at high temperatures. This,

in particular explains the partial compensation apparent in the results of [9]. More important, for this case the effect of EES cross sections is dramatic. A careful analysis of eq. (14) shows that the diffusion of EES is weighted with their energy so that also high lying states (which are more affected by EES cross sections) contribute.
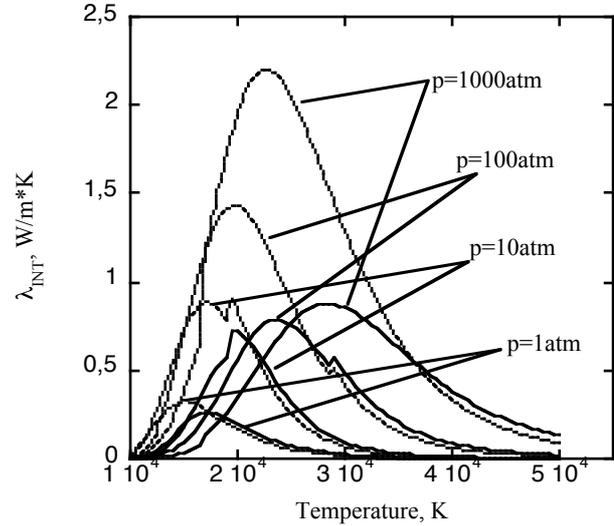

Figure 3. Internal thermal conductivity of equilibrium hydrogen plasma at different pressures. (Solid line: abnormal; dashed line: usual).

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