New Approach, Taking into Account Elastic and Inelastic Processes, for Transport Properties of a two Temperature Plasma

C. Bonnefoi, J. Aubreton, and J.-M. Mexmain *
U.E.R. des Sciences (LA 320), 87060 Limoges, France

Z. Naturforsch. **40 a,** 885–891 (1985); received March 18, 1985

We have developed a modified Chapman-Enskog method for a two-temperature partially ionized plasma: electron temperature (T_e) and heavy particles temperature (T_h). We introduce a new definition of the diffusion forces and then calculate the reactive thermal conductivity λ_R.

I. Introduction

Actual thermal plasmas are not necessarily in thermodynamic equilibrium: near the walls and the electrodes, or when injecting a cold gas, or when reducing the pressure. The plasma may be considered as, at least, a two-temperature medium with the mean kinetic energy of the electrons (electron temperature T_e) different from the one of the heavy particles (T_h). It becomes then necessary to develop a theoretical calculation of the transport properties in a two temperature plasma at atmospheric or reduced pressure.

The kinetic study of such a plasma has been partly developed by de Voto [1] and by Chmieleski [2] using a method similar to the classical one of Chapman-Enskog at equilibrium [3]. However, our purpose being to develop equations usable for numerical calculations, we have not used the approach of Chmieleski. In spite of a rigourous mathematical development, the introduction of his delta functions in the electron collision bracket integrals leads to questionable considerations of convergence. On the contrary, de Voto's development allows the use of the classical collision integrals.

Thus, starting from a given known composition of the two-temperature plasma, for example through the method of Potapov [4] or of Tuma [5], we study the transport properties by taking into account [1] the low value of the mass ratio ($m_e/m_h \ll 1$). The set of Boltzmann's equations is splitted in two: electron equations and heavy particles equations.

No significant discordance between our results and those of the Voto arising when only elastic processes are involved (chemical reactions being neglected), we shall limit ourselves to a brief review and refer to the formalism of elastic transport coefficients given else where [6, 7]. However, some reactions such as dissociation, ionization, ... occur in the plasma leading to the introduction of a new transport coefficient, λ_R, the so called reactive thermal conductivity depending on diffusion.

In the first part of this paper we emphasize that our definition of diffusion forces is new and actually leads to a verified closure equation. The second part is devoted to the calculation of λ_R through a quite new approach, close to the one of Butler and Brokaw [8], but developed specially for a two-temperature frame.

II. Definition of New Diffusion Forces and Consequences

We will not repeat here the complete development of the modified Chapman-Enskog method extended by de Voto [1] to a two-temperature partially ionized plasma. Instead, we quote only the

---

Reprint requests to J. Aubreton, U.E.R. des Sciences, Universitè de Limoges, 123, Avenue Albert-Thomas, F-87060 Limoges Cedex, France.

* Present address: CEA-DAM – Limeil Brevannes – France.

relevant results and definitions for later discussion. For all details of the derivations we refer to de Voto's work [1]. The distribution functions are given by

$$f_i = f_i^{(0)}(1+\varphi_i)\,, \quad i=1,\dots,N\,, \tag{1}$$

where φ_i is a perturbation and N the number of components of the mixture.

If n_i, m_i, $\boldsymbol{v}_i$, T_i are respectively the number density, mass, velocity, and kinetic temperature of species i Maxwell's distribution $f_i^{(0)}$ is given by

$$f_i^{(0)} = n_i \left(\frac{m_i}{2\pi k T_i}\right)^{1/2} \exp(-w_i^2) \tag{2}$$

with

$$\begin{aligned} \boldsymbol{w}_i &= (m_i/2kT_i)^{1/2}\,\boldsymbol{V}_i\,,\\ \boldsymbol{V}_i &= \boldsymbol{v}_i - \boldsymbol{v}_0\,,\\ \varrho\,\boldsymbol{v}_0 &= \sum_{i=1}^{N} m_i \int f_i^{(0)}\,\boldsymbol{v}_i \cdot d\boldsymbol{v}_i\,,\\ \varrho &= \sum_{i=1}^{N} m_i n_i\,,\\ T_1 &= T_\mathrm{e}\,,\\ T_i &= T_\mathrm{h}\,; \quad i=2,\dots,N\,. \end{aligned}$$

Separating Boltzmann's equation for the electrons from those for the heavy particles and taking into account the low value of the ratio m_1/m_i, we obtain, for the diffusion forces $\boldsymbol{d}_i'$, $\frac{\boldsymbol{V}_1}{n_1 k T_\mathrm{e}}\,\boldsymbol{d}_1'$ and $\frac{\boldsymbol{V}_i}{n_i k T_\mathrm{h}}\,\boldsymbol{d}_i'$ instead of $\frac{m_1 \boldsymbol{V}_1}{k T_\mathrm{e}}\,\boldsymbol{d}_1'$ and $\frac{m_i \boldsymbol{V}_i}{k T_\mathrm{h}}\,\boldsymbol{d}_i'$ given by de Voto [1] in his Eqs. (7.18) and (7.21). This results from a different choice for the diffusion forces.

$\boldsymbol{F}_i$ being the external force on the ith species, the partial pressure of which is P_i, and P being the total pressure of the mixture, we take by definition

$$\boldsymbol{d}_i' = \frac{n_i m_i}{\varrho} \sum_{j=1}^{N} n_j \boldsymbol{F}_j - n_i \boldsymbol{F}_i - n_i m_i \frac{\nabla P}{\varrho} + \nabla P_i \tag{3}$$

while de Voto [1] takes

$$\boldsymbol{d}_i' = \frac{1}{\varrho} \sum_{j=1}^{N} n_j \boldsymbol{F}_j - \frac{\boldsymbol{F}_i}{m_i} - \frac{\nabla P}{\varrho} + \frac{\nabla P_i}{n_i m_i}\,. \tag{4}$$

Our choice for $\boldsymbol{d}_i'$ is imperative to obtain the closure equation

$$\sum_{i=1}^{N} \boldsymbol{d}_i' = 0\,. \tag{5}$$

We must emphasize that the definition (4) adopted by de Voto [1] does not satisfy this condition. (It can be easily verified that $\sum_{i=1}^{N} \boldsymbol{d}_i' \neq 0$.)

Remark

For $T_\mathrm{e} = T_\mathrm{h}$, we obtain $\boldsymbol{d}_i' = P\,\boldsymbol{d}_i$, where $\boldsymbol{d}_i$ is the diffusion force adopted by Chapman-Cowling [3] (18.2, 5).

If we impose that the ordinary diffusion coefficients D_{11} (for the electrons) and D_{ij} (for the heavy particles) reduce to the binary diffusion coefficient in the first approximation, our transport coefficients are in complete agreement with those given by other authors [1], [6].

Up to now, the introduction of new diffusion forces does not represent a significant deviation from the well known results of de Voto because only elastic phenomena are under consideration.

In an actual plasma dissociation and ionization take place. These phenomena were studied [8], [9] for plasmas at equilibrium. For studying inelastic processes where the diffusion forces are directly involved we obtain slightly different expressions for the diffusion velocities [7]:

For the electrons we get

$$\langle \boldsymbol{V}_1 \rangle = -\frac{1}{n_1 k T_\mathrm{e}} D_{11}\,\boldsymbol{d}_1' - \frac{D_1^\mathrm{T}}{n_1 m_1 T_\mathrm{e}} \nabla T_\mathrm{e}\,, \tag{6}$$

and for the heavy particles ($i \neq 1$)

$$\langle \boldsymbol{V}_i \rangle = \frac{n}{n_i \varrho k T_\mathrm{h}} \sum_{j=2}^{N} m_j D_{ij}\,\boldsymbol{d}_j' - \frac{D_i^\mathrm{T}}{n_i m_i T_\mathrm{h}} \nabla T_\mathrm{h}\,. \tag{7}$$

Here D_i^T ($i = 1,\dots,N$) is a thermal diffusion coefficient [1], [7].

II.1. Binary diffusion and self-diffusion coefficients

a) If among the heavy species we consider only two species i and j, it is possible to introduce [7], as did Hirschfelder at equilibrium, a so-called binary diffusion coefficient

$$\mathcal{D}_{ij}(1) = \frac{3(m_i + m_j)}{16\,n\,m_i m_j} \cdot \frac{k T_\mathrm{h}}{\Omega_{i,j}^{(1,1)}}\,, \tag{8}$$

where $\Omega_{ij}^{(1,1)}$ is a collision integral [9] such that

$$\Omega_{ij}^{(1,1)} = \Omega_{ji}^{(1,1)}\,. \tag{9}$$

b) The symmetry property (9) has the immediate consequence

$$\mathscr{D}_{ij}(1) = \mathscr{D}_{ji}(1)\,,$$

and it allows us to define, for $i \neq 1$, a so-called self diffusion coefficient, noted $\mathscr{D}_{ii}$ and sometimes $\mathscr{D}$, such as

$$\mathscr{D}_{ii} = \lim_{j \to i} \mathscr{D}_{ij}(1) = \lim_{i \to j} \mathscr{D}_{ji}(1) = \frac{3}{8\, n_i m_i} \cdot \frac{k\, T_{\mathrm{h}}}{\Omega_{ii}^{(1,1)}}\,. \quad (10)$$

We have to remark that (9) is true only at the first order of the Sonine expansion [10] (consequently we write $\mathscr{D}_{ij}(1) = \mathscr{D}_{ij}$).

II.2. Relationships between the heavy particle diffusion velocities

Starting from (7) and using steps similar to those of Hirschfelder at equilibrium [9], we have established the relationship [7]

$$\sum_{\substack{j=2\\ j \neq i}}^{N} \frac{n_i n_j}{n^2 \mathscr{D}_{ij}} [\langle \boldsymbol{V}_j \rangle - \langle \boldsymbol{V}_i \rangle] \quad (11)$$

$$= \frac{\boldsymbol{d}_i'}{n\, k\, T_{\mathrm{h}}} - \boldsymbol{\nabla} L n\, T_{\mathrm{h}} \sum_{\substack{j=2\\ j \neq i}}^{N} \frac{n_i n_j}{n^2 \mathscr{D}_{ij}} \left(\frac{D_j^{\mathrm{T}}}{n_j m_j} - \frac{D_i^{\mathrm{T}}}{n_i m_i} \right).$$

III. Calculation of λ_{R}

In the development of this calculation more accurate new notations must be adopted for describing the reactions occurring among the components of the plasma.

III.1. Notations

The plasma under consideration consists of electrons (X_1), atoms ($X_2, \ldots, X_\mu$), molecules ($X_{\mu+1}, \ldots, X_\nu$) and of ions noted X_i^r with $i = 2, \ldots, \nu$.

In X_i^r, the superscript r ($r = 0, 1, \ldots, N$) stands for the ionization degree of the ith species. We will write $X_i^0 = X_i$ and to species X_i^r we associate the number density n_i^r and the mole fraction $x_i^r = n_i^r/n$.

Furthermore, for an easier notation we define $(i, r) \equiv q$ such that

$$q = i\,, \qquad i = 1, \ldots, \mu\,; \quad r = 0$$

$$q = \mu + r + \sum_{l=2}^{i-1} N(l)\,, \quad i = 2, \ldots, \mu\,; \quad r \neq 0$$

$$q = i + r + \sum_{l=2}^{i-1} N(l)\,, \quad i = \mu + 1, \ldots, \nu\,. \quad (12)$$

The superscript q is introduced in order to obtain a way of separation for the different chemical species present in the plasma. Some first values of q refer to elements constituting a base, namely electrons and atoms, the other values of q refer to species able to be expressed in terms of the base elements. However, sometimes this simpler notation lacks precision and we will consider the couple (i, r) again.

The total number of species is therefore

$$N = \nu + \sum_{l=2}^{\nu} N(l)\,,$$

and we denote

$$Q = \mu + \sum_{l=2}^{\mu} N(l)\,.$$

III.2. Simplifying assumptions (S.A.)

The quantities

$\boldsymbol{\nabla} P$ the gradient of the total pressure,
$\boldsymbol{F}_i^r$ the external force on X_i^r,
$D_i^{\mathrm{T}r}$ the diffusion coefficient relative to X_i^r

are assumed to be negligible.

Then, the diffusion forces, given by (3), reduce to

$$\boldsymbol{d}_q' = \boldsymbol{\nabla} P_q\,; \quad q = 1, \ldots, N\,. \quad (13)$$

Consequently, (6) and (11) take the simplified form

$$\boldsymbol{\nabla} L n\, P_1 = \frac{\langle \boldsymbol{V}_1 \rangle}{D_{11}}\,, \quad (14)$$

$$\boldsymbol{\nabla} L n\, P_q = \sum_{j=2}^{N} \frac{x_j}{\mathscr{D}_{qj}} [\langle \boldsymbol{V}_j \rangle - \langle \boldsymbol{V}_q \rangle]\,; \quad q = 2, \ldots, N\,. \quad (15)$$

Furthermore, internal partition functions (Z_{int}) of electrons, atoms and atomic ions are supposed to be at the electron temperature T_{e} while those of molecules and of their ions are supposed to be at the kinetic temperature T_{h}.

III.3. The reactional heat flux vector

We introduce the heat flux vector

$$\boldsymbol{q}_{\mathrm{R}} = \sum_{i=1}^{\nu} \sum_{r=0}^{N(i)} n_i^r h_i^r \langle \boldsymbol{V}_i^r \rangle\,, \quad (16)$$

where h_i^r is the enthalpy of the species X_i^r.

Now, the enthalpies of different species can be written using S.A. and following [4].

One gets:

- for the electrons, as $Z_{\mathrm{int}}(T_{\mathrm{e}}) = 2$,

$$h_1 = \frac{5}{2} k T_{\mathrm{e}} + e_{01} ; \tag{17}$$

- for monatomic species

$$h_q = k T_{\mathrm{e}}^2 \frac{\partial Ln Z_{\mathrm{int}}^q (T_{\mathrm{e}})}{\partial T_{\mathrm{e}}} + \frac{5}{2} k T_{\mathrm{h}} + e_{0q} ; \quad q = 2, \ldots, Q ; \tag{18}$$

- for diatomic species

$$h_q = k T_{\mathrm{h}} \left(T_{\mathrm{h}} \frac{Ln Z_{\mathrm{int}}^q (T_{\mathrm{h}})}{\partial T_{\mathrm{h}}} + \frac{5}{2} \right) + e_{0q} ; \quad q = Q+1, \ldots, N . \tag{19}$$

Here, e_{0q} $(q = 1, \ldots, N)$ stands for an energy relative to an arbitrary reference state.

III.4. Definition of λ_{R}

We assume that θ can be locally expressed as $\theta = \theta(\boldsymbol{r})$ through T_{e} or T_{h}. We write $\boldsymbol{\nabla} T_{\mathrm{h}}$ in terms of $\boldsymbol{\nabla} T_{\mathrm{e}}$:

$$\boldsymbol{\nabla} T_{\mathrm{h}} = \frac{1}{\theta} \left(1 - \frac{T_{\mathrm{e}}}{\theta} \frac{\partial \theta}{\partial \boldsymbol{T}_{\mathrm{e}}} \right) \boldsymbol{\nabla} T_{\mathrm{e}} , \tag{20}$$

and by definition we get

$$\boldsymbol{q}_{\mathrm{R}} = - \lambda_{\mathrm{R}} \boldsymbol{\nabla} T_{\mathrm{e}} . \tag{21}$$

III.5. Expression of λ_{R} in terms of averaged diffusion velocities

From (16) and (21) it follows that

$$\begin{aligned} \lambda_{\mathrm{R}} \boldsymbol{\nabla} T_{\mathrm{e}} &= - \sum_{l=1}^{\nu} \sum_{r=0}^{N(i)} n_i^r h_i^r \langle \boldsymbol{V}_i^r \rangle \\ &= - \sum_{q=1}^{N} n_q h_q \langle \boldsymbol{V}_q \rangle . \end{aligned} \tag{22}$$

In order to determine the reactional thermal conductivity λ_{R}, we seak to write a set of linear equations having a solution expressing $\langle \boldsymbol{V}_i^r \rangle$ in terms of $\boldsymbol{\nabla} T_{\mathrm{e}}$. The flux conservation for different species yields μ equations, the chemical reactions lead to $M = N - \mu$ equations giving $\boldsymbol{\nabla} Ln P_i^r$ in terms of $\boldsymbol{\nabla} T_{\mathrm{e}}$ (here P_i^r is the partial pressure of the species X_i^r). Firstly a relationship between $\boldsymbol{\nabla} Ln P_i^r$ and $\langle \boldsymbol{V}_i^r \rangle$ is obtained, secondly the expression of λ_{R} is derived from the N above equations.

III.6. Equations deduced from the flux conservation

It is possible to express each chemical species in terms of the elementary ones choosen for a base, namely electrons and atoms. This enables us to write

$$\sum_{k=1}^{\mu} \alpha_{ik}^r X_k - X_i^r = 0 ; \tag{23}$$

$$\begin{aligned} i &= 2, \ldots, \mu ; & r &= 1, \ldots, N(i) , \\ i &= \mu + 1, \ldots, \nu ; & r &= 0, \ldots, N(i) . \end{aligned}$$

To obtain easier notations, we introduce a new relationship in addition to the one defined in paragraph (III.1.):

$$[i, r] \rightarrow m \quad \text{with} \quad m = q - \mu \quad (\text{for } q > \mu) , \qquad \alpha_{ik}^r \equiv \alpha_{mk} . \tag{24}$$

The subscript m refers to the number of the reaction, and $m = 1, 2, \ldots, M$ with $M = N - \mu$.

Taking (23) and (24) into account, we write the flux conservation for each base element (in a steady state there are no charge or mass accumulations on either side of a surface element). Thus we get

$$\langle \boldsymbol{V}_k \rangle = - \sum_{q=\mu+1, m}^{N} \alpha_{mk} \frac{x_q}{x_k} \langle \boldsymbol{V}_q \rangle ; \quad k = 1, \ldots, \mu . \tag{25}$$

Following (16) and (23), one can write

$$\boldsymbol{q}_{\mathrm{R}} = - \sum_{q=\mu+1, m}^{N} n_q \Delta h_m \langle \boldsymbol{V}_q \rangle$$

with

$$\Delta h_m = \sum_{k=1}^{\mu} \alpha_{mk} h_k - h_m . \tag{26}$$

The quantity Δh_m is the enthalpy variation of the mth reaction described by (23).

III.7. Equations related to the chemical reactions

When the plasma is out of equilibrium, chemical equations, used to determine the species composition, cannot be written in terms of the base elements (cf. (23)). For example, the ionization of a molecule may be given as

$$X_m \rightarrow X_{m+1}^+ + e .$$

Consequently, introducing new coefficients, a reaction is described by

$$\sum_{i=1}^{\nu} \sum_{r=0}^{N(i)} \alpha_{ji}^{sr} X_i^r = 0 \,; \tag{27}$$

$$j = 2, \dots, \mu \,; \qquad s = 1, \dots, N(j) \,,$$
$$j = \mu + 1, \dots, \nu \,; \quad s = 0, \dots, N(j) \,.$$

Using (12) and (24), we set

$$\alpha_{ji}^{sr} \equiv \alpha_{mq} \,; \quad m = 1, \dots, M \,; \quad q = 1, \dots, N \,. \tag{28}$$

III.7.1. Chemical reactions in a medium out of equilibrium

The chemical potentials of the species in the gas can take the forms [4]

$$\mu_1 = \mu_1^0 + k\, T_{\mathrm{e}}\, L n \frac{P_1}{P} \,,$$

$$\mu_q = \mu_q^0 + k\, T_{\mathrm{h}}\, L n \frac{P_q}{P} \,, \tag{29}$$

where μ_q^0 stand for the chemical potentials of the qth element:

$$\mu_1^0 = -\, k\, T_{\mathrm{e}}\, L n \left[\frac{k\, T_{\mathrm{e}}}{P} \left(\frac{2\,\pi\, m_1\, k\, T_{\mathrm{e}}}{h^2} \right)^{3/2} \right]$$
$$-\, k\, T_{\mathrm{e}}\, L n\, Z_{\mathrm{int}}^1 (T_{\mathrm{e}}) + e_{01} \,,$$

$$\mu_q^0 = -\, k\, T_{\mathrm{h}}\, L n \left[\frac{k\, T_{\mathrm{h}}}{P} \left(\frac{2\,\pi\, m_q\, k\, T_{\mathrm{h}}}{h^2} \right)^{3/2} \right]$$
$$-\, k\, T_{\mathrm{e}}\, L n\, Z_{\mathrm{int}}^q (T_{\mathrm{e}}) + e_{0q} \,; \quad q = 2, \dots, Q \,,$$

$$\mu_q^0 = -\, k\, T_{\mathrm{h}}\, L n \left[\frac{k\, T_{\mathrm{h}}}{P} \left(\frac{2\,\pi\, m_q\, k\, T_{\mathrm{h}}}{h^2} \right)^{3/2} \right] \tag{30}$$
$$-\, k\, T_{\mathrm{h}}\, L n\, Z_{\mathrm{int}}^q (T_{\mathrm{h}}) + e_{0q} \,;$$
$$q = Q + 1, \dots, N \,.$$

In the above equations h is the Planck's constant.

The chemical equilibrium condition for the reaction may be obtained as [4]

$$\sum_{q=1}^{N} a_{mq}\, \mu_q = 0 \,; \quad m = 1, \dots, M \tag{31}$$

and gives

$$K_m (P) = P_1^{a_{m1}\theta} \prod_{q=2}^{N} P_q^{a_{mq}} = \left[k\, T_{\mathrm{e}} \left(\frac{2\,\pi\, m_1\, k\, T_{\mathrm{e}}}{h^2} \right)^{3/2} \right]^{a_{m1}\theta}$$
$$\times \prod_{q=2}^{N} \left[k\, T_{\mathrm{h}} \left(\frac{2\,\pi\, m_q\, k\, T_{\mathrm{h}}}{h^2} \right)^{3/2} \right]^{a_{mq}} \prod_{q=1}^{Q} \left[Z_{\mathrm{int}}^q (T_{\mathrm{e}}) \right]^{a_{mq}\theta}$$
$$\times \prod_{q=Q+1}^{N} \left[Z_{\mathrm{int}}^q (T_{\mathrm{h}}) \right]^{a_{mq}} \times \exp \left(- \frac{\theta \prod_{q=1}^{N} a_{mq}\, e_{0q}}{k\, T_{\mathrm{e}}} \right) ;$$
$$m = 1, \dots, M \,. \tag{32}$$

In the following we assume θ as a given parameter ($\theta = \text{constant}$) and write instead of (20)

$$\nabla T_{\mathrm{h}} = \frac{1}{\theta} \nabla T_{\mathrm{e}} \,. \tag{33}$$

From the derivative of $K_m (P)$ and (33), $\nabla L n\, P_q$ can be deduced.

Consequently derivatives, such as $\partial L n\, Z_{\mathrm{int}}^q / \partial T_{\mathrm{e}}$, expressed in terms of enthalpies (16)−(18), will occur in the formulation and lead to a law quite similar to the one of equilibrium:

$$\frac{\mathrm{d} L n\, K(P)}{\mathrm{d} T} = - \frac{\Delta H}{R T^2} \,, \tag{34}$$

where ΔH is the enthalpy variation.

III.7.2. Expression of $\nabla L n\, P_q$ from derivation of $K_m (P)$

Following the just defined steps one gets the equation

$$a_{m1}\theta \frac{\partial L n\, P_1}{\partial T_{\mathrm{e}}} + \sum_{q=2}^{N} a_{mq} \frac{\partial L n\, P_q}{\partial T_{\mathrm{e}}} = \frac{\theta \Delta h_m^*}{k\, T_{\mathrm{e}}^r} \,;$$
$$m = 1, \dots, M \tag{35}$$

which yields the expected expression

$$a_{m1}\theta\, \nabla L n\, P_1 + \sum_{q=2}^{N} a_{mq}\, \nabla P_q = \frac{\theta \Delta h_m^*}{k\, T_{\mathrm{e}}^r} \nabla T_{\mathrm{e}} \,;$$
$$m = 1, \dots, M \,. \tag{36}$$

Note that the energy, evaluated from the reference state, can be written as

$$e_{0q} \equiv e_{0i}^r = e_{0i}^{1r} - \sum_{s=1}^{r} \Delta e_i^{s-1} \,. \tag{37}$$

Here e_{0i}^{1r} is in reality a constant (accounting for dissociation and ionization energies) and Δe_i^{s-1} stands for a corrective term related to the Coulombic field and given as [11]

$$\Delta e_i^{s-1} = \frac{s\, e^r}{4\,\pi\, \varepsilon_0} d^{-1} \,, \tag{38}$$

e being the electron charge, ε_0 the vacuum permittivity and d the Debye's length [12]

$$d^{-1} = \frac{e}{(\varepsilon_0\, k)^{1/2}} \left[\frac{n_1}{T_\mathrm{e}} + \frac{1}{T_\mathrm{h}} \sum_{i=2}^{v} \sum_{r=0}^{N(i)} r^2 n_i^r \right]^{1/2} . \quad (39)$$

To obtain the derivative of $K_m(P)$, the quantities Δe_i^{s-1} have been regarded as constants. The determination of the derivative would be otherwise tedious: d is depending on T_e, T_h and, through the densities n_i^r, on the partial pressures. Furthermore, performing such calculations in the quite simple case of argon (with no dissociation and only a first ionization as a chemical reaction), it has been checked that the numerical results were almost unaffected by that assumption.

III.8. Expressions of $\boldsymbol{\nabla} L n\, P_q$ *for* $q = 1, \ldots, N$ *in terms of* $\langle \boldsymbol{V}_q \rangle$ *for* $q = \mu + 1, \ldots, N$

Inserting (25) into (14) and (15), one gets three sets of expressions according to the numbering of the species.

III.8.1. Electrons

The equations (14) and (25) enable us to obtain the expression for the electrons as

$$\boldsymbol{\nabla} L n\, P_1 = \frac{1}{D_{11}} \sum_{q=\mu+1,m}^{N} a_{m1} \frac{x_q}{x_1} \langle \boldsymbol{V}_q \rangle . \quad (40)$$

III.8.2. Elements from 2 up to μ

Equation (15) may be written as

$$\boldsymbol{\nabla} L n\, P_l = \sum_{k=2}^{\mu} \frac{x_k}{\mathcal{D}_{lk}} [\langle \boldsymbol{V}_k \rangle - \langle \boldsymbol{V}_l \rangle] + \sum_{q=\mu+1}^{N} \frac{x_q}{\mathcal{D}_{lq}} [\langle \boldsymbol{V}_q \rangle - \langle \boldsymbol{V}_l \rangle] , \quad (41)$$

and using (25) one finds

$$\boldsymbol{\nabla} L n\, P_l = \sum_{q=\mu+1,m}^{N} \left(\frac{x_q}{\mathcal{D}_{lq}} + a_{ml} \frac{x_q}{x_l} \sum_{j=2}^{N} \frac{x_j}{\mathcal{D}_{lj}} - \sum_{k=2}^{\mu} \alpha_{mk} \frac{x_q}{\mathcal{D}_{lk}} \right) \langle \boldsymbol{V}_q \rangle ; \quad l = 2, \ldots, \mu . \quad (42)$$

III.8.3. Species from $\mu + 1$ *up to* N

Starting from a splitting similar to the one occurring in (41) and substituting (25), one obtains the expression

$$\boldsymbol{\nabla} L n\, P_u = \sum_{q=\mu+1,m}^{N} \left(\frac{x_q}{\mathcal{D}_{uq}} - \sum_{k=2}^{\mu} \alpha_{mk} \frac{x_q}{\mathcal{D}_{uk}} \right) \langle \boldsymbol{V}_q \rangle - \langle \boldsymbol{V}_u \rangle \sum_{v=2}^{N} \frac{x_v}{\mathcal{D}_{uv}} ; \quad u = \mu + 1, \ldots, N . \quad (43)$$

IV. Final Expression for λ_R

Equation (36) can be written as

$$a_{n1}\, \theta\, \boldsymbol{\nabla} L n\, P_1 + \sum_{l=2}^{\mu} a_{nl} \boldsymbol{\nabla} L n\, P_l + \sum_{u=\mu=1}^{N} a_{nu} \boldsymbol{\nabla} L n\, P_u = \frac{\theta\, \Delta h_n^*}{k\, T_\mathrm{e}^2} \boldsymbol{\nabla} T_\mathrm{e} ; \quad n = 1, \ldots, M . \quad (44)$$

Taking into account that $m = q - \mu$ $(m = 1, \ldots, M)$ and using (40), (42) and (43) we obtain

$$\sum_{q=\mu+1,m}^{N} A_{nm} \langle \boldsymbol{V}_q \rangle = \frac{\theta\, \Delta h_n^*}{k\, T_\mathrm{e}^2} \boldsymbol{\nabla} T_\mathrm{e} ; \quad n = 1, \ldots, M \quad (45)$$

by setting

$$A_{nm} = \frac{a_{n1}\, \theta}{D_{11}} \alpha_{m1} \frac{x_q}{x_1} + \sum_{l=2}^{\mu} a_{nl} \left(\frac{x_q}{\mathcal{D}_{lq}} + \alpha_{ml} \frac{x_q}{x_l} \sum_{v=2}^{N} \frac{x_v}{\mathcal{D}_{v}} - \sum_{k=2}^{N} \alpha_{mk} \frac{x_q}{\mathcal{D}_{lk}} \right) + \sum_{u=\mu+1}^{N} a_{nu} \left(\frac{x_q}{\mathcal{D}_{uq}} - \sum_{k=2}^{\mu} \alpha_{mk} \frac{x_q}{\mathcal{D}_{uk}} \right) - a_{nq} \sum_{v=2}^{N} \frac{x_v}{\mathcal{D}_{qv}} .$$

From the definition (22) of λ_R in terms of $\langle \boldsymbol{V}_q \rangle$ satisfying (26), the classical reduced form for λ_R is obtained, by using the Cramer's rule, as

$$\lambda_\mathrm{R} = \frac{\theta}{k\, T_\mathrm{e}^2} \left| \begin{array}{cccc} 0 & n_{\mu+1} \Delta h_1 & \ldots & n_N \Delta h_M \\ \Delta h_1^* & A_{11} & \ldots\ldots & A_{1M} \\ \cdot & \cdot & & \cdot \\ \cdot & \cdot & & \cdot \\ \cdot & \cdot & & \cdot \\ \Delta h_M^* & A_{M1} & \ldots\ldots & A_{MM} \end{array} \right| \Bigg/ \left| \begin{array}{ccc} A_{11} & \ldots & A_{1M} \\ \cdot & & \cdot \\ \cdot & & \cdot \\ \cdot & & \cdot \\ A_{M1} & \ldots & A_{MM} \end{array} \right| .$$

V. Conclusion

Starting from the ideas of de Voto, by introducing different diffusion forces which lead to a closure equation, we have developed a new theory for a non equilibrium two-temperature plasma, allowing to take into account inelastic processes. The use of our theory is relatively easy because all the transport coefficients can be expressed in terms of the classical collision integrals [1], [6], [7], [9].

For elastic processes we have, in spite of theoretical modifications, obtained the formulas given in [6]. Furthermore, close attention must be paid to the adequacy of the introduction of new diffusion terms (forces, ordinary and binary coefficients, velocities). Owing to that, in order to calculate the reactional thermal conductivity λ_R, we have established a new procedure close to the one of Butler and Brokaw [8] but developed specially for the two-temperature case.

We have tested our theory, as a whole, for an Ar-H_2 mixture at atmospheric pressure. Our so computed values agree very well, at equilibrium, with those previously published [13], [14]. It is a nice verification of our theory entirely developed out of equilibrium and for which $T_e = T_h$ is merely a particular case. We will publish in a next paper all the numerical results obtained for the Ar-H_2 mixture.

[1] R. S. de Voto, Ph.D. Thesis, Standford University (1965).
[2] R. M. Chmieleski, Ph.D. Thesis, Standford University (1967).
[3] S. Chapman and T. Cowling, The Mathematical Theory of Non-Uniform Gases, Cambridge Univ. Press, New York 1970.
[4] A. V. Potapov, High Temp. **4,** 48 (1966).
[5] E. Richley and D. T. Tuma, J. Appl. Physics **53,** 12, 8, 537 (1982).
[6] R. S. de Voto, Phys. Fluids **10,** 2, 105 (1967).
[7] C. Bonnefoi, Thèse, Université de Limoges 1983.
[8] J. N. Butler and R. S. Brokaw, J. Chem. Physics **26,** n° 6, 1, 636 (1957).
[9] J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, Molecular Theory of Gases and Liquids, John Wiley & Sons, New York 1964.
[10] C. Bonnefoi and P. Fauchais, Phys. Fluids **19,** n° 11 (1976).
[11] H. R. Griem, Plasma Spectroscopy, Mac Graw Hill, New York 1964.
[12] L. R. Liboff, Phys. of Fluids **2,** 40 (1959).
[13] J. Aubreton and P. Fauchais, Rev. Phys. Appl. **18,** 51 (1983).
[14] C. Gorse, Thèse 3e cycle, Limoges 1975.