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**ASYMPTOTIC SOLUTION OF THE
BOLTZMANN-KROOK EQUATION FOR A
REACTING MIXTURE OF GASES**

by

OLIVIER PEROT

Ingenieur de l'Ecole Polytechnique, Promotion 1983,
Ingenieur de l'Ecole Nationale Supérieure de l'Aéronautique et de l'Espace, Promotion 1988,

Submitted in partial fulfillment
of the requirements of the degree of

**MASTER OF SCIENCE
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at the

MASSACHUSETTS INSTITUTE OF TECHNOLOGY

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Submitted to the Department of Aeronautics and Astronautics
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Sciences in Aeronautics and Astronautics.

ABSTRACT

A theoretical description of a flow composed of reacting monoatomic and diatomic oxygen molecules in the neighborhood of a flat plate is performed. The recombination reaction is assumed to take place at the surface of the plate only. The molecular flow is described by the mean of species distribution functions which satisfy a sequence of coupled Boltzmann-Krook equations. This kinetic model is completely determined by requiring it to admit the usual collision invariants and to be compatible with the H theorem.

An asymptotic solution of this Boltzmann-Krook equation is constructed. The distribution functions are expanded in power of the square root of the Knudsen number of the problem assumed small. They are required to satisfy boundary conditions on the averaged hydrodynamic quantities. The first component of the solution yields a contribution similar to the solution of the Navier-Stokes equations with no-slip condition. The next components satisfy a sequence of linear equations whose coefficients depend on the solution of the Navier-Stokes equations. The boundary conditions associated with these higher order iterates yield a slip proportional to the gradient normal to the surface of lower order quantities.

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Section I

INTRODUCTION

Given some of the current and future applications of the aerospace sciences (e.g. Space Shuttle, Aerospace Plane, AOTV), a very active area of research in fluid mechanics today is concerned with hypersonic flight. In particular, hypersonic aerodynamics involve high temperatures, hence dissociation reactions and the appearance of several reacting chemical species in the fluid, which greatly complicates the classical treatment. Moreover, the interaction of such an high-temperature reacting gas with a surface is far from being well understood. Consequently, the specification of boundary conditions for such flows is somewhat arbitrary, especially in the case of a transition regime flow where one needs to consider a slip-condition (see for example the treatment of Gokcen and MacCormack (1989)). To understand the process going on at a surface, one needs to consider the microscopic motion of molecules. The theoretical tool for such a study is the particle distribution function, whose evolutions are described by the Boltzmann equation.

The problem of clarifying the relationship between the Boltzmann equation and the equations of motion of a continuous gas has been extensively studied during the last decades (see for instance Grad (1963) and Grad (1963, II)). One of the major issues was that of boundary conditions, to which Trilling (1964) made an important contribution. He considered a simple boundary value problem: the motion of an infinite flat plate parallel to itself, when it bounds a half-space filled with a monoatomic gas. In particular, he constructed an asymptotic solution of the Boltzmann-Krook equation for this Rayleigh shear flow problem (By Boltzmann-Krook equation we mean the simplified model of the Boltzmann equation proposed by Bhatnagar *et al* (1954) and by Gross and Krook (1956)).

The purpose of this thesis is to investigate a simplified model of an hypersonic flow over

an infinite flat plate, by using, and eventually adapting, the theoretical approach developed by Trilling (1964). Before proceeding any further, we need to set the basic hypotheses of the problem we want to study.

We consider an infinite flat plate of temperature $T_w(t)$ which occupies the plane $y=0$ and moves in its own plane in a direction parallel to the x axis at a velocity $U_w(t)$. Initially the upper-half space is filled with monoatomic oxygen, and the plate is impulsively set into motion at $t=0$. Far from the plate, the gas is at rest at a density ρ_∞ , a temperature T_∞ and a pressure p_∞ . The plate is assumed to be adiabatic; that means there is no heat transfer at the wall. We want to investigate the molecular layer near the wall, after a period of time long enough for intermolecular collisions to have smoothed out the specific initial conditions, and still take into account the hypersonic nature of the flow.

Assuming that the wall is cold compared to the flow temperature, the recombination reaction occurs mostly in a layer very close to the wall. In fact, we will consider that the recombination process occurs only at the wall, and that the O_2 molecules created at the surface are reemitted diffusely, with full momentum and energy accommodation with the wall. Far from the surface, in the outer layer of the flow, the O_2 molecules are dissociated back into O atoms, as a result of the many energetic collisions they encounter in the outer flow. However, in the inner layer, we assume that this dissociation reaction does not occur. Therefore, we will treat the flow of a two component non reacting mixture of O and O_2 , the recombination process being taking into account through the specification of the boundary conditions only (Fig. 1). Furthermore, we assume that the Knudsen number of the flow is small compared to unity. In other words, we will consider a continuum or near continuum flow.

In this investigation, we proceed as follows. Starting from the Boltzmann equation, we derive the general form of the equation of motion of this mixture (Sec. II). Next, we replace the Boltzmann equation by a simplified kinetic model (Sec. III). Then, we formally expand the distribution functions, the equations of motion and the corresponding boundary conditions in power of a small parameter ϵ , related later to physical parameters of the problem (Sec. IV).

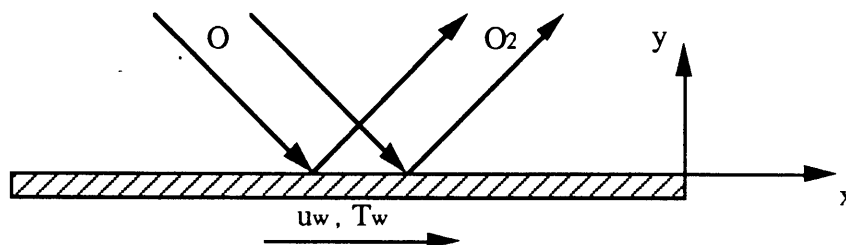


Fig. 1. Recombination at the surface.

This allows us to construct an iterative solution of our kinetic equation (Sec. V) and the first order and second order systems will be discussed thoroughly later (Sec VI).

Section II

EQUATIONS OF MOTION

In this section, we define the variables needed to study the motion of a mixture of gases and derive the general form of the equations of motion of a non reacting mixture of gases. These equations will be useful later as reference.

II.1 Boltzmann equation

To describe the behavior of a mixture of gases, we introduce different distribution functions for the components of the mixture - $f_s(\mathbf{x}_s, \xi_s, t)$ - (in our case $s=1$ for O molecules and $s=2$ for O_2 molecules). Any change in the distribution function f_s in the 6 dimension phase space (\mathbf{x}, ξ) is due to collisions both with molecules of the same kind and with molecules of a different kind. Assuming that the molecules possess only translational degrees of freedom, the evolution of each distribution function f_s in phase space is described by a Boltzmann equation of the form

$$\frac{Df_s}{Dt} = \sum_{r=1,2} Q_{sr}(f_s, f_r) \quad , \quad s = 1, 2 \quad (\text{II.1})$$

The left-hand-side is the convective derivative in phase space

$$\frac{Df_s}{Dt} = \frac{\partial f_s}{\partial t} + \xi_s \cdot \frac{\partial f_s}{\partial \mathbf{x}_s} + \frac{\mathbf{F}_s}{m_s} \cdot \frac{\partial f_s}{\partial \xi_s} \quad (\text{II.2})$$

where \mathbf{F}_s represents the external forces acting on molecules of the s -th kind, and m_s is the mass of a molecule of kind s . The right-hand-side is the sum of the collision integrals over various components of the mixture, each of which taking account of collisions of molecules of the s th kind with molecules of the r th kind

$$Q_{sr}(f_s, f_r) = \int_{\mathfrak{X}^5} (f'_s f'_r - f_s f_r) g_{sr} b db d\epsilon d\xi_{sr} \quad (\text{II.3})$$

where g_{sr} is the module of the relative velocity, b is the impact parameter and ϵ the collision angle (for a detailed description of the theory, see Kogan (1969)). Thus, the change in the state of a mixture is described by a system of equations for the distribution functions f_s , all the functions f_s appearing in each of the equations of the system (II.1).

II.2 Hydrodynamic variables

Multiplying the distribution function f_s by various quantities and integrating over the whole velocity space yield the familiar hydrodynamic variables, depending on position and time only. We need to define:

- the mass density of particles of kind s

$$\rho_s = \int_{\mathfrak{X}^3} f_s d\xi_s \quad (\text{II.4})$$

- the number density of particles of kind s

$$n_s = \frac{\rho_s}{m_s} \quad (\text{II.5})$$

- the mean velocity of particles of kind s

$$\rho_s v_s = \int_{\mathfrak{X}^3} \xi_s f_s d\xi_s \quad (\text{II.6})$$

- the mass density of the mixture

$$\rho = \sum_s \rho_s \quad (\text{II.7})$$

- the number density of the mixture

$$n = \sum_s n_s \quad (\text{II.8})$$

- the mean velocity of the mixture

$$\rho v = \sum_s \rho_s v_s \quad (\text{II.9})$$

- the diffusion velocity of particles of kind s

$$V_s = v_s - v \quad (\text{II.10})$$

- the peculiar velocity of particles of kind s

$$c_s = \xi_s - v \quad (\text{II.11})$$

- the partial stress tensor of the s th component

$$(P_s)_{ij} = \int_{\mathfrak{R}^3} (c_s)_i (c_s)_j f_s d\xi_s \quad (\text{II.12})$$

- the stress tensor of the mixture

$$P_{ij} = \sum_s (P_s)_{ij} \quad (\text{II.13})$$

- the temperature of the sth component

$$\frac{3}{2} n_s k T_s = \frac{1}{2} \int_{\mathfrak{R}^3} c_s^2 f_s d\xi_s \quad (\text{II.14})$$

- the temperature of the mixture

$$\frac{3}{2} nkT = \sum_s \frac{3}{2} n_s k T_s \quad (\text{II.15})$$

- the scalar pressure, and accordingly the equation of state for a perfect gas

$$p = \frac{1}{3} (P_{xx} + P_{yy} + P_{zz}) = nkT \quad (\text{II.16})$$

- the partial heat-flux of the sth component

$$\mathbf{q}_s = \frac{1}{2} \int_{\mathfrak{R}^3} \mathbf{c}_s c_s^2 f_s d\xi_s \quad (\text{II.17})$$

- the heat-flux in the mixture

$$\mathbf{q} = \sum_s \mathbf{q}_s \quad (\text{II.18})$$

Moreover, we introduce another species temperature, denoted T_{ss} , and defined with respect to the mean velocity of species s , instead of the mean velocity of the mixture as for T_s

$$\frac{3}{2} n_s k T_{ss} = \frac{1}{2} \int_{\mathfrak{R}^3} (\xi_s - \mathbf{v}_s)^2 f_s d\xi_s \quad (\text{II.19})$$

It is then easy to show the relation, valid in the two-component case (Appendix A.1):

$$T_1 = T_{11} + \frac{m_1 \rho_2^2}{3k \rho^2} (\mathbf{v}_2 - \mathbf{v}_1)^2 \quad (\text{II.20})$$

and the analog for species 2.

Remark: the components of the vectors $\mathbf{x}, \xi, \mathbf{v}$ are respectively denoted by (x, y, z) , (ξ, η, ζ) , (u, v, w) , a bold character stands for a vector.

II.3 Macroscopic equations of motion

In a general problem of aerodynamics, we are not interested in a detailed description of the distribution functions in the whole position-velocity phase space. What we need is a

macroscopic description of the flow involving the hydrodynamic quantities we have just introduced. However, this macroscopic description is not independent of the microscopic one. It is even closely related to it. The equations of motion, involving only the hydrodynamic variables, are derived by taking moments of the Boltzmann equation.

Integrating equation (II.1) with respect to ξ_s yields

$$\int_{\mathfrak{R}^3} \frac{Df_s}{Dt} d\xi_s = 0 \quad (\text{II.21})$$

The vanishing of the right-hand side is simply interpreted as the conservation of the total number of molecules of kind s per unit volume, since we have not allowed chemical changes to occur as a result of collisions.

If we multiply (II.1) by ξ_s and integrate with respect to ξ_s , the right-hand side does not disappear, because molecules of kind s may exchange momentum with molecules of a different kind. However, if we sum up the species momentum equations over s , the right-hand side vanishes because of the conservation of the total momentum. Thus we may write

$$\sum_s \int_{\mathfrak{R}^3} \xi_s \frac{Df_s}{Dt} d\xi_s = 0 \quad (\text{II.22})$$

Similarly, if we multiply (II.1) by ξ_s^2 , integrate with respect to ξ_s and sum up over s , we obtain

$$\sum_s \int_{\mathfrak{R}^3} \frac{1}{2} \xi_s^2 \frac{Df_s}{Dt} d\xi_s = 0 \quad (\text{II.23})$$

The sum of the right-hand-side vanishes because of the conservation of total energy. For a mathematical proof of the vanishing of the right hand sides of (II. 21, 22, 23), see Hirschfelder *et al*, page 460 (1954).

Equations (II.21), (II.22) and (II.23) represent respectively the species density, the total momentum and the total energy conservation equations. By replacing the hydrodynamic variables by their definition, taking into account the spatial variation along the y axis only, and assuming no external forces (according to the terms of our problem), we derive the equations of motion of a continuous gas mixture (the derivation of the energy equation is detailed in appendix A.2)

- conservation of mass of species s ($s=1,2$)

$$\frac{\partial \rho_s}{\partial t} + \frac{\partial \rho_s v_s}{\partial y} = 0 \quad (\text{II.24.a})$$

- conservation of total momentum along the x axis

$$\rho \left(\frac{\partial u}{\partial t} + v \frac{\partial u}{\partial y} \right) + \frac{\partial P_{xy}}{\partial y} = 0 \quad (\text{II.24.b})$$

- conservation of total momentum along the y axis

$$\rho \left(\frac{\partial v}{\partial t} + v \frac{\partial v}{\partial y} \right) + \frac{\partial P_{yy}}{\partial y} = 0 \quad (\text{II.24.c})$$

- conservation of total energy

$$\frac{3}{2}nk \left(\frac{\partial T}{\partial t} + v \frac{\partial T}{\partial y} \right) + \frac{\partial q_y}{\partial y} + P_{xy} \frac{\partial u}{\partial y} + P_{yy} \frac{\partial v}{\partial y} = \frac{3}{2}kT \frac{\partial \left(\sum_s n_s V_s \right)}{\partial y} \quad (\text{II.24.d})$$

Now, we are left with a system of 5 equations for the 5 main unknowns of the problem: ρ_1 , ρ_2 , u , v , T , and 5 additional unknowns v_1 , v_2 , P_{xy} , P_{yy} , q_y . Of course, this system is not closed. The Boltzmann equation can not be replaced by a closed set of partial differential equations. To obtain a closed set of equations, we need to relate the additional unknowns to the main hydrodynamic quantities. One way to obtain these so called constitutive relations is to look for an asymptotic solution of the Boltzmann equation. This is the purpose of the theory of Chapman and Enskog. However, in practice one uses a slightly simplified version of the theory. In the next paragraph we review these usual constitutive relations, which one could establish by using a phenomenological approach.

II.4 The Navier-Stokes equations

The constitutive relations commonly adopted, as found in Anderson (1989, Ch 16), are presented below:

- Fick's law of diffusion

$$\rho_s V_s = -\rho D_s \frac{\partial C_s}{\partial y} \quad (\text{II.25})$$

where C_s is the concentration of species s : $C_s = n_s/n$, and D_s is the diffusion coefficient (In our case where only two species are present, D_1 and D_2 are equal: $D_1 = D_2 = D$)

- Law of viscosity

$$P_{xy} = -\mu \frac{\partial u}{\partial y} \quad (\text{II.26.a})$$

$$P_{yy} = p - \frac{4}{3} \mu \frac{\partial v}{\partial y} \quad (\text{II.26.b})$$

- Law of conduction

$$q_y = -\lambda \frac{\partial T}{\partial y} - \sum_s \rho_s V_s h_s \quad (\text{II.27})$$

where h_s is the specific enthalpy per unite mass. Assuming no chemical reaction in the flow and particles with no internal degree of freedom, h_s is given by

$$h_s = \frac{5kT}{2m_s} \quad (\text{II.28})$$

Combining (II.25),(II.27) and (II.28), we get

$$q_y = -\lambda \frac{\partial T}{\partial y} - \frac{5}{2} kT \rho D \sum_s \frac{1}{m_s} \cdot \frac{\partial C_s}{\partial y} \quad (\text{II.29})$$

Putting these expressions into the equations of motion (II.24.a) through (II.24.d) yields the following equations, which will be referred to as the Navier-Stokes equations

$$\frac{\partial \rho_s}{\partial t} + \frac{\partial(\rho_s v)}{\partial y} = \frac{\partial}{\partial y} \left(\rho D \frac{\partial C_s}{\partial y} \right) \quad (\text{II.30.a})$$

$$\rho \left(\frac{\partial u}{\partial t} + v \frac{\partial u}{\partial y} \right) = \mu \frac{\partial^2 u}{\partial y^2} \quad (\text{II.30.b})$$

$$\rho \left(\frac{\partial v}{\partial t} + v \frac{\partial v}{\partial y} \right) + \frac{\partial p}{\partial y} = \frac{4}{3} \mu \frac{\partial^2 v}{\partial y^2} \quad (\text{II.30.c})$$

$$\begin{aligned} \frac{3}{2} nk \left(\frac{\partial T}{\partial t} + v \frac{\partial T}{\partial y} \right) - \lambda \frac{\partial^2 T}{\partial y^2} - \frac{\partial}{\partial y} \left(\rho D \sum_s h_s \frac{\partial C_s}{\partial y} \right) - \mu \left(\frac{\partial u}{\partial y} \right)^2 + p \frac{\partial v}{\partial y} - \frac{4}{3} \mu \left(\frac{\partial v}{\partial y} \right)^2 = \\ - \frac{3}{2} kT \frac{\partial}{\partial y} \left(\rho D \sum_s \frac{1}{m_s} \cdot \frac{\partial C_s}{\partial y} \right) \end{aligned} \quad (\text{II.30.d})$$

Furthermore, it is interesting for reference purposes to give the corresponding boundary-layer equations. In order for us to define independent and dependent dimensionless variables, we need to introduce an arbitrary length reference L and a small parameter ϵ . The small parameter ϵ is used to stretch the quantities along the y direction, as required by the theory of matched asymptotic expansions (see Van Dyke, Ch V, 1964). The dimensionless variables are

$$\begin{aligned} \bar{y} = \frac{y}{\epsilon L}, \quad \bar{t} = \frac{t c_\infty}{L} \quad (\text{with } c_\infty = \sqrt{\frac{2n_\infty k T_\infty}{\rho_\infty}}) \\ \bar{\rho} = \frac{\rho}{\rho_\infty}, \quad \bar{T} = \frac{T}{T_\infty}, \quad \bar{u} = \frac{u}{c_\infty}, \quad \bar{v} = \frac{v}{c_\infty}, \quad \bar{P}_{xy} = \frac{P_{xy}}{\epsilon \rho_\infty c_\infty^2}, \quad \bar{P}_{yy} = \frac{P_{yy}}{\rho_\infty c_\infty^2}, \quad \bar{q}_y = \frac{q_y}{\epsilon \rho_\infty c_\infty^3} \end{aligned} \quad (\text{II.31})$$

Then, we will obtain up to the first order the following system of equations by expanding the system (II.30) in power of ϵ and by identifying ϵ as the inverse of the square root of the Reynolds number (in order to retain the viscous terms in the boundary-layer, as exposed by Van Dyke, Ch VII, 1964)

$$\frac{\partial \rho_s}{\partial t} + \frac{\partial(\rho_s v)}{\partial y} = \frac{Le}{Pr} \frac{\partial}{\partial y} \left(\rho \frac{\partial C_s}{\partial y} \right) \quad (\text{II.32.a})$$

$$\rho \left(\frac{\partial u}{\partial t} + v \frac{\partial u}{\partial y} \right) = \frac{\partial^2 u}{\partial y^2} \quad (\text{II.32.b})$$

$$\frac{\partial p}{\partial y} = 0 \Rightarrow nT = 1 \quad (\text{II.32.c})$$

$$\frac{5\partial v}{4\partial y} - \left(\frac{\partial u}{\partial y} \right)^2 - \frac{\partial^2 T}{\text{Pr}\partial y^2} - \frac{5\text{Le}\partial}{2\text{Pr}\partial y} \left\{ \rho T \frac{\partial}{\partial y} \left[(n_1 R_1 + n_2 R_2) T \right] \right\} = 0 \quad (\text{II.32.d})$$

where the bars have been omitted but all quantities are dimensionless. R_1 is defined as

$$R_1 = \frac{\rho_\infty}{2n_\infty m_1} \quad (\text{II.33})$$

and R_2 is defined similarly. The Prandtl, Lewis and Reynolds numbers are defined as

$$\text{Pr} = \frac{2n_\infty k \mu}{\lambda}, \text{Le} = \frac{\rho_\infty D 2n_\infty k}{\lambda}, \text{Re} = \frac{\rho_\infty L c_\infty}{\mu} = \frac{1}{\varepsilon^2} \quad (\text{II.34})$$

Remark : In this process, the length reference L is a formal parameter. As a matter of fact, since the plate is infinite, there is no physical length reference. However, once the formal development has been performed, L may be replaced by a length obtained from a combination of other variables. In particular, it may be replaced by $c_\infty t$. This choice gives for ε

$$\varepsilon = \sqrt{\frac{\mu}{\rho_\infty c_\infty^2 t}} \quad (\text{II.35})$$

and yields the variable η

$$\eta = \bar{y} = y \left(\frac{\rho_\infty}{\mu t} \right)^{1/2} \quad (\text{II.36})$$

which leads to a self-similar solution valid in the boundary-layer.

Section III

KINETIC MODEL

The object of this section is to replace the Boltzmann equation by a simpler model equation, which will be better adapted to our particular problem. We will introduce the general form of the kinetic model and the parameters upon which it will depend (Sec. III.1). Then, we will specify these parameters by requiring that the kinetic model be compatible both with the physical assumptions of our problem and with the main properties of the true Boltzmann equation (Sec. III.2.). Finally, we will make a few remarks on this model equation (Sec.III.3.).

III.1 General form of the model

As pointed out in Sec.II., as soon as we are interested in the microscopic motion of the molecules of the mixture, we are led to consider species distribution functions, whose evolutions are described by the Boltzmann equation (II.1). However, the Boltzmann collision integrals (II.3), which appear on the right-hand side, make the system of equations (II.1) particularly intractable. It is, therefore, not surprising that alternative expressions have been proposed for these collision terms. The idea behind any kinetic model is to replace the true collision integral $Q_{sr}(f_s, f_r)$ by a simpler operator $J_{sr}(f_s)$, which retains the main qualitative and averaged properties of the true operator, but whose manipulation is easier. The most widely used kinetic model is that of Bhatnagar *et al* (1954), later extended to the case of gas mixtures by Gross and Krook (1956), and which turns out to be particularly appropriate when one needs to perform power expansions of the distribution functions.

Following these authors and the presentation of Burgers (1969, Ch 6), we postulate that

the distribution function f_s satisfies a Boltzmann-like-equation in the form

$$\frac{\partial f_s}{\partial t} + \eta_1 \frac{\partial f_s}{\partial y} = -f_s \sum_{r=1,2} \frac{1}{\tau_{sr}} + \sum_{r=1,2} \frac{1}{\tau_{sr}} \Psi_{sr} \quad (s = 1,2) \quad (\text{III.1})$$

- $\tau_{sr} = 1/\nu_{sr}$ represents a characteristic time for collisions between species s and r , ν_{sr} being the corresponding collision frequency. A priori, these parameters can depend on time, position and velocity. The total average collision frequency for species s is given by

$$\nu_s = \frac{1}{\tau_s} = \sum_{r=1,2} \nu_{sr} \quad (\text{III.2})$$

- The first sum, $-f_s \nu_s$, on the right-hand side of (III.1), represents the number of particles of type s which are thrown out of the group $f_s d\xi_s$ per second as a result of collisions. In the true Boltzmann model, it replaces the term

$$-f_s \sum_{r=1,2} \int_{\mathfrak{X}} f_r g_{sr} b db d\epsilon d\xi_r \quad (\text{III.3})$$

- The second sum represents the number of s particles which are restored to the group $f_s d\xi_s$ as a result of collisions. We introduce the auxiliary distribution function Ψ_{sr} in order to represent the average distribution of the velocity components of a particle of kind s when it comes out of a collision with a particle of kind r . The form chosen for the functions Ψ_{sr} is a Maxwellian distribution

$$\Psi_{sr} = \rho_s \left(\frac{m_s}{2\pi k T_{sr}} \right)^{3/2} \exp \left\{ - \frac{m_s}{2k T_{sr}} (\xi_s - v_{sr})^2 \right\} \quad (\text{III.4})$$

III.2 Determination of the parameters of the model

The parameters introduced in the model are the four collision times τ_{sr} , the four temperatures T_{sr} and the four velocities v_{sr} .

Concerning the square term Ψ_{ss} , it is reasonable to assume that, as a result of like collisions, particles of kind s are re-emitted with a Maxwellian distribution centered about the species velocity v_s and temperature T_{ss} defined in (II.6) and (II.14). In other words, Ψ_{ss} is the local Maxwellian distribution for species s

$$\Psi_{ss} = \rho_s \left(\frac{m_s}{2\pi k T_{ss}} \right)^{3/2} \exp \left\{ - \frac{m_s}{2k T_{ss}} (\xi_s - v_s)^2 \right\} \quad (\text{III.5})$$

and any moments of Ψ_{ss} and f_s , of order less or equal than 2, are equal.

Next, we need to make some assumptions about the characteristic collision times τ_{sr} . First of all, we assume them to be constant parameters. Then, let us look at a layer very close to the wall, whose thickness is less than the mean free path of either O or O₂ molecules. In this

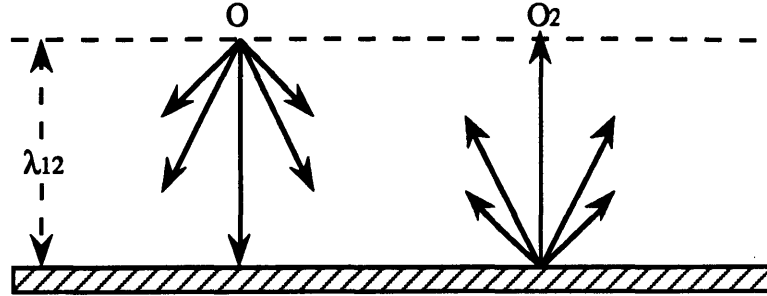


Fig. 2. O and O₂ free trajectories near the wall.

layer, neither O nor O₂ molecules encounter any collision. Moreover, due to our basic assumption of total recombination of the O molecules at the wall, in this layer, all the O molecules have a velocity directed towards the wall, because they all "vanish" at the wall, whereas all the O₂ molecules have their velocity directed away from the wall, since they all are created at the wall (see figure 2). Now, let us consider a slightly thicker layer than the previous one, whose thickness is of the order of a few mean-free paths of either O or O₂. A few collisions occur in this layer, but a collision between unlike molecules is much more probable than a collision between like molecules. On the average, an O₂ molecule leaves the wall with a velocity directed along the positive y axis. Similarly an average O molecule reaches the wall with a velocity directed along the negative y axis. Thus, if we follow an average O₂ molecule, it may collide with an O molecule coming in the opposite direction. It may also encounter another O₂ molecule, but this implied that the latter has previously collided with an O molecule and hence, reversed the sign of the y component of its velocity. Therefore, the probability of a collision between like molecules is at least of one order of magnitude smaller than the probability of a collision between unlike molecules (see figure 3).

Consistently with this physical discussion, since the characteristic collision times are inversely proportional to the probabilities of collision, we make the assumption that the characteristic time for collisions between like molecules is much longer than the one between unlike molecules:

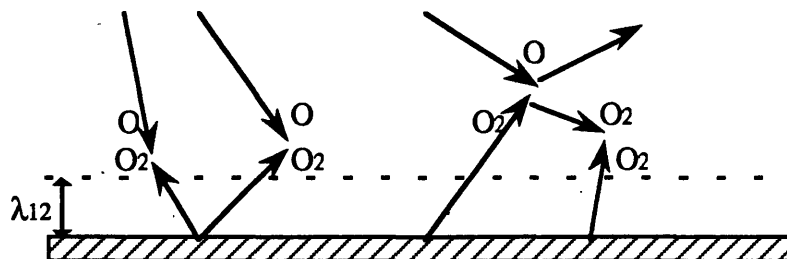


Fig. 3. O-O₂ collisions and O₂-O₂ collisions near the wall.

$$\tau_{sr} \ll \tau_{ss} \quad (\text{with } s=1,2, \text{ and } s \neq r)$$

Lastly, since O and O₂ molecules play in a way a symmetric role, both τ_{11} and τ_{22} , and τ_{12} and τ_{21} , are of the same order of magnitude. This leads us to make another simpler assumption that $\tau_{11} = \tau_{22}$ and that $\tau_{12} = \tau_{21}$. Finally, we are left with

$$\tau_{12} = \tau_{21} \ll \tau_{11} = \tau_{22} \quad (\text{III.6})$$

The remaining unspecified parameters of our model are the velocities v_{12} , v_{21} and the temperatures T_{12} , T_{21} appearing in the cross distribution functions Ψ_{12} , Ψ_{21} . To determine them, we require that the model reproduce some of the properties of the true collision operator. Following Cercignani (1988, ch II), the essential features of a collision operator $J_s(f_s)$ are

i) to admit the collisions invariants: mass, total momentum and total energy. Therefore it must satisfy the identities

$$\int_{\mathfrak{R}^3} J_s(f_s) d\xi_s = 0 \quad (\text{III.7.a})$$

$$\sum_{s=1,2,3} \int_{\mathfrak{R}^3} \xi_s J_s(f_s) d\xi_s = 0 \quad (\text{III.7.b})$$

$$\sum_{s=1,2,3} \int_{\mathfrak{R}^3} \xi_s^2 J_s(f_s) d\xi_s = 0 \quad (\text{III.7.c})$$

ii) to satisfy the H theorem. Defining the quantity H_s for species s by

$$H_s = \int_{\mathfrak{R}^3} \frac{f_s}{m_s} \ln \frac{f_s}{m_s} d\xi_s \quad (\text{III.8})$$

and the total quantity H for the mixture by: $H = H_1 + H_2$, where f_s satisfies the kinetic model equation (III.1), we require that the inequality

$$\frac{DH}{Dt} \leq 0 \quad (\text{III.9})$$

hold, the equality being satisfied if and only if the mixture is in an equilibrium state (i.e. f_1 and f_2 are maxwellian with the same parameters).

The condition (III.7.a) has already been taken into account by the form (III.5) imposed to Ψ_{sr} . Plugging the expression (III.4) into the conditions (III.7.b), (III.7.c), and making use of the results (III.5) and (III.6) yields the following identities (see appendix B.1 for details)

$$\rho_1 v_{12} + \rho_2 v_{21} = \rho_1 v_1 + \rho_2 v_2 = \rho v \quad (\text{III.10})$$

$$3n_1 k (T_{12} - T_1) + 3n_2 k (T_{21} - T_2) + \rho_1 (v_{12}^2 - v^2) + \rho_2 (v_{21}^2 - v^2) = 0 \quad (\text{III.11})$$

Furthermore, when the inequality (III.9) is written explicitly in terms of the unspecified coefficients, it appears that sufficient conditions to satisfy the H theorem are (Appendix B.2)

$$T_{12} = T_{21} = T = \frac{n_1 T_1 + n_2 T_2}{n} \quad (\text{III.12})$$

$$\mathbf{v}_{12} = \mathbf{v}_{21} = \mathbf{v} = \frac{\rho_1 \mathbf{v}_1 + \rho_2 \mathbf{v}_2}{\rho} \quad (\text{III.13})$$

This means that molecules of both species, after a collision with an unlike molecule, are re-emitted with a maxwellian distribution centered about the velocity and the temperature of the mixture.

Finally, the kinetic model we are going to use from now on shall be called a "Boltzmann-Krook" equation after the main author of the initial articles, and is given by

$$\begin{aligned} \frac{\partial f_1}{\partial t} + \eta_1 \frac{\partial f_1}{\partial y} &= \frac{\Psi_{11} - f_1}{\tau_{11}} + \frac{\Psi_{12} - f_1}{\tau_{12}} \\ \frac{\partial f_2}{\partial t} + \eta_2 \frac{\partial f_2}{\partial y} &= \frac{\Psi_{21} - f_2}{\tau_{12}} + \frac{\Psi_{22} - f_2}{\tau_{11}} \end{aligned} \quad (\text{III.14})$$

where all the parameters entering the various functions Ψ_{sr} have been defined in (III.5), (III.6), (III.12) and (III.13).

III.3 Remarks

i) The system of equations (III.14), though apparently simple in appearance, is still a set of non-linear integro-differential equations. It couples the unknown distribution functions f_1 and f_2 by the intermediate of the parameters \mathbf{v} and T appearing in both Ψ_{12} and Ψ_{21} and which are integrated quantities of both f_1 and f_2 (recall the definitions (II.6), (II.9), (II.14) and (II.15)). However, although the mathematical structure of this model is still extremely complicated, its manipulation is much easier than the original Boltzmann equation. Moreover, it is better suited when one needs to perform power expansions of the unknowns, as we shall see later on.

ii) The solution (III.12), (III.13) to the system (III.10),(III.11) is of course not unique. However it has the great advantage of satisfying the H theorem, as demonstrated in Appendix B.1. It might not be the only solution compatible with the H theorem, but it seems to be the only one for which a demonstration is so easily possible. Furthermore it has the physical meaning underlined above.

iii) Because this model has the same collision invariants as the true one, the derivation of the macroscopic equations of motion (II.24) remains valid. Therefore, the hydrodynamic quantities (II.4) through (II.18), defined with respect to the distribution functions f_1 and f_2 , whose evolutions are described by the Boltzmann-Krook equation (III.14) instead of the true Boltzmann equation (II.1), will still satisfy the equations (II.24).

iv) The authors we have used as references (Bhatnagar *et al* (1954), Gross and Krook (1956), Burgers (1969, Ch 6)) present a slightly different form of the model. They introduce additional parameters:

$$\sigma_{sr} = \frac{\tau_{sr}}{n_r} \quad (s,r = 1,2) \quad (\text{III.15})$$

which they assume, instead of τ_{sr} , to be constant. Moreover, they use the equality $\sigma_{12} = \sigma_{21}$, instead of $\tau_{12} = \tau_{21}$. Accordingly, the equations for v_{12} , v_{21} and T_{12} , T_{21} that they may deduce from the conditions (III.7.b), (III.7.c) are different from our own (III.10), (III.11.) Lastly, to determine the final expressions of these parameters, they consider relaxation rates instead of the H theorem. Of course, there result a set of parameters of the model different from our (III. 12, 13). Actually both solutions involve the same amount of arbitrary assumptions and are separately self-consistent. Therefore, there is no contradiction between the two models, simply each of them relies on a different physical assumption. Nevertheless, as pointed out by Morse (1964), a demonstration of the H theorem for their solution is not possible in general, whereas we are able to demonstrate it for our model.

Section IV

FORMAL EXPANSION AND BOUNDARY CONDITIONS

In our defined model, we can seek an asymptotic solution of the Boltzmann-Krook equation (III.14). For this purpose we introduce a small parameter ϵ together with reference values of the flow variables. This allows us to define dimensionless variables and to rewrite the equations of motion (III.14), (II.24) in dimensionless form (Sec. IV.1). Next, ϵ is related to other small physical parameters of the problem (Sec. IV.2). Finally, in order for us to solve the system (II.24), we need to specify boundary conditions at the wall. These boundary conditions must account for the recombination process at the wall, as postulated in our formulation of the problem. We specify averaged boundary conditions on the hydrodynamic quantities, leaving aside the problem of specifying boundary conditions on the distribution functions (Sec. IV.3).

IV.1 Dimensionless formulation

We consider a parameter ϵ , small in a sense to be stated precisely later when we will relate it to other parameters of the problem, an arbitrary length reference L , and the parameters of the flow at rest far from the plate: T_∞ , ρ_∞ , n_∞ . We have already defined dimensionless variables (Sec.II.). We rewrite them below

$$\bar{y} = \frac{y}{\epsilon L}, \bar{t} = \frac{t c_\infty}{L} \quad (\text{with } c_\infty = \sqrt{\frac{2n_\infty k T_\infty}{\rho_\infty}}) \quad (\text{II.31})$$

$$\bar{\rho} = \frac{\rho}{\rho_\infty}, \bar{T} = \frac{T}{T_\infty}, \bar{u} = \frac{u}{c_\infty}, \bar{v} = \frac{v}{c_\infty}, \bar{P}_{xy} = \frac{P_{xy}}{\epsilon \rho_\infty c_\infty^2}, \bar{P}_{yy} = \frac{P_{yy}}{\rho_\infty c_\infty^2}, \bar{q}_y = \frac{q_y}{\epsilon \rho_\infty c_\infty^3}$$

In addition, we introduce

$$\bar{f}_s = \frac{c_\infty^3}{\rho_\infty} f_s, \quad \bar{\xi}_s = \frac{\xi_s}{c_\infty}, \quad \bar{\tau}_{sr} = \frac{\tau_{sr} c_\infty}{L} \quad (\text{IV.1})$$

and define R_∞ as $n_\infty k / \rho_\infty$. The form of (II.31) and (IV.1) emphasizes the fact that we are seeking an asymptotic solution valid for large values of time. This means, according to the general formulation exposed in section I, that we do not consider the problem of the so-called initial-layer, which lasts a few mean-free times immediately after the plane has been set in motion. Consequently, for our purpose, the characteristic time we have introduced $-L / c_\infty$ is representative of the time-scale of the macroscopic changes in the flow. Furthermore, as pointed out by Trilling (1964), the definition of y , v as well as P_{xy} and q_y is selected by analogy with the boundary-layer equations (II.32) and to provide a solution in which the motion normal to the plate might play a role.

When all the dimensionless variables have been defined, we are able to work out dimensionless equations. The Boltzmann-Krook equation (IV.14) becomes in dimensionless variables

$$\frac{\partial f_1}{\partial t} + \frac{\eta_1}{\varepsilon} \frac{\partial f_1}{\partial y} = \frac{\Psi_{11} - f_1}{\tau_{11}} + \frac{\Psi_{12} - f_1}{\tau_{12}} \quad (\text{IV.2.a})$$

$$\frac{\partial f_2}{\partial t} + \frac{\eta_2}{\varepsilon} \frac{\partial f_2}{\partial y} = \frac{\Psi_{21} - f_2}{\tau_{12}} + \frac{\Psi_{22} - f_2}{\tau_{11}} \quad (\text{IV.2.b})$$

Likewise, the macroscopic equations of motion (II.24) become

$$\frac{\partial \rho_s}{\partial t} + \frac{\partial \rho_s v_s}{\partial y} = 0 \quad (\text{IV.3.a})$$

$$\rho \left(\frac{\partial u}{\partial t} + v \frac{\partial u}{\partial y} \right) + \frac{\partial P_{xy}}{\partial y} = 0 \quad (\text{IV.3.b})$$

$$\varepsilon^2 \rho \left(\frac{\partial v}{\partial t} + v \frac{\partial v}{\partial y} \right) + \frac{\partial P_{yy}}{\partial y} = 0 \quad (\text{IV.3.c})$$

$$\frac{3}{4} n \left(\frac{\partial T}{\partial t} + v \frac{\partial T}{\partial y} \right) + \frac{\partial q_y}{\partial y} + P_{xy} \frac{\partial u}{\partial y} + P_{yy} \frac{\partial v}{\partial y} = \frac{3}{4} T \frac{\partial (n_1 V_1 + n_2 V_2)}{\partial y} \quad (\text{IV.3.d})$$

Again, we have dropped the bars but all the quantities appearing in these equations are dimensionless, as defined above by (II.31) and (IV.1).

At this point, our strategy becomes clear. First, we will formally expand in power of ε the unknown distribution functions f_1 and f_2

$$f_s = f_s^{(0)} + \varepsilon f_s^{(1)} + \varepsilon^2 f_s^{(2)} + \dots \quad (s=1, 2) \quad (\text{IV.4})$$

Then, when these expansions are put into the definitions (II.4) to (II.18) of the hydrodynamic variables, we obtain likewise expansions of these variables. For instance,

$$\begin{aligned} \rho_s &= \rho_s^{(0)} + \varepsilon \rho_s^{(1)} + \varepsilon^2 \rho_s^{(2)} + \dots \quad (s=1,2) \\ T &= T^{(0)} + \varepsilon T^{(1)} + \varepsilon^2 T^{(2)} + \dots \end{aligned} \quad (\text{IV.5})$$

and similar developments hold for all the integrated quantities of the distribution functions. Lastly, the reference maxwellian distributions Ψ_{11} , Ψ_{12} , Ψ_{21} and Ψ_{22} can in turn be expanded, since they depend on integrated quantities which have just been expanded in power of ϵ

$$\Psi_{sr} = \Psi_{sr}^{(0)} + \epsilon \Psi_{sr}^{(1)} + \epsilon^2 \Psi_{sr}^{(2)} + \dots \quad (s, r = 1, 2) \quad (IV.6)$$

Thus, by substituting these expansions into the Boltzmann-Krook equation (IV.2), we will be left with a hierarchy of terms. Once this hierarchy is put into order, we will obtain a hierarchy of equations. Solving each of these equations will provide us with a recursive solution of the form

$$f_s^{(n)} = \Phi \left(f_s^{(0)}, f_s^{(1)}, \dots, f_s^{(n-1)} \right) \quad (IV.7)$$

At every step n , the solution $f_s^{(n)}$ will depend on quantities of lower order and on hydrodynamic quantities of order n . These hydrodynamic variables will satisfy the n th component of the hierarchy of equations obtained by expanding the system (IV.3), together with the n th component of the expansion of the appropriate boundary conditions.

We shall discuss this program, which is an extension of the approach of Trilling (1964), in some details in the next sections. But beforehand, it is necessary to relate ϵ to the physical parameters of the model τ_{11} and τ_{12} , and to specify the boundary conditions of the problem.

IV.2 Determination of the expansion parameter

To begin with, let us consider carefully the mean-free path of each species. As demonstrated by Vincenti and Kruger (1965, Ch.II.), the total collision frequency of a given species is the summation extended over all the species in the mixture of the collision frequencies with these species. Specified to our particular model, this statement has already been worked out by equation (III.2), which we reproduce here

$$v_s = \frac{1}{\tau_s} = \sum_{r=1,2} v_{sr} \quad (III.2)$$

The mean-free path λ_s of species s is simply defined by introducing a characteristic molecular velocity, which we choose to be c_∞ , previously defined in Sec.II.4.

$$\lambda_s = \frac{c_\infty}{\sum_{r=1,2} v_r} \quad (IV.8)$$

Because of our assumption (III.6) about the collision times, the mean-free paths of both O and O₂ are equal

$$\lambda_1 = \lambda_2 = \lambda = \frac{c_\infty}{\frac{1}{\tau_{11}} + \frac{1}{\tau_{12}}} \quad (\text{IV.9})$$

Consistent with the assumption made in section III.2., we neglect τ_{11} compared to τ_{12} , and we are left with

$$\lambda \approx c_\infty \tau_{12} = \lambda_{12} = \lambda_{21} \quad (\text{IV.10})$$

where λ_{12} or λ_{21} stand for the mean-free path for collisions between O molecules and O₂ molecules. This quasi equality means that there are so few collisions between like molecules that they don't affect the mean-free path.

Next, we recall that we are investigating a continuum or near-continuum regime flow. In other words, we keep the Knudsen number of the flow small compared to unity

$$\text{Kn} = \lambda / L \ll 1 \quad (\text{IV.11})$$

Taking into account (IV.10) yields

$$\text{Kn} \approx \text{Kn}_{12} = \text{Kn}_{21} = \lambda_{12} / L \ll 1 \quad (\text{IV.12})$$

Furthermore, this assumption implies also that we may allow a slip velocity and a temperature jump at the wall as long as they remain small compared to the velocity and the temperature of the wall. This is possible only if the Knudsen layer near the wall is thin. This is equivalent to saying that the dimensionless thickness of the Knudsen layer is small compared to unity, or that the Knudsen layer is small compared to the boundary layer. This thickness is of the order of magnitude of one mean-free path λ , and the dimensionless thickness along the y axis is therefore

$$\bar{\lambda} = \frac{\lambda}{\varepsilon L} \cong \frac{\tau_{12} c_\infty}{\varepsilon L} = \frac{\overline{\tau_{12}}}{\varepsilon} \quad (\text{IV.13})$$

where the dimensionless quantities are defined according to (II.31) and (IV.1). Hence, our assumptions and definitions lead us to the statement

$$\frac{\overline{\tau_{12}}}{\varepsilon} \ll 1 \quad \text{and} \quad \frac{\overline{\tau_{12}}}{\tau_{11}} \ll 1 \quad (\text{IV.14})$$

where we recall the inequality (III.6) established in section III.2. In order to get systematic expansions for our case, we select simply

$$\overline{\tau_{12}} = \varepsilon^2 \quad \text{and} \quad \overline{\tau_{11}} = \varepsilon \quad (\text{IV.15})$$

We have also

$$\overline{\tau_{12}} = \frac{\tau_{12} c_\infty}{L} = \frac{\lambda_{12}}{L} = \text{Kn}_{12} \cong \text{Kn} \quad (\text{IV.16})$$

which allows us to write

$$\varepsilon = \sqrt{\text{Kn}_{12}} \approx \sqrt{\text{Kn}} \quad (\text{IV.17})$$

Eventually, the small parameter of our expansion turns out to be the square root of the Knudsen number of the flow.

IV.3 Specification of the averaged boundary conditions

The ideal would be to specify boundary conditions on the distribution functions f_1 and f_2 themselves, in order to determine them in a unequivocal way. However, this would require a better knowledge of the mechanical and chemical interactions of the gas with the surface, which is simply not available. Furthermore, as pointed out by Trilling (1964), one might view the distribution functions more as convenient tools for the analysis of the problem than as actual physical quantities. In this case, an unequivocal determination of the distribution functions is not necessary and could appear somewhat artificial. As a velocity potential, the distribution functions may retain a certain degree of indeterminacy, as long as this does not imply an indeterminacy of the hydrodynamic quantities, which have a clear and measurable physical meaning. Thus, we need only to specify boundary conditions on the hydrodynamic quantities, which will be uniquely determined. In other words, we apply boundary conditions on integrated quantities of the distribution functions; this is why we call them averaged boundary conditions. Let us now determine these boundary conditions.

The simplest boundary condition is the one regarding v , the y component of the velocity. Since there is no transfer of fluid through the wall, we have

$$v(0) = 0 \quad (\text{IV.18})$$

Developed in power of ϵ , this identity yields the same condition for each order

$$v^{(0)}(0) = v^{(1)}(0) = \dots = v^{(n)}(0) = \dots = 0 \quad (\text{IV.19})$$

Next, we define the boundary condition for u , the x component of the flow velocity. Recalling the definition (II.9), we have

$$\rho u(0) = \rho_1 u_1(0) + \rho_2 u_2(0) \quad (\text{IV.20})$$

Since the O molecules vanish at the wall, at the point $y = 0$ they are all incoming towards the wall with a velocity acquired after their last collision, which occurred one mean-free path away in average. Hence,

$$\rho_1 u_1(0) = \rho_1 u_1(\lambda_{12}) = \rho_1 u_1\left(\frac{\tau_{12}}{\epsilon}\right) = \rho_1 u_1(\epsilon) \quad (\text{IV.21})$$

where we have used the results of the last paragraph (we have again omitted the bars, but all the quantities are dimensionless).

For the O_2 molecules, the situation is slightly more complicated. As a matter of fact, incoming and outgoing O_2 molecules coexist at the wall, although in different proportions. Once they have left the wall, O_2 molecules may collide with incoming O molecules and therefore be reflected towards the wall. Let us call θ the fraction of O_2 molecules incoming towards the wall. We have

$$\rho_2 u_2(0) = \theta \rho_2 u_2(0) + (1-\theta) \rho_2 u_2(0) \quad (\text{IV.22})$$

Like the incoming O molecules, the incoming O₂ molecules have acquired their velocity after their last collision, one mean-free path away in average. Hence, we can write the incoming flux as

$$\theta \rho_2 u_2(0) = \theta \rho_2 u_2(\lambda_{12}) = \theta \rho_2 u_2 \left(\frac{\tau_{12}}{\epsilon} \right) = \theta \rho_2 u_2(\epsilon) \quad (\text{IV.23})$$

On the other hand, the outgoing flux is assumed to be fully accommodated with the wall

$$(1 - \theta) \rho_2 u_2(0) = (1 - \theta) \rho_2(0) u_w \quad (\text{IV.24})$$

where u_w is the velocity of the wall. In these conditions, we obtain for u after a simple arrangement of terms

$$(\rho u)(0) - (\rho u)(\epsilon) = (1 - \theta) \left(\rho_2(0) u_w - (\rho_2 u_2)(\epsilon) \right) \quad (\text{IV.25})$$

Lastly, we need to identify the formal parameter θ with some physical parameter of the flow. Once the O₂ molecules are far from the surface, in the outer layer of the flow (which we do not treat), they are dissociated back into O atoms, due to the high temperature T_∞ of the external flow. Consequently, there is a global balance between O and O₂ populations, and the O₂ molecules can be seen as a transitory species. For this reason, the proportion θ of O₂ molecules which are reflected back towards the wall is small compared to unity. More precisely, we assume that this proportion is of the same order of magnitude as ϵ , and we impose, therefore, the following boundary condition on u

$$(\rho u)(0) - (\rho u)(\epsilon) = (1 - \epsilon) \left(\rho_2(0) u_w - (\rho_2 u_2)(\epsilon) \right) \quad (\text{IV.26})$$

Any quantity appearing in this equation can be expanded in power of ϵ , and any function calculated at the value ϵ can be developed in a Taylor series with respect to the value 0. Therefore, the identity (IV.26) can be expressed as a power series of ϵ , yielding a hierarchy of boundary condition for each term $u^{(n)}$ of the expansion of u . We will explicitly develop it up to the second order in a subsequent section.

To specify the boundary condition on the temperature T , we follow exactly the same approach as for u . We write directly the condition on T

$$(nT)(0) - (nT)(\epsilon) = (1 - \epsilon) \left(n_2(0) T_w - (n_2 T_2)(\epsilon) \right) \quad (\text{IV.27})$$

where T_w is the temperature of the wall. Likewise, the development of this equation yields a succession of boundary conditions for $T^{(0)}$, $T^{(1)}$...

Lastly, we need to specify a boundary condition for the density of one of the species. This condition is provided by the adiabatic hypothesis. At the wall, to take into account the chemical reaction, we have to add to the heat-flux vector q_y calculated from the distribution functions the energy flux due to the recombination process. We denote by E ($E > 0$) the energy released by the formation of one molecule of O₂. Then, in the notation of Anderson (1989,

Ch17), the specific heat of formation of O_2 is

$$(Dh_f)_2^0 = -\frac{E}{m_2} \quad (IV.28)$$

and the corresponding contribution to the heat-flux vector is

$$(\rho_2 v_2)(0)(Dh_f)_2^0 = -E(n_2 v_2)(0) = \frac{E}{2}(n_1 v_1)(0) \quad (IV.29)$$

where we have used the boundary condition (IV.18). Therefore, we obtain the following boundary condition

$$q_y(0) + \frac{E}{2}(n_1 v_1)(0) = 0 \quad (IV.30)$$

When written in dimensionless variables this identity retains the same form. Developing it in power of ϵ yields a sequence of conditions of the form

$$q_y^{(n)}(0) + \frac{E}{2}(n_1 v_1)^{(n)}(0) = 0 \quad (IV.31)$$

These equalities will provide us with a boundary condition for the O density; we will write it explicitly for the two first orders systems in section VI.

Section V

CONSTRUCTION OF THE DISTRIBUTION FUNCTIONS

Now, we will apply the strategy outlined in the previous section. The development of the Boltzmann-Krook equations leads to an iterative construction of the solution (Sec V.1.). This solution depends on parameters which satisfy a closed set of partial differential equations, associated with the appropriate boundary conditions (Sec V.2.).

V.1 Recursive equations for the components of the distribution functions

The results of previous sections prepare for the construction of the molecular distribution functions f_1 and f_2 . We substitute in the Boltzmann-Krook equation the formal developments (IV.4) and (IV.6) of the distribution functions f_s and Ψ_{sr} , and replace the characteristic times τ_{12} and τ_{11} by ϵ^2 and ϵ respectively, as dictated by the choice of ordering relations (IV.15).

We obtain for f_1 the following equation

$$\begin{aligned} & \epsilon^2 \left(\frac{\partial f_1^{(0)}}{\partial t} + \epsilon \frac{\partial f_1^{(1)}}{\partial t} + \epsilon^2 \frac{\partial f_1^{(2)}}{\partial t} + \dots \right) + \epsilon \eta_1 \left(\frac{\partial f_1^{(0)}}{\partial y} + \epsilon \frac{\partial f_1^{(1)}}{\partial y} + \epsilon^2 \frac{\partial f_1^{(2)}}{\partial y} + \dots \right) \\ & = \epsilon \left(\left(\Psi_{11}^{(0)} - f_1^{(0)} \right) + \epsilon \left(\Psi_{11}^{(1)} - f_1^{(1)} \right) + \dots \right) + \left(\Psi_{12}^{(0)} - f_1^{(0)} \right) + \epsilon \left(\Psi_{12}^{(1)} - f_1^{(1)} \right) + \dots \quad (V.1) \end{aligned}$$

and a similar equation for f_2 . A particular solution of this equation is obtained by regrouping the terms of the same order in ϵ . We get a power series in ϵ on one side of the equation and 0 on the other one. Equating every coefficient of the series with 0 leads to the following sequence of equations for the components of f_1

$$f_1^{(0)} = \Psi_{12}^{(0)} \quad (V.2)$$

$$f_1^{(1)} = \Psi_{11}^{(0)} - f_1^{(0)} + \Psi_{12}^{(1)} - \eta_1 \frac{\partial f_1^{(0)}}{\partial y} \quad (V.3)$$

$$f_1^{(2)} = \Psi_{11}^{(1)} - f_1^{(1)} + \Psi_{12}^{(2)} - \eta_1 \frac{\partial f_1^{(1)}}{\partial y} - \frac{\partial f_1^{(0)}}{\partial t} \quad (V.4)$$

$$f_1^{(n)} = \Psi_{11}^{(n-1)} - f_1^{(n-1)} + \Psi_{12}^{(n)} - \eta_1 \frac{\partial f_1^{(n-1)}}{\partial y} - \frac{\partial f_1^{(n-2)}}{\partial t} \quad (V.5)$$

and a similar sequence for the components of f_2 . We write only the equation for the n th component of f_2

$$f_2^{(n)} = \Psi_{22}^{(n-1)} - f_2^{(n-1)} + \Psi_{21}^{(n)} - \eta_2 \frac{\partial f_2^{(n-1)}}{\partial y} - \frac{\partial f_2^{(n-2)}}{\partial t} \quad (V.6)$$

We note that the n th component $f_1^{(n)}$ of the solution is explicitly given by (V.5) as a function of components of order less than n on the one hand, and of the n th component of the reference distribution Ψ_{12} . Thus, an iterative construction of the solution is possible if we are able to determine $\Psi_{12}^{(n)}$ at each step of the process. This maxwellian distribution depends on parameters which are integrated quantities of f_1 . In the next paragraph, we expose how these free parameters can be determined in theory.

V.2 Determination of the free parameters

Assuming that the solution has been constructed up to the order $n-1$, $f_1^{(n)}$ and $f_2^{(n)}$ can be calculated through the use of equations (V.5) and (V.6). However, as have been noticed, these equations involve the components of order n of the reference maxwellian distributions Ψ_{12} and Ψ_{21} . These components will introduce 5 free quantities, namely the n th components of the 5 parameters upon which Ψ_{12} and Ψ_{21} depend: $\rho_1^{(n)}$, $\rho_2^{(n)}$, $u^{(n)}$, $v^{(n)}$, $T^{(n)}$. Thus, at this point, $f_1^{(n)}$ and $f_2^{(n)}$ are of the form

$$f_s^{(n)} = \Phi_n \left(\rho_1^{(n)}, \rho_2^{(n)}, u^{(n)}, v^{(n)}, T^{(n)} \right) \quad (V.7)$$

To determine these parameters, we expand the system of equations (IV.3) and get a sequence of systems of order 0, 1, ..., n . $\rho_1^{(n)}$, $\rho_2^{(n)}$, $u^{(n)}$, $v^{(n)}$, $T^{(n)}$ are the main unknowns of the system of order n , in which the quantities of order less than n , already determined in the previous steps of the process, appear as forcing terms. Moreover, still present in this system are the additional hydrodynamic quantities of order n : $v_1^{(n)}$, $v_2^{(n)}$, $P_{xy}^{(n)}$, $P_{yy}^{(n)}$, $q_y^{(n)}$. But now, we dispose of a simple and systematic way to relate these quantities to the main

unknowns. Since $f_1^{(n)}$ and $f_2^{(n)}$ are of the form given by (V.7), if we simply apply the definitions of these hydrodynamic quantities (recall (II.6), (II.12), (II.13), (II.17) and (II.18)), and perform the required integrations, we will find expressions of the form

$$v_1^{(n)} = v_1^{(n)} \left(\rho_1^{(n)}, \rho_2^{(n)}, u^{(n)}, v^{(n)}, T^{(n)} \right) \quad (\text{V.8})$$

and similar form for $v_2^{(n)}$, $P_{xy}^{(n)}$, $P_{yy}^{(n)}$, $q_y^{(n)}$. By this process, we eliminate the additional unknowns of the system and are left with a closed set of equations for the main unknowns $\rho_1^{(n)}$, $\rho_2^{(n)}$, $u^{(n)}$, $v^{(n)}$, $T^{(n)}$. This system yields an unambiguous solution once the appropriate boundary conditions are specified. The proper boundary conditions for this system are found by expanding the equations (IV.18), (IV.26), (IV.27) and (IV.30) (obtained in IV.3.) and by writing the corresponding equations of order n . The solution of this well-posed problem will provide us with the expressions of $\rho_1^{(n)}$, $\rho_2^{(n)}$, $u^{(n)}$, $v^{(n)}$, $T^{(n)}$ as functions of the variables y and t . By replacing these functions in the expression (V.7), one finally obtains the definitive forms of $f_1^{(n)}$ and $f_2^{(n)}$. Then, one is ready to repeat the whole process at the order $n+1$. Therefore, this iterated construction provides us with an asymptotic solution of our Boltzmann-Krook equation.

In this investigation, we have to keep in mind that we perform an inner expansion of the problem. The physical assumptions made in section III, and the solution outlined above, are valid only in the inner layer, whose thickness is of the order ϵ . To get a solution valid in the whole flow field, one has to consider the outer layer of the flow, where an outer expansion must be performed. Then, one has to match the outer expansion with the inner one. The theory of matched asymptotic expansions requires, in particular, that the outer limit of the inner expansion coincide with the inner limit of the outer expansion (see Van Dyke, 1964). Therefore, the outer boundary conditions for our problem are provided by the inner boundary conditions of the outer layer, which we do not treat in this report. However, because of the assumption that the diatomic oxygen is dissociated back into oxygen atoms in the outer flow, we can consider that the outer limit of the O_2 density in the inner layer is equal to zero.

Section VI

FIRST AND SECOND ORDER SYSTEMS

In this section, we will work out the explicit form of the first and second order components of the solution, as well as the corresponding system of equations for the hydrodynamic quantities.

VI.1 First order system

The dimensionless expression of the maxwellian distribution Ψ_{12} is

$$\Psi_{12} = \frac{\rho_1}{(2\pi R_1 T)^{3/2}} \exp \left\{ - \frac{(\xi_1 - v)^2}{2R_1 T} \right\} \quad (\text{VI.1})$$

We recall the definition (II.33) of R_1

$$R_1 = \frac{\rho_\infty}{2m_1 n_\infty} \quad (\text{II.33})$$

and note the relation between n_1 and ρ_1

$$n_1 = 2R_1 \rho_1 \quad (\text{VI.2})$$

Of course, the other reference distributions Ψ_{11} , Ψ_{21} , Ψ_{22} have similar dimensionless forms and relations similar to (II.33) and (VI.2) hold for species 2.

By expanding up to the first order the dimensionless distribution Ψ_{12} , we obtain the form of the first iterate of the solution

$$f_1^{(0)} = \Psi_{12}^{(0)} = \frac{\rho_1^{(0)}}{(2\pi R_1 T^{(0)})^{3/2}} \exp \left\{ - \frac{(\xi_1 - u^{(0)})^2 + \eta_1^2 + \zeta_1^2}{2R_1 T^{(0)}} \right\} \quad (\text{VI.3})$$

and a similar expression for the first component of f_2 . To achieve the determination of $f_1^{(0)}$, we have to write explicitly the system of equations for the first-order hydrodynamic quantities $\rho_1^{(0)}$, $\rho_2^{(0)}$, $u^{(0)}$, $v^{(0)}$, $T^{(0)}$. As explained in the previous section, we need to eliminate the additional unknowns by expressing them as functions of the main unknowns of the problem. However, before expanding in power of ϵ these additional unknowns, we have to rewrite their definitions in dimensionless variables. The dimensionless forms of the definitions (II.6,12,17) are

$$\rho_s u_s = \int_{\mathfrak{R}^3} \xi_s f_s d\xi_s \quad (\text{VI.4})$$

$$\rho_s v_s = \frac{1}{\epsilon} \int_{\mathfrak{R}^3} \eta_s f_s d\xi_s \quad (\text{VI.5})$$

$$(P_s)_{xy} = \frac{1}{\epsilon} \int_{\mathfrak{R}^3} (\xi_s - u) (\eta_s - \epsilon v) f_s d\xi_s \quad (\text{VI.6})$$

$$(P_s)_{yy} = \int_{\mathfrak{R}^3} (\eta_s - \epsilon v)^2 f_s d\xi_s \quad (\text{VI.7})$$

$$(q_s)_y = \frac{1}{2\epsilon} \int_{\mathfrak{R}^3} (\eta_s - \epsilon v) \left\{ (\xi_s - u)^2 + (\eta_s - \epsilon v)^2 + \zeta_s^2 \right\} f_s d\xi_s \quad (\text{VI.8})$$

In this form, one is able to perform expansions of these variables. The first order quantities are given by

$$(\rho_1 u_1)^{(0)} = \int_{\mathfrak{R}^3} \xi_1 f_1^{(0)} d\xi_1 \quad (\text{VI.9})$$

$$(\rho_1 v_1)^{(0)} = \int_{\mathfrak{R}^3} \eta_1 f_1^{(1)} d\xi_1 \quad (\text{VI.10})$$

$$(P_1)_{xy}^{(0)} = \int_{\mathfrak{R}^3} (\xi_1 - u^{(0)}) \eta_1 f_1^{(1)} d\xi_1 \quad (\text{VI.11})$$

$$(P_1)_{yy}^{(0)} = \int_{\mathfrak{R}^3} \eta_1^2 f_1^{(0)} d\xi_1 \quad (\text{VI.12})$$

$$\begin{aligned}
(q_1)_y^{(0)} = & \frac{1}{2} \int_{\mathfrak{R}^3} \eta_1 \left\{ \left[\xi_1 - u^{(0)} \right]^2 + \eta_1^2 + \zeta_1^2 \right\} f_1^{(1)} d\xi_1 - \frac{1}{2} v^{(0)} \int_{\mathfrak{R}^3} \left\{ \left[\xi_1 - u^{(0)} \right]^2 + \eta_1^2 + \zeta_1^2 \right\} f_1^{(0)} d\xi_1 \\
& - \int_{\mathfrak{R}^3} \eta_1 \left\{ \left[\xi_1 - u^{(0)} \right] u^{(1)} + \eta_1 v^{(0)} \right\} f_1^{(0)} d\xi_1
\end{aligned} \tag{VI.13}$$

The first and the fourth of the latter quantities are immediately calculable, whereas the other require that the component $f_1^{(1)}$ be calculated beforehand. A straightforward integration yields

$$u_1^{(0)} = u_2^{(0)} = u^{(0)} \tag{VI.14}$$

$$(P_1)_{yy}^{(0)} = \frac{1}{2} n_1^{(0)} T^{(0)}, \quad (P_2)_{yy}^{(0)} = \frac{1}{2} n_2^{(0)} T^{(0)} \tag{VI.15}$$

and hence, with the definition (II. 13) of the stress tensor of the mixture

$$P_{yy}^{(0)} = \frac{1}{2} n^{(0)} T^{(0)} \tag{VI.16}$$

With these results, we can determine the various temperatures up to the first order. A simple manipulation (see Appendix C. 1) leads to the equality of all of the first order components of the different temperatures defined in II. 2.

$$T_{11}^{(0)} = T_1^{(0)} = T_{22}^{(0)} = T_2^{(0)} = T^{(0)} \tag{VI.17}$$

Moreover, the first and second order expansions of the y momentum equation (IV. 3.c) are

$$\frac{\partial P_{yy}^{(0)}}{\partial y} = 0, \quad \frac{\partial P_{yy}^{(1)}}{\partial y} = 0 \tag{VI.18}$$

namely, the pressure is constant up to the second order. Using equation (VI. 16), we are led to

$$P_{yy}^{(0)} = \frac{1}{2}, \quad n^{(0)} T^{(0)} = 1 \tag{VI.19}$$

Equations (VI. 14) and (VI. 16) allows us also to write for the square maxwellian distributions

$$\Psi_{11}^{(0)} = \Psi_{12}^{(0)} = f_1^{(0)} \tag{VI.20}$$

$$\Psi_{22}^{(0)} = \Psi_{21}^{(0)} = f_2^{(0)} \tag{VI.21}$$

so that equation (V.3) defining $f_1^{(1)}$ becomes finally

$$f_1^{(1)} = \Psi_{12}^{(1)} - \eta_1 \frac{\partial f_1^{(0)}}{\partial y} \tag{VI.22}$$

and after some manipulations, one is led to

$$\frac{f_1^{(1)}}{f_1^{(0)}} = \frac{\rho_1^{(1)}}{\rho_1^{(0)}} + \left(W_1^2 \frac{3}{2} \right) \frac{T^{(1)}}{T^{(0)}} + W_2^2 - \eta_1 \left[\frac{1}{\rho_1^{(0)}} \cdot \frac{\partial \rho_1^{(0)}}{\partial y} + \left(W_1^2 \frac{3}{2} \right) \frac{1}{T^{(0)}} \cdot \frac{\partial T^{(0)}}{\partial y} + \frac{\left(\xi_1 - u^{(0)} \right)}{R_1 T^{(0)}} \cdot \frac{\partial u^{(0)}}{\partial y} \right] \quad (\text{VI.23})$$

where

$$W_1^2 = \frac{\left(\xi_1 - u^{(0)} \right)^2 + \eta_1^2 + \zeta_1^2}{2R_1 T^{(0)}} \quad (\text{VI.24})$$

$$W_2^2 = \frac{\left(\xi_1 - u^{(0)} \right) u^{(1)} + \eta_1 v^{(0)}}{R_1 T^{(0)}} \quad (\text{VI.25})$$

With the expression of $f_1^{(1)}$, we can perform the remaining integrations (VI. 10, 11, 13) and obtain (Appendix C. 2)

$$\rho_1^{(0)} v_1^{(0)} = \rho_1^{(0)} v^{(0)} - \frac{\partial}{2\partial y} (n_1 T)^{(0)} \quad (\text{VI.26})$$

$$(P_1)_{xy}^{(0)} = - \frac{n_1^{(0)} T^{(0)}}{2} \cdot \frac{\partial u^{(0)}}{\partial y} \quad (\text{VI.27})$$

$$(q_1)_y^{(0)} = - \frac{5}{4} \frac{\partial}{\partial y} \left[n_1^{(0)} R_1 \left(T^{(0)} \right)^2 \right] \quad (\text{VI.28})$$

as well as the analog equations for species 2. Summing up the partial stress tensor and heat-flux vector over the two species gives the mixture quantities

$$P_{xy}^{(0)} = - \frac{1}{2} \cdot \frac{\partial u^{(0)}}{\partial y} \quad (\text{VI.29})$$

$$q_y^{(0)} = - \frac{5}{4} \frac{\partial}{\partial y} (\bar{n} T^2)^{(0)} \quad (\text{VI.30})$$

where

$$\bar{n} = n_1 R_1 + n_2 R_2 \quad (\text{VI.31})$$

Moreover, using equation (VI. 26), we can check that the sum of the first order components of the diffusion velocities vanishes

$$\left(\rho_1 V_1 + \rho_2 V_2 \right)^{(0)} = - \frac{\partial}{2\partial y} (nT)^{(0)} = 0 \quad (\text{VI.32})$$

Eventually, the additional unknowns are expressed in terms of the main unknowns of the

problem. Thus, by collecting the terms independent of ϵ in the development of system (IV. 3) where the additional unknowns have been replaced by the identities (VI. 14, 15, 26, 29, 30), one can write the first order system of hydrodynamic equations

$$\frac{\partial n_1^{(0)}}{\partial t} + \frac{\partial \left(n_1^{(0)} v^{(0)} \right)}{\partial y} = \frac{\partial^2 \left(n_1^{(0)} R_1 T^{(0)} \right)}{\partial y^2} \quad (\text{VI.33a})$$

$$\frac{\partial n_2^{(0)}}{\partial t} + \frac{\partial \left(n_2^{(0)} v^{(0)} \right)}{\partial y} = \frac{\partial^2 \left(n_2^{(0)} R_2 T^{(0)} \right)}{\partial y^2} \quad (\text{VI.33b})$$

$$n^{(0)} T^{(0)} = 1 \quad (\text{VI.33c})$$

$$\rho^{(0)} \left(\frac{\partial u^{(0)}}{\partial t} + v^{(0)} \frac{\partial u^{(0)}}{\partial y} \right) - \frac{1}{2} \frac{\partial^2 u^{(0)}}{\partial y^2} = 0 \quad (\text{VI.33d})$$

$$\frac{5}{4} \frac{\partial v^{(0)}}{\partial y} - \frac{1}{2} \left(\frac{\partial u^{(0)}}{\partial y} \right)^2 - \frac{5}{4} \frac{\partial^2 \left[\left(n_1^{(0)} R_1 + n_2^{(0)} R_2 \right) \left(T^{(0)} \right)^2 \right]}{\partial y^2} = 0 \quad (\text{VI.33e})$$

(More details of the first order energy equation (VI. 33e) will be discussed in Appendix C. 3). This first order system is subject to the following boundary conditions, obtained by collecting the first order terms in the expansion of the averaged boundary conditions (IV. 18, 26, 27, 30) and substituting the equation (VI. 30) in (IV. 30) (see Appendix C. 4)

$$u^{(0)}(0) = u_w \quad (\text{VI.34a})$$

$$v^{(0)}(0) = 0 \quad (\text{VI.34b})$$

$$T^{(0)}(0) = T_w \quad (\text{VI.34c})$$

$$\frac{\partial}{\partial y} \left\{ \left[\frac{5}{4} (R_1 - R_2) \left(T^{(0)} \right)^2 + \frac{ER_1 T^{(0)}}{2} \right] n_1^{(0)} \right\}_{y=0} = \frac{5}{4} R_2 \frac{\partial}{\partial y} \left(T^{(0)} \right)_{y=0} \quad (\text{VI.34d})$$

This system is similar to the Navier-Stokes system, and particularly to the boundary-layer equations (II.32). Moreover, the appropriate boundary condition for this first order system is the non-slip condition in velocity and temperature.

VI.2 Second order system

The approach used to determine the second order components $f_1^{(1)}$, $f_2^{(1)}$ of the distribution functions is similar to the one used for the first order system, although it requires far lengthier calculations. The successive steps of the process reproduce the ones we have just followed.

The expression of the second order distribution $f_1^{(1)}$ has been already given in (VI. 23). The free parameters to be determined to complete the description of $f_1^{(1)}$ and $f_2^{(1)}$ are $\rho_1^{(1)}$, $\rho_2^{(1)}$, $u^{(1)}$, $v^{(1)}$, $T^{(1)}$. These quantities satisfy the second order system obtained by collecting the terms of order ϵ in the expansion of the hydrodynamic equations (IV. 3). Before writing this system, one has to eliminate the second order additional unknowns. Expanding the dimensionless definitions (VI. 4) through (VI. 8) of these variables and collecting the terms of order ϵ yield the following identifications

$$(\rho_1 u_1)^{(1)} = \int_{\mathfrak{R}^3} \xi_1 f_1^{(1)} d\xi_1 \quad (\text{VI.35})$$

$$(\rho_1 v_1)^{(1)} = \int_{\mathfrak{R}^3} \eta_1 f_1^{(1)} d\xi_1 \quad (\text{VI.36})$$

$$\begin{aligned} (P_1)_{xy}^{(1)} = & \int_{\mathfrak{R}^3} \left[\xi_1 - u^{(0)} \right] \eta_1 f_1^{(2)} d\xi_1 + \rho_1^{(0)} u^{(1)} v^{(0)} - u^{(1)} \int_{\mathfrak{R}^3} \eta_1 f_1^{(1)} d\xi_1 - \\ & - v^{(0)} \int_{\mathfrak{R}^3} \left[\xi_1 - u^{(0)} \right] f_1^{(1)} d\xi_1 \end{aligned} \quad (\text{VI.37})$$

$$(P_1)_{yy}^{(1)} = \int_{\mathfrak{R}^3} \eta_1^2 f_1^{(1)} d\xi_1 \quad (\text{VI.38})$$

$$\begin{aligned} (q_1)_y^{(1)} = & \frac{1}{2} \int_{\mathfrak{R}^3} \eta_1 \left[\left(\xi_1 - u^{(0)} \right)^2 + \eta_1^2 + \zeta_1^2 \right] f_1^{(2)} d\xi_1 - \frac{1}{2} v^{(1)} \int_{\mathfrak{R}^3} \left[\left(\xi_1 - u^{(0)} \right)^2 + 3\eta_1^2 + \zeta_1^2 \right] f_1^{(0)} d\xi_1 \\ & - \int_{\mathfrak{R}^3} \eta_1 \left[\left(\xi_1 - u^{(0)} \right) u^{(1)} + \eta_1 v^{(0)} \right] f_1^{(1)} d\xi_1 - \frac{1}{2} v^{(0)} \int_{\mathfrak{R}^3} \left[\left(\xi_1 - u^{(0)} \right)^2 + \eta_1^2 + \zeta_1^2 \right] f_1^{(1)} d\xi_1 \end{aligned} \quad (\text{VI.39})$$

As above, the first and the fourth of these quantities are immediately calculable, whereas the other three involve the third order component $f_1^{(2)}$, which will be explicitated below. An integration of the former quantities yields

$$u_1^{(1)} = u_2^{(1)} = u^{(1)} \quad (\text{VI.40})$$

$$(P_1)_{yy}^{(1)} = \frac{1}{2} (n_1 T)^{(1)}, \quad (P_2)_{yy}^{(1)} = \frac{1}{2} (n_2 T)^{(1)} \quad (\text{VI.41})$$

Hence, we obtain the mixture stress-tensor

$$P_{yy}^{(1)} = \frac{1}{2} (nT)^{(1)} = \frac{1}{2} \left(n^{(1)} T^{(0)} + n^{(0)} T^{(1)} \right) \quad (\text{VI.42})$$

As in the previous case, one may calculate the second order components of the various temperatures defined in II.2. and find all of them to be equal (Appendix D.1)

$$T_1^{(1)} = T_{11}^{(1)} = T_2^{(1)} = T_{22}^{(1)} = T^{(1)} \quad (\text{VI.43})$$

Furthermore, recalling the form (VI. 18) of the y momentum equation, one gets the equalities

$$\frac{n^{(1)}}{n^{(0)}} + \frac{T^{(1)}}{T^{(0)}} = 0, \quad P_{yy}^{(1)} = 0 \quad (\text{VI.44})$$

(since the perturbed values at $y = \infty$ are equal to 0).

To proceed further and express the three remaining additional unknowns in terms of the main unknowns, we need to calculate moments of the third order component $f_1^{(2)}$. This component is obtained by direct substitution of the formula (V. 4). After some manipulation, one is left with

$$\begin{aligned} \frac{f_1^{(2)}}{f_1^{(0)}} = & \frac{\rho_1^{(2)}}{\rho_1^{(0)}} + \left(W_1^2 - \frac{3}{2} \right) \frac{T^{(2)}}{T^{(0)}} + \frac{T^{(1)}}{T^{(0)}} \left[\left(\frac{W_1^4}{2} - \frac{5}{2} W_1^2 + \frac{15}{8} \right) \frac{T^{(1)}}{T^{(0)}} + \left(W_1^2 - \frac{3}{2} \right) \frac{\rho_1^{(1)}}{\rho_1^{(0)}} + \left(W_1^2 - \frac{5}{2} \right) W_2^2 \right] \\ & + W_2^2 \frac{\rho_1^{(1)}}{\rho_1^{(0)}} + \frac{1}{2} W_2^4 - W_3^2 \left[\frac{1}{\rho_1^{(0)}} \frac{\partial \rho_1^{(0)}}{\partial t} + \left(W_1^2 - \frac{3}{2} \right) \frac{1}{T^{(0)}} \frac{\partial T^{(0)}}{\partial t} + \frac{\left(\xi_1 - u^{(0)} \right)}{R_1 T^{(0)}} \frac{\partial u^{(0)}}{\partial t} \right] \\ & + \eta_1 \left[\left(W_1^2 - \frac{5}{2} \right) \frac{1}{T^{(0)}} \frac{\partial T^{(0)}}{\partial y} + \frac{\xi_1 - u^{(0)}}{R_1 T^{(0)}} \frac{\partial u^{(0)}}{\partial y} \right] + \eta_1^2 \left[\frac{1}{\rho_1^{(0)}} \frac{\partial \rho_1^{(0)}}{\partial y} + \left(W_1^2 - \frac{3}{2} \right) \frac{1}{T^{(0)}} \frac{\partial T^{(0)}}{\partial y} \right. \\ & \left. + \frac{\xi_1 - u^{(0)}}{R_1 T^{(0)}} \frac{\partial u^{(0)}}{\partial y} \right]^2 + \eta_1^2 \frac{\partial}{\partial y} \left[\frac{1}{\rho_1^{(0)}} \frac{\partial \rho_1^{(0)}}{\partial y} + \left(W_1^2 - \frac{3}{2} \right) \frac{1}{T^{(0)}} \frac{\partial T^{(0)}}{\partial y} + \frac{\xi_1 - u^{(0)}}{R_1 T^{(0)}} \frac{\partial u^{(0)}}{\partial y} \right] \\ & - \eta_1 \left[\frac{\rho_1^{(1)}}{\rho_1^{(0)}} + \left(W_1^2 - \frac{3}{2} \right) \frac{T^{(1)}}{T^{(0)}} + \frac{\left(\xi_1 - u^{(0)} \right) u^{(1)} + \eta_1 v^{(0)}}{R_1 T^{(0)}} \right] \left[\frac{1}{\rho_1^{(0)}} \frac{\partial \rho_1^{(0)}}{\partial y} + \left(W_1^2 - \frac{3}{2} \right) \frac{1}{T^{(0)}} \frac{\partial T^{(0)}}{\partial y} \right. \\ & \left. + \frac{\xi_1 - u^{(0)}}{R_1 T^{(0)}} \frac{\partial u^{(0)}}{\partial y} \right] - \eta_1 \frac{\partial}{\partial y} \left[\frac{\rho_1^{(1)}}{\rho_1^{(0)}} + \left(W_1^2 - \frac{3}{2} \right) \frac{T^{(1)}}{T^{(0)}} + \frac{\left(\xi_1 - u^{(0)} \right) u^{(1)} + \eta_1 v^{(0)}}{R_1 T^{(0)}} \right] \quad (\text{VI.45}) \end{aligned}$$

where W_1^2 and W_2^2 have been given above, and W_3^2 is given by

$$W_3^2 = \frac{\left(u^{(1)}\right)^2 + \left(v^{(0)}\right)^2 - 2\left[\xi_1 - u^{(0)}\right]u^{(2)} + \eta_1 v^{(1)}}{2R_1 T^{(0)}} \quad (\text{VI.46})$$

With the expression of $f_1^{(2)}$, we are able to perform various integrations involved in (VI. 36, 37, 39), and we obtain after cumbersome algebraic calculations (Appendix D. 2)

$$\left(\rho_1 v_1\right)^{(1)} = \left(\rho_1 v\right)^{(1)} - \frac{\partial}{2\partial y} \left(n_1 T\right)^{(1)} \quad (\text{VI.47})$$

$$\begin{aligned} \left(P_1\right)_{xy}^{(1)} = & \rho_1^{(0)} u^{(1)} \left[v^{(0)} - v_1^{(0)}\right] - \frac{1}{2} \left(n_1 T\right)^{(1)} \frac{\partial u^{(0)}}{\partial y} - \frac{\partial}{2\partial y} \left[u^{(1)} n_1^{(0)} T^{(0)}\right] + \\ & + \frac{1}{2} n_1^{(0)} T^{(0)} \frac{\partial u^{(0)}}{\partial y} \end{aligned} \quad (\text{VI.48})$$

$$\left(q_1\right)_y^{(1)} = -\frac{5}{4} \frac{\partial}{\partial y} \left[R_1 \left(n_1 T^2\right)^{(1)}\right] + \frac{5}{4} R_1 n_1^{(0)} T^{(0)} \frac{\partial T^{(0)}}{\partial y} \quad (\text{VI.49})$$

Analog expressions hold for the corresponding quantities of species 2. By summing up over both species the partial stress-tensor and heat-flux vector, we obtain the mixture variables

$$P_{xy}^{(1)} = -\frac{\partial u^{(1)}}{2\partial y} + \frac{\partial u^{(0)}}{2\partial y} \quad (\text{VI.50})$$

$$q_y^{(1)} = \frac{5}{4} \frac{\partial}{\partial y} \left(\bar{n} T^2\right)^{(1)} + \frac{5}{4} \bar{n}^{(0)} T^{(0)} \frac{\partial T^{(0)}}{\partial y} \quad (\text{VI.51})$$

where we have made use of the equations (VI.19) and (VI. 44). Moreover, using equation (VI. 47), we may verify that the sum of the second order components of the diffusion velocities vanish, as for the first order components

$$\left(\rho_1 V_1 + \rho_2 V_2\right)^{(1)} = -\frac{1}{2} \frac{\partial (nT)^{(1)}}{\partial y} = 0 \quad (\text{VI.52})$$

Having determined all the constitutive relations for the quantities of second order, we can write the system of equations satisfied by the second order components of the main unknowns: $\rho_1^{(1)}$, $\rho_2^{(1)}$, $u^{(1)}$, $v^{(1)}$, $T^{(1)}$. This system is obtained by collecting the terms of order ϵ in the development of the system (IV.3)

$$\frac{\partial n_1^{(1)}}{\partial t} + \frac{\partial}{\partial y} \left(n_1 v\right)^{(1)} = \frac{\partial^2}{\partial y^2} \left(n_1 R_1 T\right)^{(1)} \quad (\text{IV.53a})$$

$$\frac{\partial n_2^{(1)}}{\partial t} + \frac{\partial}{\partial y} \left(n_2 v\right)^{(1)} = \frac{\partial^2}{\partial y^2} \left(n_2 R_2 T\right)^{(1)} \quad (\text{VI.53b})$$

$$\frac{n^{(1)}}{n^{(0)}} + \frac{T^{(1)}}{T^{(0)}} = 0 \quad (\text{VI.53c})$$

$$\rho^{(0)} \left(\frac{\partial u^{(1)}}{\partial t} + v^{(0)} \frac{\partial u^{(1)}}{\partial y} \right) - \frac{1}{2} \frac{\partial^2 u^{(1)}}{\partial y^2} = -\rho^{(0)} v^{(1)} \frac{\partial u^{(0)}}{\partial y} - \frac{\partial^2 u^{(0)}}{2 \partial y^2} \left(1 + \frac{\rho^{(1)}}{\rho^{(0)}} \right) \quad (\text{VI.53d})$$

$$\frac{5}{4} \frac{\partial v^{(1)}}{\partial y} - \frac{\partial u^{(0)}}{\partial y} \frac{\partial u^{(1)}}{\partial y} - \frac{5}{4} \frac{\partial^2 (\bar{n} T^2)^{(1)}}{\partial y^2} = -\frac{1}{2} \left(\frac{\partial u^{(0)}}{\partial y} \right)^2 - \frac{5}{4} \frac{\partial}{\partial y} \left(\bar{n} T \frac{\partial T}{\partial y} \right)^{(0)} \quad (\text{VI.53e})$$

(some details about the derivation of the second order energy equation (VI. 53e) are given in Appendix D. 3). This system is subject to the following set of boundary conditions, obtained by expanding up to second order the conditions (IV. 18, 26, 27, 30) (see Appendix D. 4 for details)

$$u^{(1)}(0) = \frac{1}{\rho_2^{(0)}(0)} \frac{\partial}{\partial y} \left(\rho_1^{(0)} u^{(0)} \right) \Big|_{y=0} \quad (\text{VI.54a})$$

$$v^{(1)}(0) = 0 \quad (\text{VI.54b})$$

$$T^{(1)}(0) = \frac{1}{n_2^{(0)}(0)} \frac{\partial}{\partial y} \left(n_1^{(0)} T^{(0)} \right) \Big|_{y=0} \quad (\text{VI.54c})$$

$$\begin{aligned} \frac{\partial}{\partial y} \left[\left(\frac{5}{4} (R_1 - R_2) \left(T^{(0)} \right)^2 + \frac{E}{2} R_1 T^{(0)} \right) n_1^{(1)} \right] \Big|_{y=0} &= -\frac{\partial}{\partial y} \left[\frac{E}{2} n_1^{(0)} R_1 T^{(1)} - \frac{5}{4} R_2 T^{(1)} + 2 \bar{n}^{(0)} T^{(0)} T^{(1)} \right] \Big|_{y=0} \\ &+ \frac{5}{4} \bar{n}^{(0)} T^{(0)} \left(\frac{\partial T^{(0)}}{\partial y} \right) \Big|_{y=0} \quad (\text{VI.54d}) \end{aligned}$$

The second order system has the same structure as the first order system. It involves additional terms, but the higher order derivatives of the main unknowns are the same as for the first order system. Therefore, it has the same network of characteristics, which depend only on the derivative terms, and refines the Navier-Stokes solution by accounting for a small slip, in a similar way as for the single species case investigated by Trilling (1964). Furthermore, the system (VI. 53) is a sequence of linear equations, which is apparent if one developed them, as it is done in Appendix D.5. The properties of the second order system are retained by the systems of higher order: they remain linear, with the same coefficients for the higher order derivatives. Moreover, derivatives of higher order than the Navier-Stokes terms may appear in these systems. However, they are derivatives of quantities of a lower index, namely quantities which have already been determined in a previous step of the construction. Thus, they do not alter the order of the system, but act as forcing terms. Accordingly, there is no need for additional boundary conditions.

SECTION VII

SUMMARY AND CONCLUSION

This thesis presents a construction of an asymptotic solution of the Boltzmann-Krook equation for a reacting mixture of gases flowing over a flat plate. The chemical process is limited to wall recombination reactions. Physical assumptions related to our problem and physical consistency lead us to a particular choice for the coefficients upon which the Boltzmann-Krook equation depends. The boundary conditions associated with this kinetic model equation are not specified directly on the distribution functions themselves, but rather on averaged quantities of the distribution functions, namely on the hydrodynamic variables.

The equations of motion and the boundary conditions are expanded in powers of the square root of the Knudsen number of the flow, leading to an iterative construction of the solution. The macroscopic equations of motion obtained from the first component of the solution constructed by this method are similar to what we have called the Navier-Stokes equations for a gas mixture, with no-slip boundary conditions. The second component of the solution yields linear macroscopic equations of motion whose coefficients are the same as those of the Navier-Stokes system, together with slip boundary conditions. The features of the second order iterate are conserved by the succeeding iterates: they will all lead to a system of linear partial differential equations whose coefficients remain the first order coefficients; the inhomogeneous forcing terms only are different from one iterate to another. Moreover, the higher order derivatives which may appear in the subsequent systems involve only lower order terms already determined in previous steps of the iteration process. Therefore, they do not alter the structure of the system, but are part of the forcing terms mentioned above.

The conclusions reached for this Boltzmann-Krook equation are very much similar to those obtained by Trilling (1964) for the single species problem. In particular, a proper

ordering of the terms for the mixture problem, as well as for the single species problem, shows that the increase in the order of the continuum equations in the course of an iterative construction is fictitious. Therefore, it would be interesting to check if this conclusion is valid for our Boltzmann-Krook model equation only, or if it is a property associated with the true Boltzmann equation. Because of the similarity of both problems, it is very probable that the positive answer given to this last question by Trilling, applies also to our case.

Lastly, it would be worthwhile to investigate the behavior of the solution when one specifies the boundary conditions on the distribution functions themselves. This would lead to the introduction a molecular sublayer whose thickness would be of order ϵ^2 , and to the construction of a solution in this layer.

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APPENDIX A

EQUATIONS OF MOTION

A.1 Relation between T_S and T_{SS}

Starting from the definition (II.14) of T_1 , we have

$$\frac{3}{2}n_1kT_1 = \frac{1}{2} \int_{\mathfrak{R}^3} (\xi_1 - \mathbf{v})^2 f_1 d\xi_1 = \frac{1}{2} \int_{\mathfrak{R}^3} (\xi_1 - \mathbf{v}_1 + \mathbf{v}_1 - \mathbf{v})^2 f_1 d\xi_1 \quad (\text{A.1})$$

$$\Rightarrow \frac{3}{2}n_1kT_1 = \frac{3}{2}n_1kT_{11} + \int_{\mathfrak{R}^3} \left[(\xi_1 - \mathbf{v}_1)(\mathbf{v}_1 - \mathbf{v}) + \frac{1}{2}(\mathbf{v}_1 - \mathbf{v})^2 \right] f_1 d\xi_1 \quad (\text{A.2})$$

$$\Rightarrow \frac{3}{2}n_1kT_1 = \frac{3}{2}n_1kT_{11} + \frac{1}{2}\rho_1(\mathbf{v}_1 - \mathbf{v})^2 \quad (\text{A.3})$$

and,

$$\mathbf{v}_1 - \mathbf{v} = \mathbf{v}_1 - \frac{\rho_1 \mathbf{v}_1 - \rho_2 \mathbf{v}_2}{\rho} = \frac{\rho_2(\mathbf{v}_1 - \mathbf{v}_2)}{\rho} \quad (\text{A.4})$$

By substituting this last result into (A.3), we will have (II.20) given in section II.2.

$$T_1 = T_{11} + \frac{m_1 \rho_2^2 (\mathbf{v}_2 - \mathbf{v}_1)^2}{3k\rho^2} \quad (\text{II.20})$$

A.2 Derivation of the energy equation

The contribution of species 1 on the left-hand side of equation (II.23) is

$$\frac{\partial}{\partial t} \left(\int_{\mathfrak{R}^3} \frac{1}{2} \xi_1^2 f_1 d\xi_1 \right) + \frac{\partial}{\partial y} \left(\int_{\mathfrak{R}^3} \eta_1 \xi_1^2 f_1 d\xi_1 \right) \quad (\text{A.5})$$

The first term is the time derivative of

$$\frac{1}{2} \int_{\mathfrak{R}^3} \xi_1^2 f_1 d\xi_1 = \frac{1}{2} \int_{\mathfrak{R}^3} (\mathbf{c}_1 + \mathbf{v})^2 f_1 d\xi_1 = \frac{3}{2} p_1 + \mathbf{v} \cdot \int_{\mathfrak{R}^3} \mathbf{c}_1 f_1 d\xi_1 + \frac{\rho_1 \mathbf{v}^2}{2} \quad (\text{A.6})$$

Adding the contribution of species 2 yields

$$\frac{3}{2} nkT + \frac{\rho \mathbf{v}^2}{2} \quad (\text{A.7})$$

The second term of (A.5) is the y derivative of

$$\begin{aligned} \frac{1}{2} \int_{\mathfrak{R}^3} \eta_1 \xi_1^2 f_1 d\xi_1 &= \frac{1}{2} \int_{\mathfrak{R}^3} \left((\mathbf{c}_1)_y + v \right) \left(\mathbf{c}_1^2 + 2\mathbf{c}_1 \cdot \mathbf{v} + v^2 \right) f_1 d\xi_1 = \\ &= \frac{1}{2} \int_{\mathfrak{R}^3} \left\{ (\mathbf{c}_1)_y \mathbf{c}_1^2 + 2v \cdot (\mathbf{c}_1)_y \mathbf{c}_1 + v^2 (\mathbf{c}_1)_y + v \mathbf{c}_1^2 + 2v \mathbf{v} \cdot \mathbf{c}_1 + v \mathbf{v}^2 \right\} f_1 d\xi_1 \end{aligned} \quad (\text{A.8})$$

By summing the similar contribution of species 2 and using the definitions of the various hydrodynamics quantities introduced in II.2., we obtain

$$q_y + uP_{xy} + vP_{yy} + \frac{3}{2} nkTv + \rho v \frac{\mathbf{v}^2}{2} \quad (\text{A.9})$$

Thus, the energy equation is

$$\frac{\partial}{\partial t} \left(\frac{3}{2} nkT + \frac{\rho \mathbf{v}^2}{2} \right) + \frac{\partial}{\partial y} \left(q_y + uP_{xy} + vP_{yy} + \frac{3}{2} nkTv + \rho v \frac{\mathbf{v}^2}{2} \right) = 0 \quad (\text{A.10})$$

Next, we need to rearrange this equation in order to find the final expression (II.24.d). The terms involving the temperature T can be rewritten as

$$\begin{aligned} \frac{\partial}{\partial t} \left(\frac{3}{2} nkT \right) + \frac{\partial}{\partial y} \left(\frac{3}{2} nkTv \right) &= \frac{3}{2} nk \left(\frac{\partial T}{\partial t} + v \frac{\partial T}{\partial y} \right) + \frac{3}{2} kT \left(\frac{\partial n}{\partial t} + \frac{\partial (nv)}{\partial y} \right) = \\ &= \frac{3}{2} nk \left(\frac{\partial T}{\partial t} + v \frac{\partial T}{\partial y} \right) + \frac{3}{2} kT \sum_{s=1,2} \left(\frac{\partial n_s}{\partial t} + \frac{\partial (n_s v_s)}{\partial y} - \frac{\partial (n_s V_s)}{\partial y} \right) = \\ &= \frac{3}{2} nk \left(\frac{\partial T}{\partial t} + v \frac{\partial T}{\partial y} \right) - \frac{3}{2} kT \frac{\partial}{\partial y} \left(\sum_{s=1,2} n_s V_s \right) \end{aligned} \quad (\text{A.11})$$

where we have used the species conservation equation (II.24.a). Among the remaining terms are

$$\frac{\mathbf{v}^2}{2} \left(\frac{\partial \rho}{\partial t} + \frac{\partial \rho v}{\partial y} \right) = 0 \quad (\text{A.12})$$

because of the overall mass conservation, and

$$\frac{\rho}{2} \left(\frac{\partial}{\partial t} (u^2 + v^2) + v \frac{\partial}{\partial y} (u^2 + v^2) \right) + u \frac{\partial P_{xy}}{\partial y} + v \frac{\partial P_{yy}}{\partial y} = \frac{\rho}{2} \left(\frac{\partial}{\partial t} (u^2 + v^2) + v \frac{\partial}{\partial y} (u^2 + v^2) \right) - \rho u \left(\frac{\partial u}{\partial t} + v \frac{\partial u}{\partial y} \right) - \rho v \left(\frac{\partial v}{\partial t} + v \frac{\partial v}{\partial y} \right) = 0 \quad (\text{A.13})$$

where we have used the momentum conservation equations (II.24.b) and (II.24.c). The non zero remaining terms are

$$\frac{\partial q_y}{\partial y} + P_{xy} \frac{\partial u}{\partial y} + P_{yy} \frac{\partial v}{\partial y} \quad (\text{A.14})$$

Adding (A.11) and (A.14) yields the final form (II.24.d) of the energy equation

$$\frac{3}{2} nk \left(\frac{\partial T}{\partial t} + v \frac{\partial T}{\partial y} \right) + \frac{\partial q_y}{\partial y} + P_{xy} \frac{\partial u}{\partial y} + P_{yy} \frac{\partial v}{\partial y} = \frac{3}{2} kT \frac{\partial \left(\sum_s n_s V_s \right)}{\partial y} \quad (\text{II.24.d})$$

APPENDIX B

KINETIC MODEL

B.1 Conditions imposed by the collision invariants

The term of the first species in the condition (III. 7.b) corresponding to the momentum conservation, is

$$\int_{\mathfrak{R}^3} \left\{ \frac{1}{\tau_{11}} (\Psi_{11}^{-f_1}) + \frac{1}{\tau_{12}} (\Psi_{12}^{-f_1}) \right\} \xi_1 d\xi_1 = \frac{1}{\tau_{11}} (\rho_1 \mathbf{v}_1 - \rho_1 \mathbf{v}_1) + \frac{1}{\tau_{12}} (\rho_1 \mathbf{v}_{12} - \rho_1 \mathbf{v}_1) =$$

$$= \frac{1}{\tau_{12}} \rho_1 (\mathbf{v}_{12} - \mathbf{v}_1) \quad (\text{B.1})$$

Adding the similar contribution due to the second species yields for (III. 7.b)

$$\frac{1}{\tau_{12}} \rho_1 (\mathbf{v}_{12} - \mathbf{v}_1) + \frac{1}{\tau_{21}} \rho_2 (\mathbf{v}_{21} - \mathbf{v}_2) = 0 \quad (\text{B.2})$$

Once we have taken into account of the assumption on the collision times (III.6), we have this condition

$$\rho_1 \mathbf{v}_{12} + \rho_2 \mathbf{v}_{21} = \rho \mathbf{v} \quad (\text{III.10})$$

Similarly, the term of the first species in the condition (III. 7.c) corresponding to the energy conservation is

$$\frac{1}{2} \int_{\mathfrak{R}^3} \left\{ \frac{1}{\tau_{11}} (\Psi_{11}^{-f_1}) + \frac{1}{\tau_{12}} (\Psi_{12}^{-f_1}) \right\} \xi_1^2 d\xi_1 =$$

$$\frac{1}{2\tau_{12}} \left\{ \int_{\mathfrak{R}^3} \Psi_{12} \left[\left(\xi_1 - \mathbf{v}_{12} \right)^2 + 2\mathbf{v}_{12} \cdot \left(\xi_1 - \mathbf{v}_{12} \right) + \mathbf{v}_{12}^2 \right] d\xi_1 - \int_{\mathfrak{R}^3} f_1 \left[\left(\xi_1 - \mathbf{v} \right)^2 + 2\mathbf{v} \cdot \left(\xi_1 - \mathbf{v} \right) + \mathbf{v}^2 \right] d\xi_1 \right\} =$$

$$= \frac{1}{\tau_{12}} \left[\frac{3}{2} n_1 k (T_{12} - T_1) + \frac{\rho_1}{2} (\mathbf{v}_{12}^2 - \mathbf{v}^2) - \rho_1 \mathbf{v} \cdot (\mathbf{v}_1 - \mathbf{v}) \right] \quad (\text{B.3})$$

The left term under the first of the integrals above vanishes because f_1 and Ψ_{11} have the same moments up to the order 2. Adding the equivalent contribution of species 2 in condition (III. 7.c), leads to the constraint (III. 11) of III.2.

$$3n_1 k (T_{12} - T_1) + 3n_2 k (T_{21} - T_2) + \rho_1 (\mathbf{v}_{12}^2 - \mathbf{v}^2) + \rho_2 (\mathbf{v}_{21}^2 - \mathbf{v}^2) = 0 \quad (\text{III.11})$$

B.2 H Theorem

In this section, any distribution function represents the number of molecules per unite volume in phase space, instead of the mass per unite volume, as in any other part of this thesis. Thus, the quantity H_1 is given by

$$H_1 = \int_{\mathfrak{R}^3} f_1 \ln f_1 d\xi_1 \quad (\text{B.4})$$

and the convective derivative of H_1 is

$$\frac{DH_1}{Dt} = \int_{\mathfrak{R}^3} \frac{Df_1}{Dt} (1 + \ln f_1) d\xi_1 = \int_{\mathfrak{R}^3} \left[\frac{1}{\tau_{11}} (\Psi_{11} - f_1) + \frac{1}{\tau_{12}} (\Psi_{12} - f_1) \right] (1 + \ln f_1) d\xi_1 \quad (\text{B.5})$$

The first part of this expression is

$$\frac{1}{\tau_{11}} \int_{\mathfrak{R}^3} \left\{ (\Psi_{11} - f_1) + (\Psi_{11} - f_1) \ln \left(\frac{f_1}{\Psi_{11}} \right) + (\Psi_{11} - f_1) \ln \Psi_{11} \right\} d\xi_1 \quad (\text{B.6})$$

Among the three terms appearing under the integral (B.6), the first one vanishes. The second one is always negative, and the third one can be developed as

$$\frac{1}{\tau_{11}} \int_{\mathfrak{R}^3} \left\{ \ln \left[n_1 \left(\frac{m_1}{2\pi k T_{11}} \right)^{3/2} \right] - \frac{m_1}{2kT_{11}} (\xi_1 - \mathbf{v}_1)^2 \right\} (\Psi_{11} - f_1) d\xi_1 \quad (\text{B.7})$$

where the form (III.5) of Ψ_{11} has been written explicitly. Since f_1 and Ψ_{11} have the same

moments up to second order, the integral (B.7) vanishes also. Thus, the only term remaining in (B.6) is the second one, and it is a negative term.

Let us now come back to the integral (B.5) and investigate the second term of the integrand. As for the first term, we can rewrite it as

$$\frac{1}{\tau_{12}} \int_{\mathfrak{R}^3} \left\{ (\Psi_{12}^{-f_1}) + (\Psi_{12}^{-f_1}) \ln \left(\frac{f_1}{\Psi_{12}} \right) + (\Psi_{12}^{-f_1}) \ln \Psi_{12} \right\} d\xi_1 \quad (\text{B.8})$$

As for (B.6), the first term under the integral vanishes, the second is negative, and the third is developed as

$$\frac{1}{\tau_{12}} \int_{\mathfrak{R}^3} \left\{ \ln \left[n_1 \left(\frac{m_1}{2\pi k T_{12}} \right)^{3/2} \right] - \frac{m_1}{2k T_{12}} (\xi_1 - \mathbf{v}_{12})^2 \right\} (\Psi_{12}^{-f_1}) d\xi_1 \quad (\text{B.9})$$

In this last integral, the first part vanishes whereas the second one may be rewritten as

$$-\frac{1}{2k T_{12} \tau_{12}} \left[3n_1 k T_{12} - 3n_1 k T_1 - \rho_1 (\mathbf{v} - \mathbf{v}_{12})^2 - 2\rho_1 (\mathbf{v} - \mathbf{v}_{12})(\mathbf{v}_1 - \mathbf{v}) \right] \quad (\text{B.10})$$

The same analysis can be done for the quantity H_2 of species 2. As for species 1, this would yield two negative terms and the following complementary term similar to (B.10)

$$\frac{1}{2k T_{21} \tau_{21}} \left[3n_2 k T_{21} - 3n_2 k T_2 - \rho_2 (\mathbf{v} - \mathbf{v}_{21})^2 - 2\rho_2 (\mathbf{v} - \mathbf{v}_{21})(\mathbf{v}_2 - \mathbf{v}) \right] \quad (\text{B.11})$$

The two characteristic times τ_{12} and τ_{21} have been assumed equal (see III.2). Therefore, it is clear from the form of (B.10) and (B.11) that the conditions

$$\mathbf{v}_{12} = \mathbf{v}_{21} \quad \text{and} \quad T_{12} = T_{21} \quad (\text{B.12})$$

are sufficient to satisfy the H theorem. As a matter of fact, (B.12) together with condition (III.10) imply

$$\mathbf{v}_{12} = \mathbf{v}_{21} = \mathbf{v} \quad (\text{B.13})$$

which, in turn, combined with (III.11), yields

$$T_{12} = T_{21} = T \quad (\text{B.14})$$

Then the sum of (B.10) and (B.11) becomes

$$\frac{3}{2T\tau_{12}} \left(n_1 (T - T_1) + n_2 (T - T_2) \right) = 0 \quad (\text{B.15})$$

In these conditions, we are left with

$$\frac{DH}{Dt} = \frac{DH_1}{Dt} + \frac{DH_2}{Dt} = \frac{1}{\tau_{11}} \int_{\mathfrak{R}^3} (\Psi_{11}^{-f_1}) \ln \left(\frac{f_1}{\Psi_{11}} \right) d\xi_1 + \frac{1}{\tau_{12}} \int_{\mathfrak{R}^3} (\Psi_{12}^{-f_1}) \ln \left(\frac{f_1}{\Psi_{12}} \right) d\xi_1$$

$$+ \frac{1}{\tau_{21}} \int_{\mathfrak{R}^3} (\Psi_{21} - f_2) \ln \left(\frac{f_2}{\Psi_{21}} \right) d\xi_2 + \frac{1}{\tau_{22}} \int_{\mathfrak{R}^3} (\Psi_{22} - f_2) \ln \left(\frac{f_2}{\Psi_{22}} \right) d\xi_2 \quad (\text{B.16})$$

Each of the terms appearing in the sum (B.16) is obviously negative. Thus, we have the inequality (III. 9)

$$\frac{DH}{Dt} \leq 0 \quad (\text{III.9})$$

Moreover, the equality in (III. 9) holds if and only if each one of the four terms in the sum (B.16) is equal to 0. This implies

$$f_1 = \Psi_{11}, f_1 = \Psi_{12}, f_2 = \Psi_{21}, f_2 = \Psi_{22} \quad (\text{B.17})$$

and consequently,

$$\mathbf{v}_1 = \mathbf{v}_2 = \mathbf{v} \quad \text{and} \quad T_1 = T_2 = T \quad (\text{B.18})$$

Thus, the equality in (III. 9) holds if and only if the mixture is in an equilibrium state. We have, therefore, demonstrated that the condition (B.12) implies the H theorem.

APPENDIX C

FIRST ORDER SYSTEM

C.1 Moments of $f_1^{(0)}$

The first order component $f_1^{(0)}$ is the maxwellian distribution function given by (VI. 3). We give below the general form of the moment of $f_1^{(0)}$

$$\int_{\mathfrak{R}^3} \left(\xi_1 - u^{(0)} \right)^n \eta_1^p \zeta_1^q f_1^{(0)} d\xi_1 = \rho_1^{(0)} \left(2R_1 T^{(0)} \right)^{\frac{n+p+q}{2}} \left(\frac{n-1}{2} \right)! \left(\frac{p-1}{2} \right)! \left(\frac{q-1}{2} \right)! \quad (C.1)$$

with

$$\left(\frac{n-1}{2} \right)! = \frac{n-1}{2} \left(\frac{n-3}{2} \right)! \quad \text{and} \quad \left(\frac{1}{2} \right)! = \frac{1}{2}$$

if each of the exponents n, p, q is even. Otherwise, if one of the exponent n, p, q is odd, the moment vanishes

$$\int_{\mathfrak{R}^3} \left(\xi_1 - u^{(0)} \right)^n \eta_1^p \zeta_1^q f_1^{(0)} d\xi_1 = 0$$

The calculations of $u_1^{(0)}$ and $P_{yy}^{(0)}$ are straight applications of this formula.

Moreover, let us derive the equation (VI. 17) for the first order components of the various temperatures. The dimensionless form of the definition (II. 14) of the species temperature is

$$\frac{3}{2}n_s T_s = \int_{\mathfrak{R}^3} \left[(\xi_s - u)^2 + (\eta_s - \varepsilon v)^2 + \zeta_s^2 \right] f_s d\xi_s \quad (\text{C.2})$$

By expanding u , v , f and collecting the terms independent of ε , we obtain the first order component of the temperature

$$\frac{3}{2}n_1^{(0)} T_1^{(0)} = \int_{\mathfrak{R}^3} \left[(\xi_1 - u^{(0)})^2 + \eta_1^2 + \zeta_1^2 \right] f_1^{(0)} d\xi_1 = 3\rho_1^{(0)} R_1 T^{(0)} = \frac{3}{2}n_1^{(0)} T^{(0)} \quad (\text{C.3})$$

where the rule (C.1) and the relation (VI. 2) have been used. A similar relation can be derived for species 2. Thus, we obtain the equality

$$T_1^{(0)} = T_2^{(0)} = T^{(0)} \quad (\text{C.4})$$

Next, we need to calculate the first order component of the species temperature T_{ss} . For this purpose, we only need to replace $u^{(0)}$ by $u_1^{(0)}$ in the equation (C.3). But $u_1^{(0)} = u^{(0)}$. Therefore, $T_{11}^{(0)} = T_1^{(0)}$, and a similar equality holds for species 2. We finally get

$$T_1^{(0)} = T_{11}^{(0)} = T_2^{(0)} = T_{22}^{(0)} = T^{(0)} \quad (\text{VI.17})$$

C.2 Moments of $f_1^{(1)}$

The second order component of the reference distribution Ψ_{12} is obtained by performing a power expansion of all the parameters appearing in the dimensionless form (VI. 1) and collecting the terms of order ε . After some calculations, this yields

$$\Psi_{12}^{(1)} = \Psi_{12}^{(0)} \left[\frac{\rho_1^{(1)}}{\rho_1^{(0)}} + \left(W_1^2 - \frac{3}{2} \right) \frac{T^{(1)}}{T^{(0)}} + W_2^2 \right] \quad (\text{C.5})$$

On the other hand, the y derivative of the maxwellian distribution $f_1^{(0)}$ is easy to calculate and is given by

$$\frac{\partial f_1^{(0)}}{\partial y} = f_1^{(0)} \left[\frac{1}{\rho_1^{(0)}} \frac{\partial \rho_1^{(0)}}{\partial y} + \left(W_1^2 - \frac{3}{2} \right) \frac{1}{T^{(0)}} \frac{\partial T^{(0)}}{\partial y} + \frac{\xi_1 - u^{(0)}}{R_1 T^{(0)}} \frac{\partial u^{(0)}}{\partial y} \right] \quad (\text{C.6})$$

Substituting (C.5) and (C.6) in the equation (VI. 22) defining $f_1^{(1)}$, yields the expression (VI. 23) of $f_1^{(1)}$. As far as the velocity space is concerned, $f_1^{(1)}$ is the product of a polynomial in the velocity variables by the maxwellian distribution $f_1^{(0)}$. Thus, any moment of $f_1^{(1)}$ can be decomposed in moments of $f_1^{(0)}$, which are calculated by the mean of the rule (C.1). However, an alternative and slightly simpler way of calculating the moments of $f_1^{(1)}$ is

available. Let h be a function of the position and velocity variables $x_1, y_1, z_1, \xi_1, \eta_1, \zeta_1$. One may easily prove the identity

$$\int_{\mathfrak{R}^3} h f_1^{(1)} d\xi_1 = \int_{\mathfrak{R}^3} h \Psi_{12}^{(1)} d\xi_1 - \frac{\partial}{\partial y} \int_{\mathfrak{R}^3} \eta_1 h f_1^{(0)} d\xi_1 + \int_{\mathfrak{R}^3} \eta_1 \frac{\partial h}{\partial y} f_1^{(0)} d\xi_1 \quad (\text{C.7})$$

Thus, one do not need any more the explicit form (C.6). The formula (C.7) turns out to be more adaptable for the actual calculations of the various hydrodynamic quantities. In particular, when applied to the quantities (VI. 10, 11, 13), it leads to the expressions (VI. 26, 27, 28) of the first order components of the species y velocity, stress-tensor and heat-flux vector .

C.3 Derivation of the first-order energy equation

The species continuity and global momentum equations are obtained by direct elimination of the additional unknowns by the mean of relations (VI. 14, 15, 26, 27). However, in order to derive the energy equation (VI. 33.e), we need to perform some additional manipulations. We start from the species continuity equation

$$\frac{\partial n_1^{(0)}}{\partial t} + v^{(0)} \frac{\partial n_1^{(0)}}{\partial y} = \frac{\partial^2}{\partial y^2} \left(n_1^{(0)} R_1 T^{(0)} \right) - n_1^{(0)} \frac{\partial v^{(0)}}{\partial y} \quad (\text{C.8})$$

Adding to (C.8) the analog equation for the second species and replacing $n^{(0)}$ by $1/T^{(0)}$ yields the equation

$$n^{(0)} \left(\frac{\partial T^{(0)}}{\partial t} + v^{(0)} \frac{\partial T^{(0)}}{\partial y} \right) = - T^{(0)} \frac{\partial^2}{\partial y^2} \left(\bar{n}^{(0)} T^{(0)} \right) + \frac{\partial v^{(0)}}{\partial y} \quad (\text{C.9})$$

After substitution of (C.9), the left-hand side of the first order energy equation becomes

$$- \frac{3}{4} T^{(0)} \frac{\partial^2}{\partial y^2} \left(\bar{n}^{(0)} T^{(0)} \right) + \frac{5}{4} \frac{\partial v^{(0)}}{\partial y} - \frac{1}{2} \left(\frac{\partial u^{(0)}}{\partial y} \right)^2 - \frac{5}{4} \frac{\partial^2}{\partial y^2} (\bar{n} T^2)^{(0)} \quad (\text{C.10})$$

On the other hand, the diffusion velocity of species 1 may be written

$$n_1^{(0)} v_1^{(0)} = - R_1 \frac{\partial}{\partial y} (n_1 T)^{(0)} \quad (\text{C.11})$$

so that the right-hand side of the energy equation becomes

$$- \frac{3}{4} T^{(0)} \frac{\partial^2}{\partial y^2} (\bar{n} T)^{(0)} \quad (\text{C.12})$$

and cancels the first term of the left-hand-side (C.10). Hence, we are left with the energy equation (VI. 33e) for the first order quantities.

C.4 Boundary conditions for the first-order system

Expanding (IV. 26) up to the first order yields

$$(\rho u)^{(0)}(0) - (\rho u)^{(0)} = \rho_2^{(0)}(0)u_w - (\rho_2 u_2)^{(0)}(0) \quad (C.13)$$

Since $u_2^{(0)} = u^{(0)}$, we get the condition

$$u^{(0)}(0) = u_w \quad (VI.34a)$$

The condition (VI.34b) for $v^{(0)}(0)$ is immediately obtained from (IV. 18), and the temperature boundary condition (VI. 34c) is derived from (IV. 27) exactly as the condition (VI.34a) is obtained above from (IV. 26).

Lastly, the boundary condition specifying the proportion of each species at the surface is obtained by working out the condition (IV. 30). On the one hand, the velocity term is

$$(n_1 v_1)^{(0)}(0) = - \frac{\partial}{\partial y} \left[n_1^{(0)} R_1 T^{(0)} \right]_{y=0} \quad (C.14)$$

on the other hand, the heat-flux vector at the surface is

$$q_y^{(0)}(0) = \frac{5}{4} \frac{\partial}{\partial y} \left[(R_1 - R_2) n_1^{(0)} \left(T^{(0)} \right)^2 + R_2 T^{(0)} \right]_{y=0} \quad (C.15)$$

Then, combining (C.14) and (C.15) leads to (VI. 34d).

C.5 Developed form of the equations

We give below the explicit form of the system (VI. 33), in order to have a reference for the second order system. The momentum equations are given explicitly by (VI. 33c) and (VI.33d), while the species continuity and the energy equations become

$$\frac{\partial n_1^{(0)}}{\partial t} + v^{(0)} \frac{\partial n_1^{(0)}}{\partial y} + n_1^{(0)} \frac{\partial v^{(0)}}{\partial y} - R_1 \left[T^{(0)} \frac{\partial^2 n_1^{(0)}}{\partial y^2} + 2 \frac{\partial T^{(0)}}{\partial y} \frac{\partial n_1^{(0)}}{\partial y} + n_1^{(0)} \frac{\partial^2 T^{(0)}}{\partial y^2} \right] \quad (C.16)$$

$$\begin{aligned} \frac{5}{4} \frac{\partial v^{(0)}}{\partial y} - \frac{1}{2} \left[\frac{\partial u^{(0)}}{\partial y} \right]^2 - \frac{5}{4} \left[\left(T^{(0)} \right)^2 \frac{\partial \bar{n}}{\partial y} + 4 T^{(0)} \frac{\partial T^{(0)}}{\partial y} \frac{\partial \bar{n}}{\partial y} + 2 \bar{n}^{(0)} T^{(0)} \frac{\partial T^{(0)}}{\partial y} \right. \\ \left. + 2 \bar{n}^{(0)} \frac{\partial^2 T^{(0)}}{\partial y^2} \right] = 0 \end{aligned} \quad (C.17)$$

APPENDIX D

SECOND ORDER SYSTEM

D.1 Moments of $f_1^{(1)}$

As pointed out in VI.2., the integrated quantities $(\rho_1 u_1)^{(1)}$ and $(P_1)_{yy}^{(1)}$ involve the component $f_1^{(1)}$ only. Therefore, they are calculated by applying the rule (C.7) given above. Moreover, as for the first order system in C.1., let us derive the equation (VI. 43) between the second order components of the various temperatures. Developing (C.2) up to the second order yields

$$\frac{3}{2}(n_1 T_1)^{(1)} = \int_{\mathfrak{R}^3} \left[\left(\xi_1 - u^{(0)} \right)^2 + \eta_1^2 + \zeta_1^2 \right] f_1^{(1)} d\xi_1 - 2 \int_{\mathfrak{R}^3} \left[u^{(1)} \left(\xi_1 - u^{(0)} \right) + v^{(0)} \eta_1 \right] f_1^{(0)} d\xi_1 \quad (D.1)$$

The second integral involves only odd moments of $f_1^{(0)}$ and vanishes, whereas calculating the second one leads to

$$\frac{3}{2}(n_1 T_1)^{(1)} = \frac{3}{2}(n_1 T)^{(1)} \quad (D.2)$$

A similar identity holds for species 2, and we may write

$$T_1^{(1)} = T_2^{(1)} = T^{(1)} \quad (D.3)$$

The other species temperature $T_{11}^{(1)}$ is defined by an identity similar to (D.1), but $u^{(1)}$ and $v^{(0)}$ are replaced by $u_1^{(1)}$ and $v_1^{(0)}$. Therefore, the second integral vanishes, as for $T_1^{(1)}$, and the first one has the same value since $u_1^{(1)} = u^{(1)}$. Hence, $T_{11}^{(1)} = T_1^{(1)}$, and a similar equality holds for species 2, so that we finally get

$$T_1^{(1)} = T_{11}^{(1)} = T_2^{(1)} = T_{22}^{(1)} = T^{(1)} \quad (VI.43)$$

D.2 Moments of $f_1^{(2)}$

The three remaining quantities, namely $(\rho_1 v_1)^{(1)}$, $(P_1)_{xy}^{(1)}$ and $(q_1)_y^{(1)}$, involve the third order component $f_1^{(2)}$ of the distribution function. This component is obtained by direct substitution of the various quantities entering equation (V. 4). We do not intend to describe in details the derivation of the identity (VI. 45), but will simply identify the various terms entering it.

By expanding up to the order ε^2 the parameters upon which the reference maxwellian distribution Ψ_{12} depends, we are able to identify the third order component of Ψ_{12}

$$\frac{\Psi_{12}^{(2)}}{\Psi_{12}^{(0)}} = \frac{\rho_1^{(2)}}{\rho_1^{(0)}} + \left(W_1^2 - \frac{3}{2} \right) \frac{T^{(2)}}{T^{(0)}} + \left\{ \left(\frac{W_1^4}{2} - \frac{5}{2} W_1^2 + \frac{15}{8} \right) \frac{T^{(1)}}{T^{(0)}} + \left(W_1^2 - \frac{3}{2} \right) \frac{\rho_1^{(1)}}{\rho_1^{(0)}} + \left(W_1^2 - \frac{5}{2} \right) W_2^2 \right\} \frac{T^{(1)}}{T^{(0)}} + W_2^2 \frac{\rho_1^{(1)}}{\rho_1^{(0)}} + \frac{1}{2} W_2^4 - W_3^2 \quad (D.4)$$

Next, the second order component of Ψ_{11} has the same form as $\Psi_{12}^{(1)}$

$$\Psi_{11}^{(1)} = \Psi_{11}^{(0)} \left\{ \frac{\rho_1^{(1)}}{\rho_1^{(0)}} + \left(W_1^2 - \frac{3}{2} \right) \frac{T^{(1)}}{T^{(0)}} + \frac{\left(\xi_{1-u}^{(0)} \right) u^{(1)} + \eta_1 v_1^{(0)}}{R_1 T^{(0)}} \right\} \quad (D.5)$$

The only difference is the term $v_1^{(0)}$ in place of $v^{(0)}$. Replacing $v_1^{(0)}$ by its expression (VI.26) and subtracting $f_1^{(1)}$, yield the difference

$$\Psi_{11}^{(1)} - f_1^{(1)} = \eta_1 f_1^{(0)} \left\{ \left(W_1^2 - \frac{5}{2} \right) \frac{1}{T^{(0)}} \frac{\partial T^{(0)}}{\partial y} + \frac{\xi_{1-u}^{(0)}}{R_1 T^{(0)}} \frac{\partial u^{(0)}}{\partial y} \right\} \quad (D.6)$$

Then, the time derivative of $f_1^{(0)}$ is

$$\frac{\partial f_1^{(0)}}{\partial t} = f_1^{(0)} \left\{ \frac{1}{\rho_1^{(0)}} \frac{\partial \rho_1^{(0)}}{\partial t} + \left(W_1^2 - \frac{3}{2} \right) \frac{1}{T^{(0)}} \frac{\partial T^{(0)}}{\partial t} + \frac{\xi_{1-u}^{(0)}}{R_1 T^{(0)}} \frac{\partial u^{(0)}}{\partial t} \right\} \quad (D.7)$$

Finally, the four last terms in the expression (VI.45) of $f_1^{(2)}$ correspond to the y derivative of $f_1^{(1)}$.

As already noticed for $f_1^{(1)}$, $f_1^{(2)}$ is a polynomial in the velocity variables, multiplied by the maxwellian distribution $f_1^{(0)}$. Therefore, any moment of $f_1^{(2)}$ can be calculated by applying the rule (C.1). However, a simpler rule of calculation similar to (C.7) can be given. Recalling (VI. 22), one gets

$$\eta_1 \frac{\partial f_1^{(1)}}{\partial y} = \eta_1 \frac{\partial \Psi_{12}^{(1)}}{\partial y} - \eta_1^2 \frac{\partial^2 f_1^{(0)}}{\partial y^2} \quad (\text{D.8})$$

so that one can easily establish the following rule, h being a function defined in the position velocity phase space,

$$\begin{aligned} \int_{\mathfrak{R}^3} h f_1^{(2)} d\xi_1 &= \int_{\mathfrak{R}^3} \left(\Psi_{12}^{(2)} + \Psi_{11}^{(1)} - f_1^{(1)} \right) h d\xi_1 - \frac{\partial^2}{\partial y^2} \int_{\mathfrak{R}^3} \eta_1^2 h f_1^{(0)} d\xi_1 + 2 \frac{\partial}{\partial y} \int_{\mathfrak{R}^3} \eta_1^2 \frac{\partial h}{\partial y} f_1^{(0)} d\xi_1 \\ &- \int_{\mathfrak{R}^3} \eta_1^2 \frac{\partial^2 h}{\partial y^2} f_1^{(0)} d\xi_1 - \frac{\partial}{\partial t} \int_{\mathfrak{R}^3} h f_1^{(0)} d\xi_1 + \int_{\mathfrak{R}^3} \frac{\partial h}{\partial t} f_1^{(0)} d\xi_1 - \frac{\partial}{\partial y} \int_{\mathfrak{R}^3} \eta_1 h \Psi_{12}^{(1)} d\xi_1 + \int_{\mathfrak{R}^3} \eta_1 \frac{\partial h}{\partial y} \Psi_{12}^{(1)} d\xi_1 \end{aligned} \quad (\text{D.9})$$

For actual calculations, dealing with this rule turns out to be more convenient than with the full explicit identity (VI. 45). It provides us with the expressions (VI. 47, 48, 49) of the components of second order of the species y velocity, stress-tensor and heat-flux vector .

D.3 Second order energy equation

As for the first order system, the species continuity and momentum equations for the second order system are easily derived by simple substitution of the relations (VI. 40, 41, 47, 48). The derivation of the energy equation is less simple and requires a few more manipulations.

We start with the left hand side

$$\begin{aligned} \frac{3}{4} n^{(1)} \left(\frac{\partial T^{(0)}}{\partial t} + v^{(0)} \frac{\partial T^{(0)}}{\partial y} \right) + \frac{3}{4} n^{(0)} \left(\frac{\partial T^{(1)}}{\partial t} + v^{(0)} \frac{\partial T^{(1)}}{\partial y} \right) + \frac{3}{4} n^{(0)} v^{(1)} T^{(0)} + \frac{\partial q_y^{(1)}}{\partial y} + P_{xy}^{(1)} \frac{\partial u^{(0)}}{\partial y} \\ + P_{xy}^{(0)} \frac{\partial u^{(1)}}{\partial y} + P_{yy}^{(1)} \frac{\partial v^{(0)}}{\partial y} + P_{yy}^{(0)} \frac{\partial v^{(1)}}{\partial y} \end{aligned} \quad (\text{D.10})$$

From the y momentum equations (VI. 19) and (VI.44), we have

$$T^{(1)} = -n^{(1)} \left(T^{(0)} \right)^2 \quad (\text{D.11})$$

which allows us to write

$$\frac{\partial T^{(1)}}{\partial t} + v^{(0)} \frac{\partial T^{(1)}}{\partial y} = - \left(T^{(0)} \right)^2 \left(\frac{\partial n^{(1)}}{\partial t} + v^{(0)} \frac{\partial n^{(1)}}{\partial y} \right) - 2n^{(1)} T^{(0)} \left(\frac{\partial T^{(0)}}{\partial t} + v^{(0)} \frac{\partial T^{(0)}}{\partial y} \right) \quad (\text{D.12})$$

Then, combining both species continuity equations yields

$$\frac{\partial n^{(1)}}{\partial t} + v^{(0)} \frac{\partial n^{(1)}}{\partial y} = \frac{\partial^2 (nT)}{\partial y^2} - n^{(1)} \frac{\partial v^{(0)}}{\partial y} - \frac{\partial}{\partial y} \left(n^{(0)} v^{(1)} \right) \quad (\text{D.13})$$

Substituting (D.13) into (D.12) and (D.12) into (D.10), together with the relations (VI. 19, 29,

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from which we deduce

$$u^{(1)}(0) = \frac{1}{\rho_2^{(0)}(0)} \cdot \frac{\partial(\rho_1 u)^{(0)}}{\partial y} \Big|_{y=0} \quad (\text{VI.54a})$$

As well as for the first order system, the condition (VI. 54b) for $v^{(0)}(0)$ is immediately obtained from (IV. 18), and the temperature second order boundary condition (VI. 54c) is derived by expanding (IV. 27) exactly as the condition (VI. 54a) is obtained above by expanding (IV. 26).

Finally, the second order velocity term of the condition (IV. 30) is

$$\frac{E(n_1 v_1)^{(1)}(0)}{2} = -\frac{E R_1}{2} \frac{\partial}{\partial y} \left[n_1^{(1)} T^{(0)} + n_1^{(0)} T^{(1)} \right] \Big|_{y=0} \quad (\text{D.21})$$

whereas the second order component of the heat-flux vector at the surface is given by

$$q_y^{(1)}(0) = -\frac{5}{4} \frac{\partial}{\partial y} \left[(R_1 - R_2) \left(T^{(0)} \right)^2 n_1^{(1)} - R_2 T^{(1)} + 2\bar{n}^{(0)} T^{(0)} T^{(1)} \right] \Big|_{y=0} + \frac{5}{4} \left(\bar{n} T \frac{\partial T}{\partial y} \right)^{(0)} \quad (\text{D.22})$$

so that combining the last two equations gives the boundary condition (VI. 54d).

D.5 Developed form of the equations

As for the first order system in C.5., we write, as below, the explicit form of the species continuity and energy equations (VI. 53a) and (VI. 53e)

$$\begin{aligned} \frac{\partial n_1^{(1)}}{\partial t} + v^{(0)} \frac{\partial n_1^{(1)}}{\partial y} + n_1^{(0)} \frac{\partial v^{(1)}}{\partial y} - R_1 \left[T^{(0)} \frac{\partial^2 n_1^{(1)}}{\partial y^2} + 2 \frac{\partial T^{(0)}}{\partial y} \frac{\partial n_1^{(1)}}{\partial y} + 2 \frac{\partial n_1^{(0)}}{\partial y} \frac{\partial T^{(1)}}{\partial y} + n_1^{(0)} \frac{\partial^2 T^{(1)}}{\partial y^2} \right] \\ = - \left[n_1^{(1)} \frac{\partial v^{(0)}}{\partial y} + v^{(1)} \frac{\partial n_1^{(0)}}{\partial y} \right] + R_1 \left[n_1^{(1)} \frac{\partial^2 T^{(0)}}{\partial y^2} + T^{(1)} \frac{\partial^2 n_1^{(0)}}{\partial y^2} \right] \end{aligned} \quad (\text{D.23})$$

$$\begin{aligned} \frac{5}{4} \frac{\partial v^{(1)}}{\partial y} - \frac{\partial u^{(0)}}{\partial y} \frac{\partial u^{(1)}}{\partial y} - \frac{5}{4} \left[\left(T^{(0)} \right)^2 \frac{\partial^2 \bar{n}^{(1)}}{\partial y^2} + 4 T^{(0)} \frac{\partial T^{(0)}}{\partial y} \frac{\partial \bar{n}^{(1)}}{\partial y} + 4 T^{(0)} \frac{\partial \bar{n}^{(0)}}{\partial y} \frac{\partial T^{(1)}}{\partial y} \right. \\ \left. + 2 \bar{n}^{(0)} T^{(0)} \frac{\partial^2 T^{(1)}}{\partial y^2} + 2 \bar{n}^{(0)} \frac{\partial T^{(0)}}{\partial y} \frac{\partial T^{(1)}}{\partial y} \right] = -\frac{1}{2} \left(\frac{\partial u^{(0)}}{\partial y} \right)^2 - \frac{5}{4} \frac{\partial}{\partial y} \left(\bar{n} T \frac{\partial T}{\partial y} \right)^{(0)} + \frac{5}{2} \left[\bar{n}^{(1)} \left(\frac{\partial T^{(0)}}{\partial y} \right)^2 \right. \\ \left. + \bar{n}^{(1)} T^{(0)} \frac{\partial^2 T^{(0)}}{\partial y^2} + T^{(0)} T^{(1)} \frac{\partial^2 \bar{n}^{(0)}}{\partial y^2} + \bar{n}^{(0)} T^{(1)} \frac{\partial^2 T^{(0)}}{\partial y^2} + T^{(1)} \frac{\partial \bar{n}^{(0)}}{\partial y} \frac{\partial T^{(0)}}{\partial y} \right] \end{aligned} \quad (\text{D.24})$$

The linear structure of the second order system appears clearly in these equations, as well as

the fact that the coefficients of the higher order terms (put on the left-hand side) are those of the first order system (see C.5.).