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**ASYMPTOTIC SOLUTION OF THE  
BOLTZMANN-KROOK EQUATION FOR THE RAYLEIGH  
FLOW**

by

**TAKUJI KUROTAKI**

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Signature of Author \_\_\_\_\_

Department of Aeronautics and Astronautics, January 1991

Certified by \_\_\_\_\_

Professor Leon Trilling, Thesis Advisor  
Department of Aeronautics and Astronautics, M.I.T.

Accepted by \_\_\_\_\_

Professor Harold Y. Wachman, Chairman  
Department Graduate Committee

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Submitted to the Department of Aeronautics and Astronautics  
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**Abstract**

An asymptotic solution of the Boltzmann-Krook equations for the Rayleigh shear flow is constructed. The flow consists of a reacting mixture of gases (O and O<sub>2</sub> molecules) and the chemical process is assumed to occur both in the flow and on the surface which is highly catalytic. The distribution functions, corresponding equations of motion and the boundary conditions on the averaged flow parameters are expanded in powers of the square root of the Knudsen number assumed to be small. The first order system is similar to the Navier-Stokes equations with no-slip boundary conditions. The second order system represents a slip flow with coefficients which depend on the solution of the first order system.

One of ways to treat with the highly catalytic surface is also presented. The relationship among the diffusion velocity of atoms, the catalytic efficiency and the catalytic recombination rate constant on the surface are clarified and the effect of the catalytic efficiency on the heat transfer rate on the surface is discussed.

Thesis Supervisor: Leon Trilling

Title: Professor of the Department of Aeronautics and Astronautics, M.I.T.

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# Chapter 1

## Introduction

### 1.1 Introduction

Recently, with the development of Space shuttle, Aerospace planes and Aeroassisted Orbital Transfer Vehicles (AOTV) etc., research on hypersonic aerodynamics has been an important area. As long as the flow is assumed to be continuum or near continuum, the basic governing equations can be Navier-Stokes equations. Therefore, most of techniques developed for both analytical and computational treatments for the subsonic and supersonic flow can be readily extended to this area.

However, in the hypersonic aerodynamics, there appear some effects which greatly complicate classical treatments. In general, it contains effects of high temperature which is caused by a strong shock wave, hence, it is necessary to consider chemical reactions such as dissociation, recombination and, sometimes, even ionization processes. These effects especially influence the heat transfer rate on the surface of the flight vehicle. Fay & Riddell [1] and Goulard [2] discussed these problems, and showed that the catalytic efficiency of dissociated atoms on the surface is important to determine the heat transfer rate.

Another important effect in the hypersonic flow is the slip of hydrodynamic values on the surface which becomes remarkable in the near continuum flow where the gas is slightly rarefied. In the treatments of this problem, the Knudsen layer near the surface whose thickness is order of one mean free path plays an important role and

it is necessary to consider the microscopic motions of molecules. For example, Sone [3, 4] analyzed this problem by dividing the flow into two parts; the Hilbert part which represents the overall behavior of the gas and the Knudsen-layer part near the surface whose thickness is the order of one mean free path. More recently, Scott [5] and Gupta et al. [6] constructed slip boundary conditions for the multicomponent gases by extending concepts by Shidlovskiy [7] in which the distribution functions in the Knudsen layer are uniform. Another important contribution in this area was made by Trilling [8]. He constructed an asymptotic solution of the Boltzmann-Krook equation proposed by Bhatnagar, Gross and Krook [9, 10] for the Rayleigh shear flow problem for a monoatomic gas by expanding in powers of the square root of the Knudsen number.

The purpose of this thesis is to investigate the gas-surface interaction in the hypersonic flow composed of a mixture of gases by using the model similar to that used by Trilling [8]. In this study, we will consider chemical reactions both in the flow and on the surface and assume that the surface is highly catalytic. We will get an asymptotic solution of this problem with the singular perturbation method by adopting the similar approach developed by Trilling [8].

## 1.2 Definition of the problem

Before the analysis, we will define the hypotheses of the problem we study (see Figure 1-1).

We consider an infinite flat plate located at  $y = 0$  whose surface temperature is  $T_w(t)$  and which moves in the  $x$ -direction at the velocity  $u_w(t)$ . Initially the upper-half space is filled with a gas mixture composed of O and O<sub>2</sub> molecules whose densities are  $\rho_{1\infty}$  and  $\rho_{2\infty}$  respectively and temperature  $T_\infty$ . At time  $t = 0$ , the plate is impulsively set into motion. We will analyze the inner layer near the plate after a period of time long enough for the initial transient to be smoothed out.

Outside the inner layer, O and O<sub>2</sub> molecules are in equilibrium, however, in the inner layer, if the time is large, the flow is a chemically non-equilibrium flow. There-



fore, we will consider the chemical reaction process in the inner layer. And we assume that the surface is highly catalytic, i.e. a large portion of the O molecules hitting the surface recombine into  $O_2$  molecules on the surface (their fraction is represented by the catalytic efficiency  $\gamma$  defined in Chapter 4). Furthermore, we assume that the flow is continuum or near continuum. This is equivalent to assuming that the Knudsen number of the flow is small.

In this thesis, we will proceed as follows. At first, we introduce the Boltzmann-Krook equations and derive the equations of motion with the macroscopic hydrodynamic properties (Chapter 2) and construct a kinetic model suitable for this problem (Chapter 3). Next, we consider boundary conditions (Chapter 4) and determine the small expansion parameter and expand governing equations with respect to it (Chapter 5, 6). Then, we construct the first and second order system of equations of motion and boundary conditions (Chapter 7, 8). Finally, we discuss the results obtained in this study (Chapter 9) and get some conclusions (chapter 10).

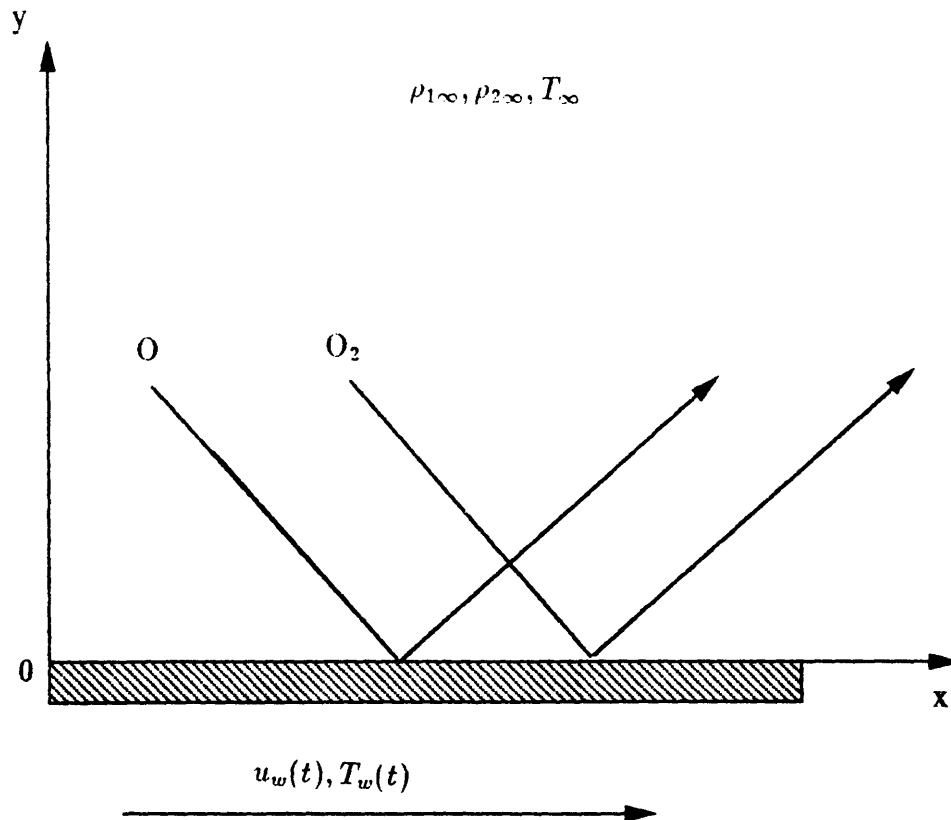


Figure 1-1: Definition of the problem.

# Chapter 2

## Equations of Motion

In the first two sections of this chapter, we introduce a concept of distribution function and the Boltzmann equation to describe the microscopic motion of a mixture of gases, and define the hydrodynamic variables which are needed in the analysis throughout this thesis. In the last section of this chapter, we derive the macroscopic equations of motion by integrating moments of the Boltzmann equation.

### 2.1 Boltzmann equation

To consider the behavior of a reacting mixture of gases at the microscopic level, we introduce distribution functions at time  $t$  for each components of the mixture;

$$f_s(\vec{x}_s, \vec{\xi}_s, t).$$

In this analysis,  $s = 1$  for O molecules and  $s = 2$  for O<sub>2</sub> molecules. The parameters  $\vec{x}_s$  and  $\vec{\xi}_s$  represent position in the physical space and in the velocity space respectively. This distribution function  $f_s$  is defined in the six-dimensional phase space  $(\vec{x}_s, \vec{\xi}_s)$ , and its value changes due to collisions both with molecules of the same kind and with molecules of the other kind.

If we ignore the excitation of internal degrees of freedom (i.e. rotational, vibrational and electronic etc.), the evolution of each distribution functions  $f_s$  in a phase

space can be described by the following Boltzmann equation,

$$\frac{Df_s}{Dt} = \left[ \frac{\partial f_s}{\partial t} \right]_{coll} . \quad (2.1)$$

The left-hand side of ( 2.1) is (see, e.g. Kogan [11] or Vincenti & Kruger [12]),

$$\frac{Df_s}{Dt} = \frac{\partial f_s}{\partial t} + \vec{\xi}_s \cdot \frac{\partial f_s}{\partial \vec{x}_s} + \frac{\vec{X}_s}{m_s} \cdot \frac{\partial f_s}{\partial \vec{\xi}_s} \quad (2.2)$$

where  $\vec{X}_s$  is the external force acting on the  $s$ -th kind and  $m_s$  is the mass of a molecule of the  $s$ -th kind. The right-hand side of ( 2.1) is the rate of increase of the species density in the  $\vec{\xi}_s$ -class resulting from collisions; the so-called collision integral. Since molecules of  $s$ -th kind interact with both the same kind and the other kind of molecules, this term is a function of both  $f_1$  and  $f_2$ . Therefore, the change in the state of a mixture gas is governed by a system of two equations for the distribution functions  $f_1, f_2$ , each of which contains the distribution function for the other kind of species.

The approximate formulation of  $\left[ \frac{\partial f_s}{\partial t} \right]_{coll}$  which is necessary for the later analysis will be considered in Chapter 3.

## 2.2 Definitions of hydrodynamic variables

In terms of the distribution function  $f_s$ , we can get a variety of familiar hydrodynamic variables. These can be basically obtained by multiplying the distribution function by various quantities and integrating over the whole velocity space. It is convenient to define them at this stage before we proceed further. They are as follows:

- The mass density of the  $s$ -th component;  $\rho_s$

$$\rho_s = \int_{\mathbb{R}^3} f_s d\vec{\xi}_s. \quad (2.3)$$

- The mass density of the mixture

$$\rho = \sum_s \rho_s. \quad (2.4)$$

- The number density of the  $s$ -th component;  $n_s$

$$n_s = \frac{\rho_s}{m_s}. \quad (2.5)$$

- The number density of the mixture;  $n$

$$n = \sum_s n_s. \quad (2.6)$$

- The mean velocity of the  $s$ -th component;  $\vec{v}_s$

$$\rho_s \vec{v}_s = \int_{\mathbb{R}^3} \vec{\xi}_s f_s d\vec{\xi}_s. \quad (2.7)$$

- The mean velocity of the mixture;  $\vec{v}$

$$\rho \vec{v} = \sum_s \rho_s \vec{v}_s. \quad (2.8)$$

- The diffusion velocity of the  $s$ -th component;  $\vec{V}_s$

$$\vec{V}_s = \vec{v}_s - \vec{v}. \quad (2.9)$$

- The peculiar velocity of the  $s$ -th component;  $\vec{c}_s$

$$\vec{c}_s = \vec{\xi}_s - \vec{v}. \quad (2.10)$$

- The stress tensor of the  $s$ -th component;  $(P_s)_{ij}$

$$(P_s)_{ij} = \int_{\mathbb{R}^3} (c_s)_i (c_s)_j f_s d\vec{\xi}_s. \quad (2.11)$$

- The stress tensor of the mixture;  $P_{ij}$

$$P_{ij} = \sum_s (P_s)_{ij}. \quad (2.12)$$

- The temperature of the  $s$ -th component;  $T_s$

$$\frac{3}{2}n_s k T_s = \frac{1}{2} \int_{\mathbb{R}^3} |\vec{c}_s|^2 f_s d\vec{\xi}_s \quad (2.13)$$

where  $k$  is the Boltzmann constant.

- The temperature of the mixture;  $T$

$$\frac{3}{2}n k T = \sum_s \frac{3}{2}n_s k T_s. \quad (2.14)$$

- The pressure of the mixture;  $p$

$$p = \frac{1}{3}(P_{xx} + P_{yy} + P_{zz}). \quad (2.15)$$

- The heat flux of the  $s$ -th component;  $\vec{q}_s$

$$\vec{q}_s = \frac{1}{2} \int_{\mathbb{R}^3} \vec{c}_s |\vec{c}_s|^2 f_s d\vec{\xi}_s. \quad (2.16)$$

- The heat flux of the mixture;  $\vec{q}$

$$\vec{q} = \sum_s \vec{q}_s. \quad (2.17)$$

The pressure, number density and temperature are connected to each other by the familiar equation of state for a perfect gas,

$$p = n k T. \quad (2.18)$$

In the analysis which treats with a mixture of gases, it is sometimes convenient to introduce another kind of species temperature  $T_{,s}$ . This is defined with respect to the mean velocity of species  $s$ , i.e.  $\vec{v}_s$ , instead of the mean velocity of the mixture  $\vec{v}$  (see Burgers [13, p.228]);

$$\frac{3}{2}n_s k T_{,s} = \frac{1}{2} \int_{\mathbb{R}^3} |\vec{\xi} - \vec{v}_s|^2 f_s d\vec{\xi}_s. \quad (2.19)$$

From ( 2.13) and ( 2.19), we can show the following relations between  $T_s$  and  $T_{,s}$  (see Appendix A.1),

$$T_1 = T_{11} + \frac{m_1 \rho_2^2}{3k\rho^2} |\vec{v}_2 - \vec{v}_1|^2 \quad (2.20)$$

$$T_2 = T_{22} + \frac{m_2 \rho_1^2}{3k\rho^2} |\vec{v}_2 - \vec{v}_1|^2. \quad (2.21)$$

## 2.3 Macroscopic equations of motion

The Boltzmann equations discussed in Section 2.1 describe the detailed motion of molecules of each species in the position-velocity phase space  $(\vec{x}_s, \vec{\xi}_s)$ . We can derive ordinary equations of motion in a fluid flow which involve the hydrodynamic quantities defined in Section 2.2 from these microscopic equations. These macroscopic equations of motion can be obtained by multiplying the Boltzmann equation by any function of molecular velocity  $\vec{\xi}_s$  and integrating over the whole velocity space. If this function is taken to be a collision invariant, i.e. the mass, momentum or energy per molecule  $(m_s, m_s \vec{\xi}_s, m_s |\vec{\xi}_s|^2/2)$ , we can get the macroscopic equations of motion of a continuous mixture of gases.

Integrating equation ( 2.1) with respect to  $\vec{\xi}_s$ , we can get,

$$\int_{\mathbb{R}^3} \frac{Df_s}{Dt} d\vec{\xi}_s = \int_{\mathbb{R}^3} \left[ \frac{\partial f_s}{\partial t} \right]_{coll} d\vec{\xi}_s. \quad (2.22)$$

Since we assume a reacting gas mixture in which  $O_2$  molecules may dissociate into  $O$  molecules, the right-hand side of ( 2.22) does not vanish. Then, we can write for

each species,

$$\int_{\mathbb{R}^3} \frac{Df_1}{Dt} d\vec{\xi}_1 = \dot{w} \quad (2.23)$$

$$\int_{\mathbb{R}^3} \frac{Df_2}{Dt} d\vec{\xi}_2 = -\dot{w} \quad (2.24)$$

where  $\dot{w}$  is the rate of increase of the mass of species 1 in a unit volume and a unit time called a source term,

$$\dot{w} = \int_{\mathbb{R}^3} \left[ \frac{\partial f_1}{\partial t} \right]_{coll} d\vec{\xi}_1. \quad (2.25)$$

However, the total mass of both species should be conserved,

$$\sum_s \int_{\mathbb{R}^3} \frac{Df_s}{Dt} d\vec{\xi}_s = 0. \quad (2.26)$$

If we multiply ( 2.1) by  $\vec{\xi}_s = (\xi_s, \eta_s, \zeta_s)$  and integrate with respect to  $\vec{\xi}_s$ , the right-hand side of equations also do not vanish because the  $s$ -th kind of molecules may exchange momentum with the other kind of molecules. However, the total momentum should be conserved. Then we can write,

$$\sum_s \int_{\mathbb{R}^3} \vec{\xi}_s \frac{Df_s}{Dt} d\vec{\xi}_s = 0. \quad (2.27)$$

By multiplying ( 2.1) by  $\frac{1}{2}|\vec{\xi}_s|^2$ , integrating with respect to  $\vec{\xi}_s$  and summing up over  $s$ , we obtain an expression for the total energy,

$$\sum_s \int_{\mathbb{R}^3} \frac{1}{2}|\vec{\xi}_s|^2 \frac{Df_s}{Dt} d\vec{\xi}_s = \sum_s \int_{\mathbb{R}^3} \frac{1}{2}|\vec{\xi}_s|^2 \left[ \frac{\partial f_s}{\partial t} \right]_{coll} d\vec{\xi}_s. \quad (2.28)$$

If we assume a reacting gas mixture, the right-hand side of ( 2.28) does not vanish because some portion of the total kinetic energy of a mixture may transfer into the heat of formation of some species, or vice versa. If we introduce the dissociation energy per  $O_2$  molecule,  $E$  (the energy obtained from the kinetic energy of a mixture of gases when  $O_2$  molecule dissociates into two  $O$  molecules;  $E > 0$ ), ( 2.28) can be written,

$$\sum_s \int_{\mathbb{R}^3} \frac{1}{2}|\vec{\xi}_s|^2 \frac{Df_s}{Dt} d\vec{\xi}_s = -\frac{E}{m_2} \dot{w}. \quad (2.29)$$

Equations ( 2.23), ( 2.24), ( 2.27) and ( 2.29) constitute a system of equations for the mass, the total momentum and the total energy conservation. By evaluating the left-hand side of each conservation equation with expressions of hydrodynamic quantities introduced in Section 2.2, we can get the macroscopic equations of motion of a continuous gas mixture,

- Conservation of mass of species 1

$$\frac{\partial \rho_1}{\partial t} + \frac{\partial(\rho_1 v_1)}{\partial y} = \dot{w} \quad (2.30)$$

- Conservation of mass of species 2

$$\frac{\partial \rho_2}{\partial t} + \frac{\partial(\rho_2 v_2)}{\partial y} = -\dot{w} \quad (2.31)$$

- Conservation of the total momentum along  $x$ -axis

$$\rho \left( \frac{\partial u}{\partial t} + v \frac{\partial u}{\partial y} \right) + \frac{\partial P_{xy}}{\partial y} = 0 \quad (2.32)$$

- Conservation of the total momentum along  $y$ -axis

$$\rho \left( \frac{\partial v}{\partial t} + v \frac{\partial v}{\partial y} \right) + \frac{\partial P_{yy}}{\partial y} = 0 \quad (2.33)$$

- Conservation of the total energy (see Appendix A.2 for more detail)

$$\begin{aligned} & \frac{3}{2}nk \left( \frac{\partial T}{\partial t} + v \frac{\partial T}{\partial y} \right) + \frac{\partial q_y}{\partial y} + P_{xy} \frac{\partial u}{\partial y} + P_{yy} \frac{\partial v}{\partial y} + \frac{\dot{w}}{m_2} \left( E + \frac{3}{2}kT \right) \\ & = \frac{3}{2}kT \frac{\partial}{\partial y} \left\{ \sum_s n_s V_s \right\} \end{aligned} \quad (2.34)$$

where notations  $\vec{x} = (x, y, z)$ ,  $\vec{\xi}_s = (\xi_s, \eta_s, \zeta_s)$ ,  $\vec{v} = (u, v, w)$  and  $\vec{q} = (q_x, q_y, q_z)$  are used. In this derivation, we assume that there is no external force  $\vec{X}_s$  defined in ( 2.2) and there is spatial variation along the  $y$ -axis only according to the basic assumption of our problem described in Chapter 1.



Equation ( 2.30)  $\sim$  ( 2.34) constitute a system of five equations for five main unknowns :  $\rho_1, \rho_2, u, v, T$  and five additional unknowns:  $v_1, v_2, P_{xy}, P_{yy}, q_y$ . This system is not a closed set of equations. In order to get a closed system of equations, these additional unknowns should be related with main unknowns by using the definitions of hydrodynamic quantities in Section 2.2.

Another important term we should evaluate is the source term  $\dot{w}$  in ( 2.30) , ( 2.31) and ( 2.34). This term depends on how the chemical reaction occurs in a mixture of gases and can be obtained by considering a collision integral term in the Boltzmann equation ( 2.1). This consideration and modeling of it will be discussed in Chapter 3.

# Chapter 3

## Kinetic Model

The main purpose of this chapter is to construct a kinetic model which is consistent with our problem. In the first two sections, we consider the case without chemical reactions as a reference and estimate the order of characteristic times for collisions introduced there. We follow the concepts by Perot [14] basically in these sections. In the next two sections, we extend this model to the case with chemical reactions which is consistent with our problem and model characteristic times for collisions between the different species. In the last section, we specify unknown parameters introduced into the kinetic model by the reasonable physical assumptions and obtain the final forms which are suitable for this analysis.

### 3.1 Kinetic model of a mixture of gases without chemical reactions

Perot [14] constructed a kinetic model for a mixture of gases under the assumption that no chemical reactions occur in it. This assumption can be interpreted as corresponding to the case in which the flow is completely frozen and as one of the limiting cases for the chemically reacting flow. Therefore, it is worth while considering a kinetic model of a mixture of gases without chemical reactions before constructing the one of a chemically reacting mixture of gases in our problem.

The collision integral for species  $s$  in ( 2.1) in Chapter 2 can be expressed in the following form,

$$\left[ \frac{\partial f_s}{\partial t} \right]_{coll} = \sum_{r=1,2} Q_{sr}(f_s, f_r) \quad (s = 1, 2). \quad (3.1)$$

$Q_{sr}(f_s, f_r)$  is the collision integral operator taking into account collisions between molecules of the  $s$ th kind and the  $r$ th kind. This term is expressed with notations used in, e.g., Kogan [11],

$$Q_{sr}(f_s, f_r) = \int_{\mathbb{R}^5} (f'_s f'_r - f_s f_r) g_{sr} b db d\varepsilon d\vec{\xi}_r \quad (3.2)$$

where  $g_{sr}$  is the relative velocity,  $b$  is the impact parameter and  $\varepsilon$  is the collision angle. The primes denote values after the collision.

In general, it is very difficult to treat with this detailed form of  $Q_{sr}$ , and several simpler models of this collision term have been proposed in which mathematical treatments are easier and main qualitative properties are still retained. One of the most widely used models is the Bhatnagar-Gross-Krook collision model ([9, 10]). This model is especially suitable for the analysis in which one needs to expand the governing equations into power series such as in Trilling [8].

Under the assumption that there are no chemical reactions, the Boltzmann equations with the Bhatnagar-Gross-Krook collision model (so-called, the Boltzmann-Krook equation) can be expressed in the following form,

$$\frac{\partial f_s}{\partial t} + \eta_s \frac{\partial f_s}{\partial y} = -f_s \sum_{r=1,2} \frac{1}{\tau_{sr}} + \Psi_{sr} \sum_{r=1,2} \frac{1}{\tau_{sr}} \quad (s = 1, 2). \quad (3.3)$$

In ( 3.3),  $\tau_{sr}$  is a characteristic time of molecules of species  $s$  for collisions with molecules of species  $r$ . The corresponding collision frequency  $\nu_{sr}$  is defined as

$$\nu_{sr} = \frac{1}{\tau_{sr}}. \quad (3.4)$$

$\tau_{sr}$  and  $\nu_{sr}$  may depend on densities of each species and temperature but not on molecular velocity. Then total average collision frequency  $\nu_s$  and the total characteristic

time  $\tau_s$  for species  $s$  are,

$$\nu_s = \sum_{r=1,2} \nu_{sr} = \sum_{r=1,2} \frac{1}{\tau_{sr}} = \frac{1}{\tau_s}. \quad (3.5)$$

The first term of the right-hand side of ( 3.3),  $-f_s \sum_{r=1,2} \frac{1}{\tau_{sr}}$ , represents the number of molecules of species  $s$  which are thrown out of the  $\vec{\xi}_s$ -class per a unit time and volume as a result of collisions, while the second term,  $+\Psi_{sr} \sum_{r=1,2} \frac{1}{\tau_{sr}}$ , represents the number of molecules of species  $s$  which are restored to the  $\vec{\xi}_s$ -class. In the Bhatnagar-Gross-Krook collision model, the distribution function  $\Psi_{sr}$  of the molecules restored to the  $\vec{\xi}_s$ -class has the form of the Maxwell distribution function. For collisions between the same species, it is reasonable to assume that molecules of species  $s$  are re-emitted with the Maxwell distribution function centered about the species velocity  $\vec{v}_s$  and species temperature  $T_{ss}$  defined in ( 2.7) and ( 2.19) respectively, then we can write for  $\Psi_{ss}$ ,

$$\Psi_{ss} = \rho_s \left( \frac{m_s}{2\pi k T_{ss}} \right)^{3/2} \exp \left\{ -\frac{m_s}{2k T_{ss}} |\vec{\xi}_s - \vec{v}_s|^2 \right\}. \quad (3.6)$$

On the other hand, for collisions between different species, the local velocity and temperature corresponding to  $\vec{v}_s$  and  $T_{ss}$  in the case of above are not known a priori. Then, we introduce the auxiliary velocity  $\vec{v}_{sr}$  and temperature  $T_{sr}$ , and define the auxiliary distribution function  $\Psi_{sr}$  as

$$\Psi_{sr} = \rho_s \left( \frac{m_s}{2\pi k T_{sr}} \right)^{3/2} \exp \left\{ -\frac{m_s}{2k T_{sr}} |\vec{\xi}_s - \vec{v}_{sr}|^2 \right\}. \quad (3.7)$$

These parameters introduced in this section, i.e.  $\tau_{sr}$ ,  $v_{sr}$  and  $T_{sr}$ , should be determined from the physical conditions.

## 3.2 Order estimation of characteristic times for collisions

Four characteristic times  $\tau_{sr}$  introduced in the previous section are, in general, functions of number densities of each species, temperature and time. In this analysis,

for simplicity, we assume that each  $\tau_{s,r}$  is independent of temperature and time. (It may still depend on number densities.)

The order of magnitude of  $\tau_{s,r}$  should depend on the problems we choose, and rough order estimation of them can be made by considering the motion of molecules near the wall in detail. In this analysis, we should remember that we try to treat with the flow very near the wall and that we assume that a large portion of O molecules hitting the wall recombine at the wall as described in Chapter 1.

First of all, we look at a very thin layer very close to the wall whose thickness is about one mean free path of either O or O<sub>2</sub> molecules. In this layer, most O molecules have a velocity directed towards the wall because a large portion of O molecules hitting the wall recombine and become O<sub>2</sub> molecules. On the other hand, these O<sub>2</sub> molecules produced at the wall have a velocity directed away from the wall in this layer (see Figure 3-1).

Next, we consider a thicker layer than the previous one whose thickness is of the order of a few mean free paths. In this layer, each molecule may experience a few collisions. Because of the influence of catalytic recombination on the wall described in the previous paragraph, O<sub>2</sub> molecules leave the wall with a positive velocity in the  $y$ -direction on the average, and, on the other hand, O molecules reach the wall with a negative velocity in the  $y$ -direction. Therefore, a collision between different species is much more probable than a collision between the same species.

Typical motions of molecules in this layer are shown in Figure 3-2. For the average O<sub>2</sub> molecules, it is most probable that they collide with incoming O molecules. They may also collide with incoming O<sub>2</sub> molecules, but most of these incoming O<sub>2</sub> molecules have experienced O-O<sub>2</sub> collisions at previous times. We should also note that there may be incoming O<sub>2</sub> molecules in the thin layer whose thickness is about one mean free path as seen in Figure 3-1. These molecules can be interpreted as the ones which are reflected as a result of O-O<sub>2</sub> collisions in this thicker layer.

From these discussions, we can assume that the chance of collisions between different species is much larger than the chance of collisions between the same species. This physical consideration is consistent with the assumption that the characteristic

time for collisions between different species is much smaller than the one between the same species,

$$\tau_{12}, \tau_{21} \ll \tau_{11}, \tau_{22}. \quad (3.8)$$

This basic relation comes from the assumption that a large portion of molecules hitting the wall recombine at the wall, in other words, the assumption of a surface which is highly catalytic. Therefore, we should note that ( 3.8) cannot be satisfied if we treat with a problem in which only a small portion of hitting O molecules recombine at the wall. In this case, the order of magnitude of  $\tau_{11}$  may be the same as the order of magnitude of  $\tau_{12}$  or  $\tau_{21}$ .

### 3.3 Kinetic model of a mixture of gases with chemical reactions

In the real situation, in a mixture of gases whose components are O and O<sub>2</sub>, it is reasonable to expect that chemical reactions occur in it. Therefore, in order to construct a suitable kinetic model for this mixture, it is necessary to include the effects of chemical reactions in the kinetic model discussed in the previous two sections.

In this mixture of gases, it is probable that the following chemical reactions occur,



In each equation, the forward reactions are the dissociation reactions and the backward reactions are the recombination ones. The second terms of the right- and left-hand side in each equation are catalytic bodies. A recombination reaction requires a three-body collision between two O molecules and some third body; O or O<sub>2</sub>. The reason for it is that if there is no such third body, the recombination energy must transfer into a vibrational mode of the newly created O<sub>2</sub> molecule and may cause the immediate dissociation after one-half period of vibration.

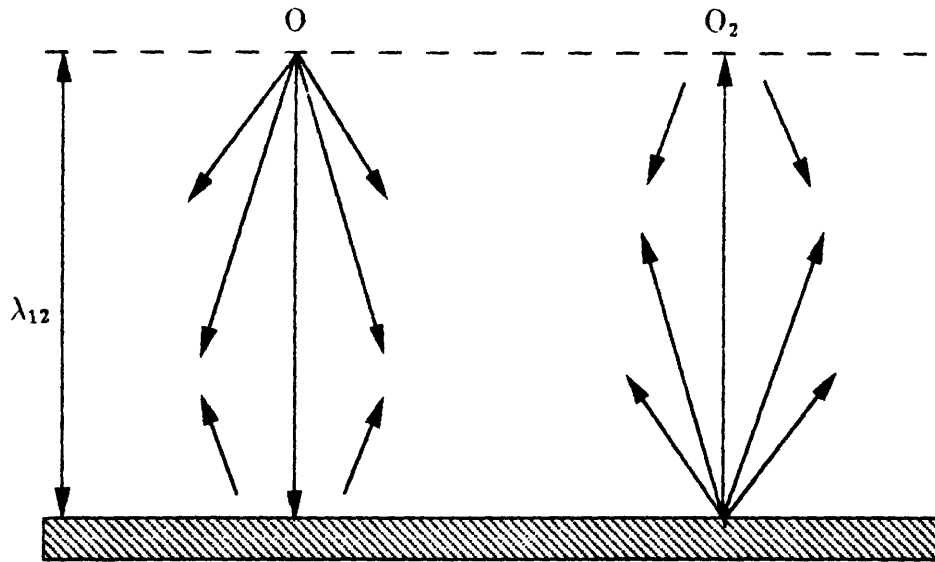


Figure 3-1: Typical motions of O and O<sub>2</sub> molecules in a thin layer whose thickness is about one mean free path.

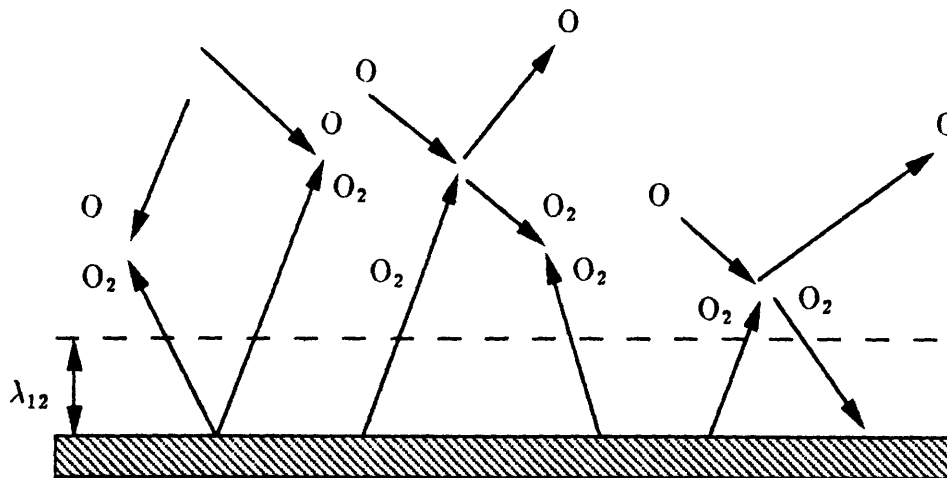
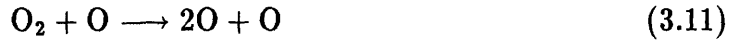


Figure 3-2: Typical collisions of O and O<sub>2</sub> molecules in a layer whose thickness is of order of a few mean free paths.

In order to judge which reactions in ( 3.9) and ( 3.10) are more probable near the wall, the physical consideration for characteristic times discussed in Section 3.2 plays an important role. If we compare the two dissociation reactions in ( 3.9) and ( 3.10), the dissociation reactions by O-O<sub>2</sub> collisions are much more probable than those by O<sub>2</sub>-O<sub>2</sub> collisions because the number of O-O<sub>2</sub> collisions is much larger than the number of O<sub>2</sub>-O<sub>2</sub> collisions in the same volume and during the same time from the result in Section 3.2. Furthermore, in this study, for simplicity, we neglect the existence of collisions which cause the recombination reactions because they require three-body collisions and they are not likely to occur very near the wall. Therefore, we can conclude that it is enough to consider the following dissociation reaction for the treatment of the flow near the wall,



A dissociation reaction occurs when the energy of two molecules involved in a collision is greater than a threshold value, i.e. the activation energy. We assume that this minimum energy required for dissociation is equal to the dissociation energy  $E$  per O<sub>2</sub> molecule. Furthermore, we make the following assumptions for both species after O-O<sub>2</sub> collisions.

- For O-O<sub>2</sub> collisions without dissociation, each O and O<sub>2</sub> molecule is replaced in the  $\vec{\xi}_1$ -class and the  $\vec{\xi}_2$ -class with a local Maxwell distribution function  $\Psi_{12}^*$  and  $\Psi_{21}^*$  respectively.
- For O-O<sub>2</sub> collisions with dissociation, O molecules newly created by dissociation are replaced in the  $\vec{\xi}_1$ -class with a local Maxwell distribution function  $\Psi_{R2}^*$ .
- For O-O<sub>2</sub> collisions with dissociation, O molecules which were the catalytic bodies are replaced in the  $\vec{\xi}_1$ -class with a local Maxwell distribution function  $\Psi_{R1}^*$ .



$\Psi_{12}^*$ ,  $\Psi_{21}^*$ ,  $\Psi_{R1}^*$  and  $\Psi_{R2}^*$  are defined as,

$$\Psi_{12}^* = \rho_{12} \left( \frac{m_1}{2\pi kT_{12}} \right)^{3/2} \exp \left\{ -\frac{m_1}{2kT_{12}} |\vec{\xi}_1 - \vec{v}_{12}|^2 \right\} \quad (3.12)$$

$$\Psi_{21}^* = \rho_{21} \left( \frac{m_2}{2\pi kT_{21}} \right)^{3/2} \exp \left\{ -\frac{m_2}{2kT_{21}} |\vec{\xi}_2 - \vec{v}_{21}|^2 \right\} \quad (3.13)$$

$$\Psi_{R1}^* = \rho_{R1} \left( \frac{m_1}{2\pi kT_{R1}} \right)^{3/2} \exp \left\{ -\frac{m_1}{2kT_{R1}} |\vec{\xi}_1 - \vec{v}_{R1}|^2 \right\} \quad (3.14)$$

$$\Psi_{R2}^* = \rho_{R2} \left( \frac{m_1}{2\pi kT_{R2}} \right)^{3/2} \exp \left\{ -\frac{m_1}{2kT_{R2}} |\vec{\xi}_1 - \vec{v}_{R2}|^2 \right\}. \quad (3.15)$$

Unknown parameters introduced in these definitions should be determined later. The assumptions mentioned above are extensions of the concepts by Morse [15]. In ( 3.12) and ( 3.13), only expressions for densities  $\rho_{12}$  and  $\rho_{21}$  are different from ( 3.7) which is for a mixture of gases without chemical reactions because the transformation of species is expected for a mixture with chemical reactions.

Under the assumptions discussed above, we can extend the Boltzmann-Krook equations ( 3.3) to the case with chemical reactions. Before doing it, we should note that O molecules are thrown out of the  $\vec{\xi}_1$ -class once they experience collisions, whether these collisions are reactive or non-reactive, and this also applies for O<sub>2</sub> molecules. Then, the extended Boltzmann-Krook equation for O molecules is,

$$\frac{\partial f_1}{\partial t} + \eta_1 \frac{\partial f_1}{\partial y} = -\frac{f_1}{\tau_{11}} + \frac{\Psi_{11}}{\tau_{11}} - \frac{f_1}{\tau_{12}} + \frac{\Psi_{12}^*}{\tau_{12}} + \frac{\Psi_{R1}^*}{\tau_{12}} + \frac{\Psi_{R2}^*}{\tau_{21}}. \quad (3.16)$$

The first two terms of the right-hand side of ( 3.16) are ordinary expressions for collisions between the same species. The third term  $-f_1/\tau_{12}$  represents the mass of O molecules thrown out of the  $\vec{\xi}_1$ -class by O-O<sub>2</sub> collisions per unit volume and unit time. The fourth term  $+\Psi_{12}^*/\tau_{12}$  represents the mass of O molecules which are replaced in the  $\vec{\xi}_1$ -class by O-O<sub>2</sub> collisions without dissociation per unit volume and unit time. The fifth and sixth terms represent the mass of O molecules which are replaced in the  $\vec{\xi}_1$ -class by O-O<sub>2</sub> collisions with dissociation per unit volume and unit time. The fifth term  $+\Psi_{R1}^*/\tau_{12}$  is the expression for O molecules which were catalytic bodies

and were originally O molecules before collisions, while the sixth term  $+\Psi_{R2}^*/\tau_{21}$  is the expression for O molecules newly created by dissociation, which were originally O<sub>2</sub> molecules.

In the same way, the Boltzmann-Krook equation for O<sub>2</sub> molecules is,

$$\frac{\partial f_2}{\partial t} + \eta_2 \frac{\partial f_2}{\partial y} = -\frac{f_2}{\tau_{22}} + \frac{\Psi_{22}}{\tau_{22}} - \frac{f_2}{\tau_{21}} + \frac{\Psi_{21}^*}{\tau_{21}}. \quad (3.17)$$

In ( 3.17), the last term of the right-hand side  $+\Psi_{21}^*/\tau_{21}$  represents the mass of O<sub>2</sub> molecules which are replaced in the  $\vec{\xi}_2$ -class by O-O<sub>2</sub> collisions without dissociation per unit volume and unit time.

The relations among unknown parameters  $\rho_{12}, \rho_{21}, \rho_{R1}$  and  $\rho_{R2}$  introduced in ( 3.12) ~ ( 3.15) can be obtained by integrating ( 3.16) and ( 3.17) over the whole velocity space and considering the balance of mass of each species. Integrating ( 3.16) and ( 3.17) over the whole space  $\vec{\xi}_1$  and  $\vec{\xi}_2$  respectively with the use of the definitions of ( 3.12) ~ ( 3.15), we get

$$\dot{w} = -\frac{\rho_1}{\tau_{12}} + \frac{\rho_{12}}{\tau_{12}} + \frac{\rho_{R1}}{\tau_{12}} + \frac{\rho_{R2}}{\tau_{21}} \quad (3.18)$$

$$-\dot{w} = -\frac{\rho_2}{\tau_{21}} + \frac{\rho_{21}}{\tau_{21}} \quad (3.19)$$

where we used the expression for a source term  $\dot{w}$  defined in ( 2.23) and ( 2.24). The first term of the right-hand side of ( 3.18)  $-\rho_1/\tau_{12}$  represents the mass of O molecules which experienced O-O<sub>2</sub> collisions in a unit volume and in a unit time. These collisions might be either reactive collisions or non-reactive collisions. If they were reactive collisions, O molecules involved in them were catalytic bodies and should become the portion of the term  $+\rho_{R1}/\tau_{12}$  after collisions. If they were non-catalytic collisions, they should become the portion of the term  $+\rho_{12}/\tau_{12}$  after collisions. Therefore, if we introduce a new parameter P, which is the fraction of collisions involving energy greater than the activation energy (i.e. dissociation energy) that is required to cause

dissociation, we can write the following expression

$$\frac{\rho_{12}}{\tau_{12}} = (1 - P) \frac{\rho_1}{\tau_{12}} \quad (3.20)$$

$$\frac{\rho_{R1}}{\tau_{12}} = P \frac{\rho_1}{\tau_{12}} \quad (3.21)$$

In the same way, for the O<sub>2</sub> molecules,

$$\frac{\rho_{21}}{\tau_{21}} = (1 - P) \frac{\rho_2}{\tau_{21}} \quad (3.22)$$

$$\frac{\rho_{R2}}{\tau_{21}} = P \frac{\rho_2}{\tau_{21}} \quad (3.23)$$

These expressions ( 3.20) ~ ( 3.23) satisfy the total mass conservation because the summation of ( 3.18) and ( 3.19) vanishes in both right- and left-hand side if ( 3.20) ~ ( 3.23) are substituted into ( 3.18) and ( 3.19).

Then, we can rewrite ( 3.16) and ( 3.17) with the newly defined auxiliary distribution functions,

$$\frac{\partial f_1}{\partial t} + \eta_1 \frac{\partial f_1}{\partial y} = \frac{\Psi_{11} - f_1}{\tau_{11}} + \frac{\Psi_{12} - f_1}{\tau_{12}} - P \frac{\Psi_{12}}{\tau_{12}} + P \frac{\Psi_{R1}}{\tau_{12}} + \frac{\rho_2}{\rho_1} P \frac{\Psi_{R2}}{\tau_{21}} \quad (3.24)$$

$$\frac{\partial f_2}{\partial t} + \eta_2 \frac{\partial f_2}{\partial y} = \frac{\Psi_{21} - f_2}{\tau_{21}} + \frac{\Psi_{22} - f_2}{\tau_{22}} - P \frac{\Psi_{21}}{\tau_{21}} \quad (3.25)$$

where

$$\Psi_{12} = \rho_1 \left( \frac{m_1}{2\pi kT_{12}} \right)^{3/2} \exp \left\{ -\frac{m_1}{2kT_{12}} |\vec{\xi}_1 - \vec{v}_{12}|^2 \right\} \quad (3.26)$$

$$\Psi_{21} = \rho_2 \left( \frac{m_2}{2\pi kT_{21}} \right)^{3/2} \exp \left\{ -\frac{m_2}{2kT_{21}} |\vec{\xi}_2 - \vec{v}_{21}|^2 \right\} \quad (3.27)$$

$$\Psi_{R1} = \rho_1 \left( \frac{m_1}{2\pi kT_{R1}} \right)^{3/2} \exp \left\{ -\frac{m_1}{2kT_{R1}} |\vec{\xi}_1 - \vec{v}_{R1}|^2 \right\} \quad (3.28)$$

$$\Psi_{R2} = \rho_1 \left( \frac{m_1}{2\pi kT_{R2}} \right)^{3/2} \exp \left\{ -\frac{m_1}{2kT_{R2}} |\vec{\xi}_1 - \vec{v}_{R2}|^2 \right\}. \quad (3.29)$$

( 3.24) and ( 3.25) are the Boltzmann-Krook equations extended to a mixture of gases with chemical reactions which are consistent with our problem. There still

be unknown parameters  $T_{12}, v_{12}$ , etc. and they will be determined in the following sections in this chapter.

### 3.4 Modeling of characteristic times $\tau_{12}$ and $\tau_{21}$

In Section 3.2, we assumed that each characteristic time  $\tau_{sr}$  is independent of temperature and time. However, they may still be functions of number densities of each species. (3.8) suggests that, in the flow very near the wall, the dominant collisions are O-O<sub>2</sub> and they play dominant role in determining the main flow characteristics. Therefore, before we proceed to determine the values of the unknown parameters in (3.26) ~ (3.29), it is necessary to consider the characteristic times  $\tau_{12}$  and  $\tau_{21}$  in more detail.

From the definition in Section 3.1,  $\tau_{sr}$  is a characteristic time for molecules of species  $s$  collisions with molecules of species  $r$ . Morse [15] and Burgers [13] modeled  $\tau_{12}$  and  $\tau_{21}$  as

$$\tau_{12} = \frac{\tau^*}{n_2}, \quad \tau_{21} = \frac{\tau^*}{n_1} \quad (3.30)$$

where  $\tau^*$  is a formal relaxation time. This model can evaluate variations of each characteristic time with respect to number densities suitably. However, Morse [15] reports that the Boltzmann-Krook equation with this model does not necessarily satisfy the H-theorem in general for a non-reacting flow.

On the other hand, Perot[14] modeled  $\tau_{12}$  and  $\tau_{21}$  in simpler forms,

$$\tau_{12} = \tau_{21}. \quad (3.31)$$

It can be interpreted that, in this model,  $\tau_{12}$  or  $\tau_{21}$  is a kind of an average value of  $\tau_{12}$  and  $\tau_{21}$  in Morse's model. When  $n_1 = n_2$ , the models are exactly the same, but when  $n_1$  and  $n_2$  are different, Perot's model cannot evaluate the difference between  $\tau_{12}$  and  $\tau_{21}$  correctly. In this sense, it seems that Perot's model is a rougher approximation compared with Morse's model. However, for a non-reacting flow, the H-theorem can be proved for Perot's model [14]. Therefore, we have enough reason to use Perot's

model for the Boltzmann-Krook equations ( 3.24) and ( 3.25).

However, for the terms related with chemical reactions in them, i.e. terms containing  $P$ , we should treat with the effect of number densities in more detail because the number of reactive collisions per unit volume and unit time should be proportional to the product of number densities.

Therefore, in our problem, it seems to be most reasonable that we adopt Perot's model for terms not containing  $P$  and Morse's model for terms containing  $P$  in ( 3.24) and ( 3.25). Once we adopt this hybrid model, the H-theorem is satisfied at least when  $P \rightarrow 0$  and we can treat with chemical reaction terms in more detail.

If we denote  $\tau_{av}$  as values for  $\tau_{12}$  and  $\tau_{21}$  in Perot's model ( $\tau_{av} = \tau_{12} = \tau_{21}$ ), the relation between  $\tau_{av}$  and  $\tau^*$  in Morse's model can be obtained by interpreting a collision frequency  $1/\tau_{av}$  in Perot's model as an average value of collision frequencies  $1/\tau_{12}$  and  $1/\tau_{21}$  in Morse's model,

$$\frac{1}{\tau_{av}} = \frac{1}{2} \left( \frac{1}{\tau_{12}} + \frac{1}{\tau_{21}} \right) = \frac{n_1 + n_2}{2} \frac{1}{\tau^*} = \frac{n}{2} \frac{1}{\tau^*}. \quad (3.32)$$

Then, applying Perot's model for terms not containing  $P$  and Morse's model for terms containing  $P$  ( 3.24) and ( 3.25), we get the forms

$$\frac{\partial f_1}{\partial t} + \eta_1 \frac{\partial f_1}{\partial y} = \frac{\Psi_{11} - f_1}{\tau_{11}} + \frac{\Psi_{12} - f_1}{\tau_{av}} - 2 \frac{n_2}{n} P \frac{\Psi_{12}}{\tau_{av}} + 2 \frac{n_2}{n} P \frac{\Psi_{R1}}{\tau_{av}} + 2 \frac{\rho_2}{\rho_1} \frac{n_1}{n} P \frac{\Psi_{R2}}{\tau_{av}} \quad (3.33)$$

$$\frac{\partial f_2}{\partial t} + \eta_2 \frac{\partial f_2}{\partial y} = \frac{\Psi_{21} - f_2}{\tau_{av}} + \frac{\Psi_{22} - f_2}{\tau_{22}} - 2 \frac{n_1}{n} P \frac{\Psi_{21}}{\tau_{av}}. \quad (3.34)$$

### 3.5 Determination of unknown parameters in the Boltzmann-Krook equations

To proceed with the analysis of our problem, it is necessary to specify the unknown parameters introduced in ( 3.26) ~ ( 3.29), i.e. the velocities  $v_{12}, v_{21}, v_{R1}$  and  $v_{R2}$  and the temperatures  $T_{12}, T_{21}, T_{R1}$  and  $T_{R2}$ . To do this, it is necessary to consider conditions which the Boltzmann-Krook equations should satisfy. The right-hand side

of ( 3.33) and ( 3.34) corresponds to collision integrals  $\left[\frac{\partial f_s}{\partial t}\right]_{coll}$  expressed with simpler collision integral operators  $J_s(f_s)$  instead of true collision integral operators  $Q_{sr}(f_s, f_r)$  in ( 3.1). Therefore, we can write, instead of ( 3.1),

$$\begin{aligned}\left[\frac{\partial f_1}{\partial t}\right]_{coll} &= J_1(f_1) \\ &= \frac{\Psi_{11} - f_1}{\tau_{11}} + \frac{\Psi_{12} - f_1}{\tau_{av}} - 2\frac{n_2}{n}P\frac{\Psi_{12}}{\tau_{av}} + 2\frac{n_2}{n}P\frac{\Psi_{R1}}{\tau_{av}} \\ &\quad + 2\frac{\rho_2}{\rho_1}\frac{n_1}{n}P\frac{\Psi_{R2}}{\tau_{av}}\end{aligned}\quad (3.35)$$

$$\begin{aligned}\left[\frac{\partial f_2}{\partial t}\right]_{coll} &= J_2(f_2) \\ &= \frac{\Psi_{21} - f_2}{\tau_{av}} + \frac{\Psi_{22} - f_2}{\tau_{22}} - 2\frac{n_1}{n}P\frac{\Psi_{21}}{\tau_{av}}.\end{aligned}\quad (3.36)$$

We require that these model collision integrals reproduce some properties which true collision integrals have. Therefore, we should admit the existence of three collision invariants, i.e. total mass, total momentum and total energy for these model collision operators (see e.g. Cercignani [16, p.95]). By the same discussions as in Section 2.3 in Chapter 2, we must impose the following relations,

$$\sum_s \int_{\mathbb{R}^3} J_s(f_s) d\vec{\xi}_s = 0 \quad (3.37)$$

$$\sum_s \int_{\mathbb{R}^3} \vec{\xi}_s J_s(f_s) d\vec{\xi}_s = 0 \quad (3.38)$$

$$\sum_s \int_{\mathbb{R}^3} \frac{1}{2} |\vec{\xi}_s|^2 J_s(f_s) d\vec{\xi}_s = -\frac{E}{m_2} \dot{w} \quad (3.39)$$

where

$$\dot{w} = \int_{\mathbb{R}^3} J_1(f_1) d\vec{\xi}_1 = - \int_{\mathbb{R}^3} J_2(f_2) d\vec{\xi}_2. \quad (3.40)$$

( 3.37) ~ ( 3.39) correspond to ( 2.26), ( 2.27) and ( 2.29) respectively and ( 3.40) corresponds to the definition in ( 2.25).

The first condition ( 3.37) has already been satisfied because of the forms imposed to ( 3.26) ~ ( 3.29). The second condition ( 3.38) gives the following equation for

unknown parameters (see Appendix B.1),

$$\begin{aligned}
& \rho_1(\vec{v}_{12} - \vec{v}_1) + \rho_2(\vec{v}_{21} - \vec{v}_2) \\
& - 2\frac{n_2}{n}P\rho_1\vec{v}_{12} - 2\frac{n_1}{n}P\rho_2\vec{v}_{21} + 2\frac{n_2}{n}P\rho_1\vec{v}_{R1} + 2\frac{n_1}{n}P\rho_2\vec{v}_{R2} \\
& = \vec{0}
\end{aligned} \tag{3.41}$$

and the third condition gives (see also Appendix B.1),

$$\begin{aligned}
& 3n_1k(T_{12} - T_1) + 3n_2k(T_{21} - T_2) + \rho_1(|\vec{v}_{12}|^2 - |\vec{v}|^2) + \rho_2(|\vec{v}_{21}|^2 - |\vec{v}|^2) \\
& - 2\frac{n_2}{n}P(3n_1kT_{12} + \rho_1|\vec{v}_{12}|^2) - 2\frac{n_1}{n}P(3n_2kT_{21} + \rho_2|\vec{v}_{21}|^2) \\
& + 2\frac{n_2}{n}P(3n_1kT_{R1} + \rho_1|\vec{v}_{R1}|^2) + 2\frac{n_1}{n}P(3 \cdot 2n_2kT_{R2} + \rho_2|\vec{v}_{R2}|^2) \\
& + \frac{4n_1n_2}{n}PE \\
& = 0.
\end{aligned} \tag{3.42}$$

In the derivation of ( 3.42), we used the following expression for the source term  $\dot{w}$  from the definition of ( 2.25),

$$\dot{w} = 2\rho_2\frac{n_1}{n}\frac{P}{\tau_{av}}. \tag{3.43}$$

We have still eight unknown parameters while there are only two conditions. To reduce the number of unknowns, it is necessary to make more assumptions for collisions between different species. As mentioned in Section 3.4, the Boltzmann-Krook equations ( 3.33) and ( 3.34) satisfy the H-theorem when  $P \rightarrow 0$  under conditions (see Appendix B.2 for the proof),

$$\vec{v}_{12} = \vec{v}_{21}, \quad T_{12} = T_{21} \quad (P \rightarrow 0). \tag{3.44}$$

In this analysis, we assume that conditions ( 3.44) can be applied when  $P \neq 0$ , i.e. when there are chemical reactions,

$$\vec{v}_{12} = \vec{v}_{21}, \quad T_{12} = T_{21} \quad (P \neq 0). \tag{3.45}$$

It corresponds to the assumption that, if collisions are non-reactive, molecules of both species, after collisions with the different species, are re-emitted with a Maxwell distribution function centered about the same velocity and the same temperature.

In the same analogy, we assume for the terms related with reactive collisions,

$$\vec{v}_{R1} = \vec{v}_{R2} = \vec{v}_R \quad (3.46)$$

$$T_{R1} = T_{R2} = T_R. \quad (3.47)$$

They are equivalent to the assumption that, if collisions are reactive, O molecules which were both originally O<sub>2</sub> molecules (newly created) and catalytic bodies are re-emitted with a Maxwell distribution function centered about the same velocity  $\vec{v}_R$  and the same temperature  $T_R$ .

By substituting these assumptions ( 3.46) and ( 3.47) into ( 3.41) and ( 3.42), we get simpler forms,

$$\rho(\vec{v}_{12} - \vec{v}) + 2\frac{n_2}{n}P\rho_1(\vec{v}_R - \vec{v}_{12}) + 2\frac{n_1}{n}P\rho_2(\vec{v}_R - \vec{v}_{12}) = \vec{0} \quad (3.48)$$

$$\begin{aligned} & 3nk(T_{12} - T) + \rho(|\vec{v}_{12}|^2 - |\vec{v}|^2) \\ & + 2\frac{n_2}{n}P \left\{ 3n_1k(T_R - T_{12}) + \rho_1(|\vec{v}_R|^2 - |\vec{v}_{12}|^2) \right\} \\ & + 2\frac{n_1}{n}P \left\{ 3n_2k(2T_R - T_{12}) + \rho_2(|\vec{v}_R|^2 - |\vec{v}_{12}|^2) \right\} \\ & + \frac{4n_1n_2}{n}PE \\ & = 0. \end{aligned} \quad (3.49)$$

( 3.48) and ( 3.49) still have four unknown parameters. Next, we should consider the limiting situation where the mixture approaches the non-reactive condition, in other words, the fraction of reactive collisions approaches zero, i.e.  $P \rightarrow 0$ . In this limit, from the results of ( B.29) in Appendix B.2, we can impose these conditions,

$$\lim_{P \rightarrow 0} \vec{v}_{12} = \lim_{P \rightarrow 0} \vec{v}_R = \vec{v} \quad (3.50)$$



$$\lim_{P \rightarrow 0} T_{12} = \lim_{P \rightarrow 0} T_R = T. \quad (3.51)$$

Under these conditions, we can derive one of reasonable forms (see Appendix B.3 for detail),

$$\vec{v}_{12} = \vec{v}_R = \vec{v} \quad (3.52)$$

$$T_{12} = T_R = \frac{3n^2kT - 4n_1n_2PE}{3n^2k + 6n_1n_2kP}. \quad (3.53)$$

( 3.52) and ( 3.53) suggest that, whether collisions are reactive or non-reactive, molecules of both species, after collisions with the different species, are re-emitted with a Maxwell distribution function centered about the velocity of the mixture and a slightly smaller temperature than the mixture. In order for a dissociative collision to occur, at least one of species or both must possess much greater kinetic energy than average molecules. After such a collision, most of this large kinetic energy transfers into the heat of formation of O molecules newly created.  $T_{12} = T_R$  in ( 3.53) suggests that, after a dissociative collision, the kinetic energy of molecules involved in it reduces to the same level as the kinetic energy of average molecules (which does not cause dissociation in general). The local temperature  $T_{12}$  or  $T_R$  must be smaller than the temperature of the total mixture because there exists a heat release process as mentioned above. And the larger the fraction of dissociative collisions becomes, the smaller the local temperature becomes. In this sense, these results are reasonable from the physical point of view.

We should note that the results obtained in this section are not unique. However, they satisfy conditions of conservation of three invariants and also satisfy the H-theorem when  $P \rightarrow 0$ . Furthermore, each assumption and result has the physical meaning discussed above. We should also note that, as mentioned in Appendix B.3, ( 3.53) is a kind of an approximation form when  $P$  is small. Therefore, it cannot be applied when  $P$  is relatively large. However, it does not affect this analysis very much because  $P$  is large only when the temperature of the mixture is very high and becomes drastically small as the temperature is smaller. For example,  $P = 1$  when temperature is more than about 60,000K because the characteristic temperature for dissociation of  $O_2$  molecules is 59,500K.

Applying the results ( 3.45) ~ ( 3.47) and ( 3.52) ~ ( 3.53) to ( 3.26) ~ ( 3.29), we get

$$\Psi_{R1} = \Psi_{R2} = \Psi_{12}. \quad (3.54)$$

Then, we get the final forms of the Boltzmann-Krook equations which are suitable for our problem,

$$\frac{\partial f_1}{\partial t} + \eta_1 \frac{\partial f_1}{\partial y} = \frac{\Psi_{11} - f_1}{\tau_{11}} + \frac{\Psi_{12} - f_1}{\tau_{av}} + 2 \frac{\rho_2 n_1}{\rho_1 n} P \frac{\Psi_{12}}{\tau_{av}} \quad (3.55)$$

$$\frac{\partial f_2}{\partial t} + \eta_2 \frac{\partial f_2}{\partial y} = \frac{\Psi_{21} - f_2}{\tau_{av}} + \frac{\Psi_{22} - f_2}{\tau_{22}} - 2 \frac{n_1}{n} P \frac{\Psi_{21}}{\tau_{av}} \quad (3.56)$$

where

$$\Psi_{11} = \rho_1 \left( \frac{m_1}{2\pi k T_{11}} \right)^{3/2} \exp \left\{ -\frac{m_1}{2k T_{11}} |\vec{\xi}_1 - \vec{v}_1|^2 \right\}. \quad (3.57)$$

$$\Psi_{22} = \rho_2 \left( \frac{m_2}{2\pi k T_{22}} \right)^{3/2} \exp \left\{ -\frac{m_2}{2k T_{22}} |\vec{\xi}_2 - \vec{v}_2|^2 \right\}. \quad (3.58)$$

$$\Psi_{12} = \rho_1 \left( \frac{m_1}{2\pi k T_{12}} \right)^{3/2} \exp \left\{ -\frac{m_1}{2k T_{12}} |\vec{\xi}_1 - \vec{v}|^2 \right\} \quad (3.59)$$

$$\Psi_{21} = \rho_2 \left( \frac{m_2}{2\pi k T_{12}} \right)^{3/2} \exp \left\{ -\frac{m_2}{2k T_{12}} |\vec{\xi}_2 - \vec{v}|^2 \right\} \quad (3.60)$$

$$T_{12} = \frac{3n^2 k T - 4n_1 n_2 P E}{3n^2 k + 6n_1 n_2 k P}. \quad (3.61)$$

When  $P$  is small, ( 3.61) can be approximated as

$$T_{12} \cong T - \frac{2n_1 n_2}{n^2} \left( T + \frac{2}{3} \Theta \right) P \quad (3.62)$$

where  $\Theta$  is the characteristic temperature for dissociation of  $O_2$ ,

$$\Theta \equiv \frac{E}{k}. \quad (3.63)$$

# Chapter 4

## Boundary Conditions

In this chapter, we construct boundary conditions for a mixture of gases which include the effects of the gas-surface interaction. In the first section, we discuss justification of specifications of averaged boundary conditions which we should apply in this study. In later sections, we construct each boundary condition. The slip conditions discussed there are an extension of the concept by Trilling [8] for the case of a monoatomic gas to the case of a mixture of gases with chemical reactions on a surface.

### 4.1 Construction of boundary conditions for a reacting mixture of gases

The most rigorous treatment of boundary conditions would be to specify each distribution function  $f_1$  and  $f_2$  on the wall, which can represent the detailed gas-surface interaction process. Several mathematical and physical models have been proposed for a monoatomic gas (see, e.g. Cercignani [16, Chap. III]). However, for the gas-surface interaction which contains chemical reactions on the catalytic surface as in our problem, the detailed treatment is not yet possible because of the lack of enough knowledge of such complicated chemical processes. And, even if the detailed treatments for distribution functions are available, these mathematical expressions

may be too intractable to handle in the singular perturbation expansion scheme which we should apply.

Trilling [8] pointed out that actual boundary conditions should be specified on the measurable properties of the flow, i.e. averaged values of the distribution functions, and the specification of the distribution functions has a degree of indeterminacy like that of a velocity potential, which does not affect the determination of the hydrodynamic properties. These concepts are based on the assumption that the detailed mechanism of the gas-surface interaction for individual molecules is independent of gas-gas collisions and distribution functions in the flow because each gas molecule interacts with the wall independently. In this study, we accept these concepts by Trilling [8] and specify boundary conditions in terms of hydrodynamic properties defined in Chapter 2, which are, so-called, averaged boundary conditions.

Another important assumption we should introduce here, also by Trilling [8], is that the molecules hitting the wall acquire their hydrodynamic properties during their previous collisions which occurred, on average, one mean free path away from the wall. To explain this, we must introduce the gradients of each property in the direction normal to the wall into the expression of each boundary conditions.

This approach makes it possible to express the gradual adjustment of distribution functions to the presence of the wall. As mentioned before, the detailed mechanism of the gas-surface interaction can be assumed to be independent of the distribution functions in the flow, therefore, the influence of the detailed effect at the surface should be blurred after a few collisions near the wall, in other words, a local rearrangement of distribution functions is allowed at the wall. And this physical aspect is consistent with the introduction of the gradients in the  $y$ -direction discussed in the previous paragraph.

In Section 2.3, we obtained a system of five equations ( 2.30)  $\sim$  ( 2.34) for five main unknowns :  $\rho_1, \rho_2, u, v$  and  $T$ . Therefore, we need specify four averaged boundary conditions, i.e. for  $u, v, T$  and one of species densities  $\rho_1$  or  $\rho_2$  because the mass fraction of species  $s$  is also one of the dependent variables.

In this study, we assume that the velocity of the wall in the  $x$ -direction  $u_w(t)$  is

given a priori, and the tangential velocity of the mixture at the wall  $u(0)$  should be determined from the relation between  $u_w$  and  $u(0)$ , the so-called slip condition which will be discussed in the later section. For the boundary condition for temperature, we consider the following two extreme cases,

- $T_w(t)$  is given a priori (including the case of constant wall temperature).
- Adiabatic boundary condition.

For the first case, the temperature of the mixture on the wall  $T(0)$  should be determined from the slip condition on the wall. For the second case,  $T(0)$  should be specified by considering the energy balance on the wall and, afterwards,  $T_w$  can be determined from the slip condition (see Gupta et al.[6]).

## 4.2 Boundary condition for the velocity $v$

The boundary condition for the velocity in the  $y$ -direction  $v$  is specified by the physical condition that there should be no mass transfer through the wall,

$$\rho v(0) = 0. \tag{4.1}$$

Consequently, we get the boundary condition for  $v$ ,

$$v(0) = 0. \tag{4.2}$$

## 4.3 Boundary condition for one of the species densities

The boundary condition for one of the species densities can be obtained by considering the catalytic process on the surface.

The mass flux of O molecules diffusing towards the wall is  $\rho_1 V_1(0)$ . This diffused mass flux must be exactly balanced by the catalytic consumption rate of O molecules

on the wall. Then we can get the general form of the boundary condition for  $\rho_1$  (see Goulard [2] and Scott [5]),

$$\rho_1 V_1(0) = -k_w [\rho_1(0)]^l \quad (1 < l < 2) \quad (4.3)$$

where  $k_w$  is the catalytic recombination rate constant and  $l$  is the order of the surface recombination process.

In general, the catalytic recombination process on the wall is not simple and it is a combination of both first-order and second-order reactions, which corresponds to  $(1 < l < 2)$  in (4.3). However, the first-order should be dominant when the density is low because the second-order reaction rate approaches zero faster than the first-order one with decreasing density (see Park [17]). In this study, we assume that this recombination process is a first-order reaction. Then, we get, from (4.3),

$$\rho_1 v_1(0) = -k_w \rho_1(0) \quad (4.4)$$

where we used the relation from (4.1),

$$\rho_1 V_1(0) = \rho_1 (v_1 - v)(0) = \rho_1 v_1(0). \quad (4.5)$$

The catalytic reaction rate constant  $k_w$  introduced in (4.3) is related to the catalytic efficiency  $\gamma$  defined as the ratio of the number  $N_r$  of O molecules recombining on a surface per unit area and unit time to the total number  $N$  of O molecules striking the surface per a unit area and a unit time,

$$\gamma = \frac{N_r}{N}. \quad (4.6)$$

The number  $N_r$  can be easily derived from the mass flux on the wall. From (4.4),

$$N_r = -\frac{\rho_1 v_1(0)}{m_1} = \frac{k_w \rho_1(0)}{m_1}. \quad (4.7)$$

The number  $N$  of O molecules hitting the wall per a unit area and a unit time can be

expressed by using the distribution function  $f_1$  at  $y = -\eta_1\tau_1$  (one mean free path away from the wall) and  $t = t - \tau$ , i.e.  $f(-\eta_1\tau_1, t - \tau_1)$  where  $\tau_s$  is the total characteristic time for the species  $s$  defined in ( 3.5), then,

$$N = -\frac{1}{m_1} \int_{-\infty}^{\infty} \int_{-\infty}^0 \int_{-\infty}^{\infty} \eta_1 f_1(-\eta_1\tau_1, t - \tau_1) d\xi_1 d\eta_1 d\zeta_1. \quad (4.8)$$

From ( 4.6)  $\sim$  ( 4.8), we can get the relation between  $k_w$  and  $\gamma$ ,

$$k_w = -\frac{\gamma}{\rho_1(0)} \int_{-\infty}^{\infty} \int_{-\infty}^0 \int_{-\infty}^{\infty} \eta_1 f_1(-\eta_1\tau_1, t - \tau_1) d\xi_1 d\eta_1 d\zeta_1. \quad (4.9)$$

When the surface is highly catalytic, i.e. the catalytic efficiency  $\gamma$  is order of unity,  $k_w$  is the same order as the speed of sound.

( 4.4) is the boundary condition for  $\rho_1$  and the catalytic rate constant  $k_w$  appearing there is connected with the catalytic efficiency  $\gamma$  which will be used mainly later through the relation ( 4.9).

## 4.4 Slip conditions on the wall for the tangential velocity $u$ and temperature $T$

For a monatomic flow, Trilling [8] constructed the averaged boundary conditions for the tangential velocity  $u$  and temperature  $T$  with the classical statements by Chapman & Cowling [18]. In this section, we will try to extend this concept to the mixture of gases. In this study, we make the following assumption.

- The momentum and energy accommodation coefficients for each species  $s$ , denoted as  $\theta_s$ , have the same value and represent the fraction of particles re-emitted diffusively.
- $O_2$  molecules created by the recombination process are fully accommodated with the wall after releasing the net adsorption energy and the dissociation energy in the adsorbed phase, and equilibrate with the wall tangential velocity  $u_w$  and the wall temperature  $T_w$ .

- Sticking time of molecules to the wall is negligible for all cases, i.e. specular reflection, simple accommodation without chemical reactions and recombination on the surface.

First of all, we define the density flux and the number density flux in the  $y$ -direction near the wall (much closer than one mean free path away from the wall) as follows,

$$\begin{aligned}
\rho_1 v_1(0) &= \rho_{1in} v_{1in} + \rho_{1out} v_{1out} \\
\rho_2 v_2(0) &= \rho_{2in} v_{2in} + \rho_{2out} v_{2out} \\
n_1 v_1(0) &= n_{1in} v_{1in} + n_{1out} v_{1out} \\
n_2 v_2(0) &= n_{2in} v_{2in} + n_{2out} v_{2out}
\end{aligned} \tag{4.10}$$

where the subscript *in* denotes properties of incoming molecules whose velocities in the  $y$ -direction are negative, while the subscript *out* denotes properties of outgoing molecules whose velocities in the  $y$ -direction are positive.

For the incoming mass flux, for example  $\rho_{1in} v_{1in}$ , by using the catalytic efficiency  $\gamma$  and the accommodation coefficient  $\theta_1$ , we can assume that

- Mass flux  $(1 - \theta_1)\rho_{1in} v_{1in}$  is reflected specularly as O molecules on the wall with the velocity in the  $y$ -direction  $-v_{1in}$ .
- Mass flux  $(\theta_1 - \gamma)\rho_{1in} v_{1in}$  is reflected diffusely as O molecules on the wall with the velocity in the  $y$ -direction  $v_{1w}$ . And the outgoing mass flux is  $-(\theta_1 - \gamma)\rho_{1in} v_{1in}$  because the incoming mass flux cannot go through the wall.
- Mass flux  $\gamma\rho_{1in} v_{1in}$  is reflected diffusely as O<sub>2</sub> molecules on the wall with the velocity in the  $y$ -direction  $v_{2w}$ . And the outgoing mass flux is  $-\gamma\rho_{1in} v_{1in}$  because of the same reason as above.

where  $v_{1w}$  and  $v_{2w}$  are the average velocities in the  $y$ -direction of accommodated O and O<sub>2</sub> molecules respectively.

If we denote the average tangential velocities of incoming O and O<sub>2</sub> molecules whose velocities in the  $y$ -direction are negative as  $u_{1in}$  and  $u_{2in}$  respectively, for O



molecules, for example, the incoming tangential momentum flux to the wall is  $\rho_{1in}u_{1in} \cdot v_{1in}$  and outgoing momentum flux is  $(1 - \theta_1)\rho_{1in}u_{1in} \cdot (-v_{1in})$  for molecules specularly reflected and  $(\theta_1 - \gamma)\rho_{1in}u_w \cdot (-v_{1in})$  for molecules accommodated on the wall (see Figure 4-1 (a)). Then, the average tangential velocity on the wall for species 1,  $u_1(0)$ , can be defined by taking a weighted mean of these momentum fluxes,

$$\begin{aligned}
& u_1(0) \\
= & \frac{\rho_{1in}u_{1in} \cdot |v_{1in}| + (1 - \theta_1)\rho_{1in}u_{1in} \cdot |-v_{1in}| + (\theta_1 - \gamma)\rho_{1in}u_w \cdot |-v_{1in}|}{\rho_{1in}|v_{1in}| + (1 - \theta_1)\rho_{1in}|-v_{1in}| + (\theta_1 - \gamma)\rho_{1in}|-v_{1in}|} \\
= & \frac{(2 - \theta_1)(\rho_{1in}v_{1in})u_{1in} + (\theta_1 - \gamma)(\rho_{1in}v_{1in})u_w}{(2 - \gamma)(\rho_{1in}v_{1in})} \tag{4.11}
\end{aligned}$$

For species 2, the incoming tangential momentum flux to the wall is  $\rho_{2in}u_{2in} \cdot v_{2in}$  and outgoing momentum flux is  $(1 - \theta_2)\rho_{2in}u_{2in} \cdot (-v_{2in})$  for molecules specularly reflected and  $\theta_2\rho_{2in}u_w \cdot (-v_{2in})$  for molecules accommodated on the wall and  $\gamma\rho_{1in}u_w \cdot (-v_{1in})$  for molecules newly created by the recombination on the surface (see Figure 4-1 (b)). Then,  $u_2(0)$  can be defined as,

$$\begin{aligned}
& u_2(0) \\
= & \frac{\rho_{2in}u_{2in} \cdot |v_{2in}| + (1 - \theta_2)\rho_{2in}u_{2in} \cdot |-v_{2in}| + \theta_2\rho_{2in}u_w \cdot |-v_{2in}| + \gamma\rho_{1in}u_w \cdot |-v_{1in}|}{\rho_{2in}|v_{2in}| + (1 - \theta_2)\rho_{2in}|-v_{2in}| + \theta_2\rho_{2in}|-v_{2in}| + \gamma\rho_{1in}|-v_{1in}|} \\
= & \frac{(2 - \theta_2)(\rho_{2in}v_{2in})u_{2in} + \theta_2(\rho_{2in}v_{2in})u_w + \gamma(\rho_{1in}v_{1in})u_w}{2(\rho_{2in}v_{2in}) + \gamma(\rho_{1in}v_{1in})}. \tag{4.12}
\end{aligned}$$

Then, the total average tangential velocity  $u_1(0)$  can be defined as,

$$\begin{aligned}
\rho u(0) &= \rho_1 u_1(0) + \rho_2 u_2(0) \\
&= \frac{2 - \theta_1}{2 - \gamma} \rho_1(0) u_{1in} + \frac{\theta_1 - \gamma}{2 - \gamma} \rho_1(0) u_w + \rho_2(0) \left( \frac{F_2}{F_1} \right) \tag{4.13}
\end{aligned}$$

where

$$F_1 = 2 + \gamma \left( \frac{\rho_{1in}v_{1in}}{\rho_{2in}v_{2in}} \right) \tag{4.14}$$

$$F_2 = (2 - \theta_2)u_{2in} + \theta_2 u_w + \gamma \left( \frac{\rho_{1in}v_{1in}}{\rho_{2in}v_{2in}} \right) u_w. \tag{4.15}$$

The incoming density flux  $\rho_{1in}v_{1in}$  and  $\rho_{2in}v_{2in}$  can be defined by the similar concepts as in Section 4.3,

$$\rho_{1in}v_{1in} = \int_{-\infty}^{\infty} \int_{-\infty}^0 \int_{-\infty}^{\infty} \eta_1 f_1(-\eta_1 \tau_1, t - \tau_1) d\xi_1 d\eta_1 d\zeta_1. \quad (4.16)$$

$$\rho_{2in}v_{2in} = \int_{-\infty}^{\infty} \int_{-\infty}^0 \int_{-\infty}^{\infty} \eta_2 f_2(-\eta_2 \tau_2, t - \tau_2) d\xi_2 d\eta_2 d\zeta_2. \quad (4.17)$$

In the same way as for the tangential momentum, by considering each energy flux towards the wall, we can get the temperature on the wall for each species (see Figure 4-2),

$$T_1(0) = \frac{(2 - \theta_1)(n_{1in}v_{1in})T_{1in} + (\theta_1 - \gamma)(n_{1in}v_{1in})T_w}{(2 - \gamma)(n_{1in}v_{1in})} \quad (4.18)$$

$$T_2(0) = \frac{(2 - \theta_2)(n_{2in}v_{2in})T_{2in} + \theta_2(n_{2in}v_{2in})T_w + \frac{\gamma}{2}(n_{1in}v_{1in})T_w}{2(n_{2in}v_{2in}) + \frac{\gamma}{2}n_{1in}(n_{1in}v_{1in})} \quad (4.19)$$

where  $T_{sin}(s = 1, 2)$  is the species temperature of the incoming molecules of species  $s$ . And the incoming density flux  $n_{1in}v_{1in}$  and  $n_{2in}v_{2in}$  are defined as,

$$n_{1in}v_{1in} = \frac{\rho_{1in}v_{1in}}{m_1} \quad (4.20)$$

$$n_{2in}v_{2in} = \frac{\rho_{2in}v_{2in}}{m_2} \quad (4.21)$$

Then, the temperature of the mixture on the wall,  $T(0)$ , can be defined as,

$$\begin{aligned} nT(0) &= n_1T_1(0) + n_2T_2(0) \\ &= \frac{2 - \theta_1}{2 - \gamma}n_1(0)T_{1in} + \frac{\theta_1 - \gamma}{2 - \gamma}n_1(0)T_w + n_2(0) \left( \frac{G_2}{G_1} \right) \end{aligned} \quad (4.22)$$

where

$$G_1 = 2 + \frac{\gamma}{2} \left( \frac{n_{1in}v_{1in}}{n_{2in}v_{2in}} \right). \quad (4.23)$$

$$G_2 = (2 - \theta_2)T_{2in} + \theta_2T_w + \frac{\gamma}{2} \left( \frac{n_{1in}v_{1in}}{n_{2in}v_{2in}} \right) T_w. \quad (4.24)$$

As mentioned in Section 4.1, variables introduced here,  $u_{1in}$ ,  $u_{2in}$ ,  $T_{1in}$  and  $T_{2in}$  are values acquired during previous collisions which have occurred one mean free path

away from the wall. Then, we can write,

$$\begin{aligned}
u_{1in} &= u_1(\lambda_1, t - \tau_1) \\
u_{2in} &= u_2(\lambda_2, t - \tau_2) \\
T_{1in} &= T_1(\lambda_1, t - \tau_1) \\
T_{2in} &= T_2(\lambda_2, t - \tau_2)
\end{aligned} \tag{4.25}$$

By using these definitions, we can get the final forms of the slip conditions on the wall for  $u(0)$  and  $T(0)$ ,

$$\rho u(0) = \frac{2 - \theta_1}{2 - \gamma} \rho_1(0) u_1(\lambda_1, t - \tau_1) + \frac{\theta_1 - \gamma}{2 - \gamma} \rho_1(0) u_w + \rho_2(0) \left( \frac{F_2}{F_1} \right) \tag{4.26}$$

where

$$F_1 = 2 + \gamma \left( \frac{\rho_{1in} v_{1in}}{\rho_{2in} v_{2in}} \right) \tag{4.27}$$

$$F_2 = (2 - \theta_2) u_2(\lambda_2, t - \tau_2) + \theta_2 u_w + \gamma \left( \frac{\rho_{1in} v_{1in}}{\rho_{2in} v_{2in}} \right) u_w. \tag{4.28}$$

And,

$$nT(0) = \frac{2 - \theta_1}{2 - \gamma} n_1(0) T_1(\lambda_1, t - \tau_1) + \frac{\theta_1 - \gamma}{2 - \gamma} n_1(0) T_w + n_2(0) \left( \frac{G_2}{G_1} \right) \tag{4.29}$$

where

$$G_1 = 2 + \frac{\gamma}{2} \left( \frac{n_{1in} v_{1in}}{n_{2in} v_{2in}} \right). \tag{4.30}$$

$$G_2 = (2 - \theta_2) T_2(\lambda_2, t - \tau_2) + \theta_2 T_w + \frac{\gamma}{2} \left( \frac{n_{1in} v_{1in}}{n_{2in} v_{2in}} \right) T_w. \tag{4.31}$$

## 4.5 Boundary condition for temperature $T$ when the wall is adiabatic

As mentioned in Section 4.1, when the wall is adiabatic, the temperature of the mixture on the wall,  $T(0)$ , is specified by considering the energy balance. The heat

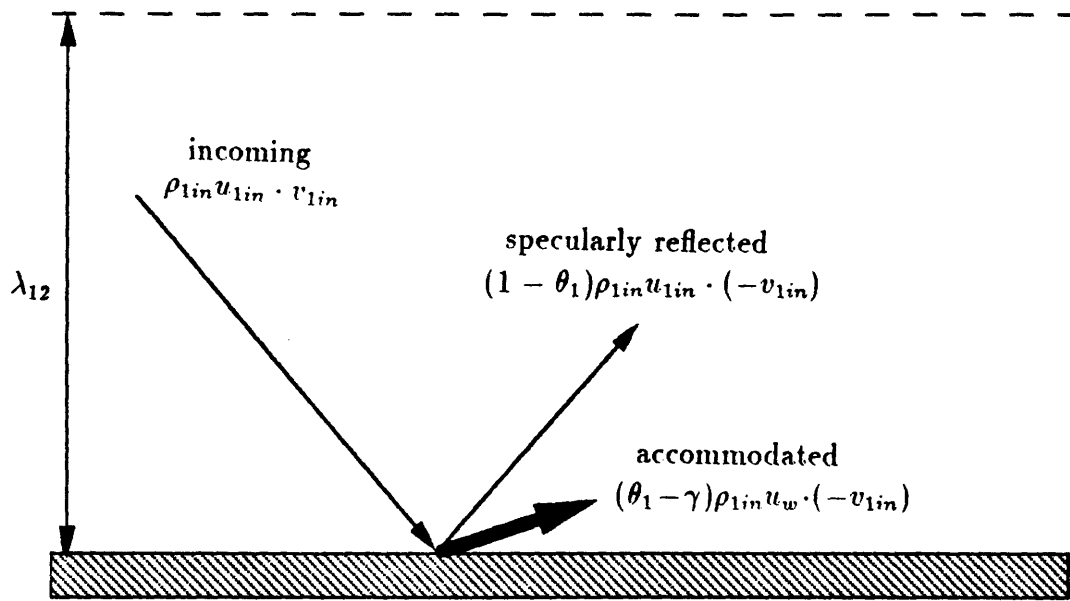
transfer rate towards the wall  $q_w$  consists of the heat flux by the conduction,  $q_y$ , and the recombination process on the surface,

$$q_w = -q_y(0) - \frac{E}{m_2} (\rho_1 V_1)(0) \quad (4.32)$$

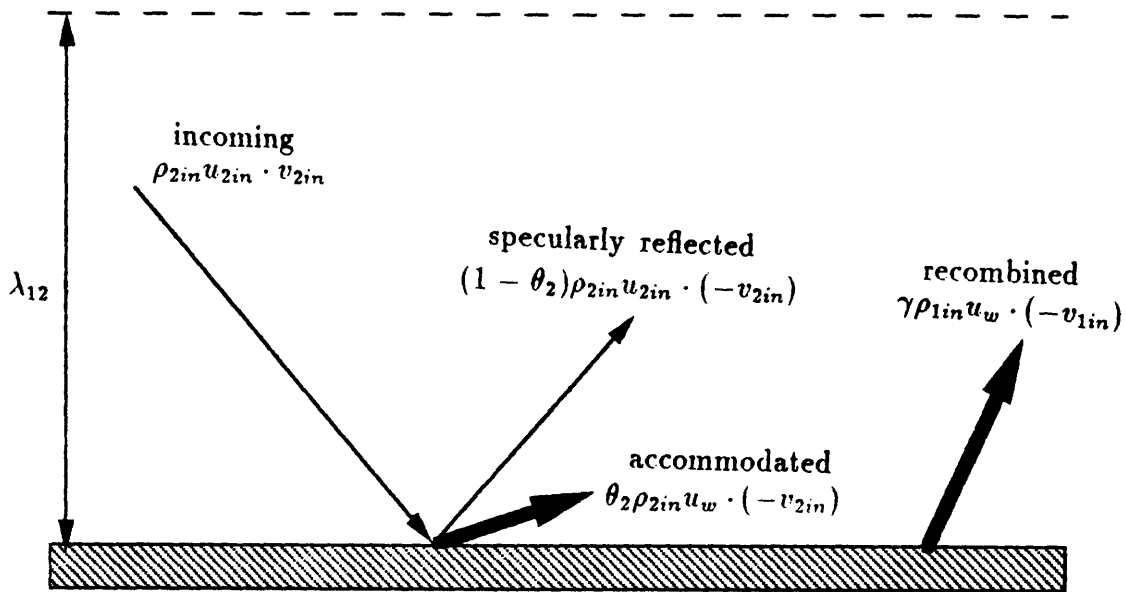
By using the expression ( 4.5), the energy balance at the wall is expressed as,

$$q_y(0) + \frac{E}{m_2} (\rho_1 v_1)(0) = 0 \quad (4.33)$$

The wall temperature  $T_w$  is determined from  $T(0)$  which should be obtained from ( 4.33).

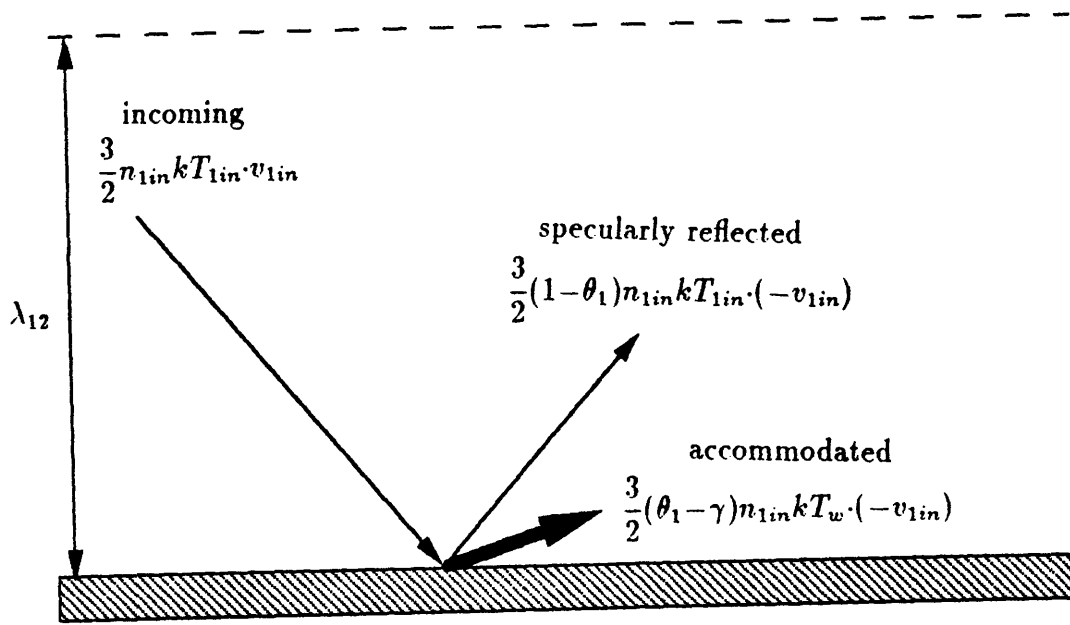


(a) O molecules

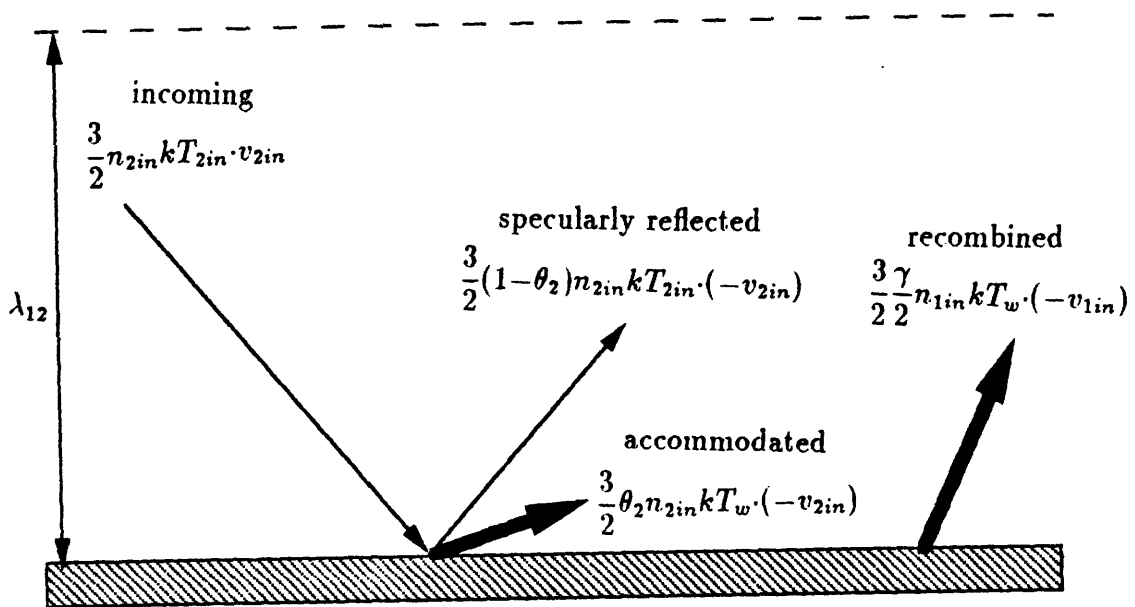


(b) O<sub>2</sub> molecules

Figure 4-1: Incoming and outgoing tangential momentum flux on the surface for each species.



(a) O molecules



(b) O<sub>2</sub> molecules

Figure 4-2: Incoming and outgoing energy flux on the surface for each species.

# Chapter 5

## Formal expansion scheme and determination of the expansion parameter

In this study, we seek an asymptotic solution of the Boltzmann-Krook equations derived in Chapter 3. In the first section of this chapter, we non-dimensionalize the Boltzmann-Krook equations and the equations of motion by introducing dimensionless independent and dependent variables. Next, we introduce the formal expansion parameter  $\epsilon$  and expand these variables in powers of  $\epsilon$ . In the following section, we relate this expansion parameter  $\epsilon$  to some physical parameters by considering the slip conditions derived in Chapter 4. This concept is an extension of the treatments of the case for a monoatomic gas by Trilling [8] to the mixture of gases.

### 5.1 The formal expansion scheme of governing equations

In order to proceed with this analysis in accordance with the theory of matched asymptotic expansions (see Van Dyke [19] for detail), it is necessary to introduce dimensionless variables and to non-dimensionalize each governing equations and bound-

ary conditions.

For this purpose, we introduce a small expansion parameter  $\epsilon$  and an arbitrary reference length  $L$ . Then, we define the dimensionless independent variables,

$$\bar{t} = \frac{tc_\infty}{L}, \quad \bar{y} = \frac{y}{\epsilon L} \quad (5.1)$$

where  $c_\infty$  is a reference velocity and is defined as,

$$c_\infty = \sqrt{\frac{2n_\infty kT_\infty}{\rho_\infty}} \quad (5.2)$$

where a suffix  $\infty$  denotes values far from the wall.

In this stage, the relationship between  $\epsilon$  and other physical small parameters, e.g.  $\tau_{av}, \tau_{11}$  or  $\tau_{22}$  is not yet specified. The form of  $\bar{t}$  in (5.1) emphasizes that changes in time are slow because we seek an asymptotic solution for large time and the characteristic time  $L/c_\infty$  represents the time scale of the macroscopic changes of the flow. And the form of  $\bar{y}$  in (5.1) is selected such that the normal motion of the flow might play a role. It corresponds to the introduction of an inner variable in the outer and inner expansion scheme.

Similarly, the dimensionless dependent variables are defined as,

$$\bar{\rho} = \frac{\rho}{\rho_\infty}, \quad \bar{T} = \frac{T}{t_\infty}, \quad \bar{u} = \frac{u}{c_\infty}, \quad \bar{v} = \frac{v}{\epsilon c_\infty} \quad (5.3)$$

$$\bar{P}_{xy} = \frac{P_{xy}}{\epsilon \rho_\infty c_\infty^2}, \quad \bar{P}_{yy} = \frac{P_{yy}}{\rho_\infty c_\infty^2}, \quad \bar{q}_y = \frac{q_y}{\epsilon \rho_\infty c_\infty^3} \quad (5.4)$$

$$\bar{f}_s = \frac{c_\infty^3}{\rho_\infty} f_s, \quad \bar{\Psi}_{sr} = \frac{c_\infty^3}{\rho_\infty} \Psi_{sr} \quad (s, r = 1, 2) \quad (5.5)$$

$$\bar{\xi}_s = \frac{\xi_s}{c_\infty}, \quad \bar{\eta}_s = \frac{\eta_s}{c_\infty}, \quad \bar{\zeta}_s = \frac{\zeta_s}{c_\infty} \quad (s = 1, 2) \quad (5.6)$$

$$\bar{\tau}_{11} = \frac{\tau_{11} c_\infty}{L}, \quad \bar{\tau}_{22} = \frac{\tau_{22} c_\infty}{L}, \quad \bar{\tau}_{av} = \frac{\tau_{av} c_\infty}{L} \quad (5.7)$$

and

$$\bar{w} = \frac{L}{\rho_\infty c_\infty} \dot{w} \quad (5.8)$$



$$\bar{E} = \bar{\Theta} = \frac{2n_\infty}{\rho_\infty c_\infty^2} E. \quad (5.9)$$

In these definitions,  $\bar{v}$ ,  $\bar{P}_{xy}$  and  $\bar{q}_y$  are selected to emphasize the normal motion of the flow in the same way as for the definition of  $\bar{y}$ .

When these dimensionless variables are defined, we can get dimensionless governing equations. The Boltzmann-Krook equations ( 3.55) and ( 3.56) become in dimensionless form,

$$\frac{\partial \bar{f}_1}{\partial \bar{t}} + \frac{\bar{\eta}_1}{\epsilon} \frac{\partial \bar{f}_1}{\partial \bar{y}} = \frac{\bar{\Psi}_{11} - \bar{f}_1}{\bar{\tau}_{11}} + \frac{\bar{\Psi}_{12} - \bar{f}_1}{\bar{\tau}_{av}} + 4 \frac{\bar{n}_2}{\bar{n}} P \frac{\bar{\Psi}_{12}}{\bar{\tau}_{av}} \quad (5.10)$$

$$\frac{\partial \bar{f}_2}{\partial \bar{t}} + \frac{\bar{\eta}_2}{\epsilon} \frac{\partial \bar{f}_2}{\partial \bar{y}} = \frac{\bar{\Psi}_{22} - \bar{f}_2}{\bar{\tau}_{22}} + \frac{\bar{\Psi}_{21} - \bar{f}_2}{\bar{\tau}_{av}} - 2 \frac{\bar{n}_1}{\bar{n}} P \frac{\bar{\Psi}_{21}}{\bar{\tau}_{av}} \quad (5.11)$$

and the macroscopic equations of motion defined in ( 2.30) ~ ( 2.34) become,

$$\frac{\partial \bar{\rho}_1}{\partial \bar{t}} + \frac{\partial(\bar{\rho}_1 \bar{v}_1)}{\partial \bar{y}} = \bar{w} \quad (5.12)$$

$$\frac{\partial \bar{\rho}_2}{\partial \bar{t}} + \frac{\partial(\bar{\rho}_2 \bar{v}_2)}{\partial \bar{y}} = -\bar{w} \quad (5.13)$$

$$\bar{\rho} \left( \frac{\partial \bar{u}}{\partial \bar{t}} + \bar{v} \frac{\partial \bar{u}}{\partial \bar{y}} \right) + \frac{\partial \bar{P}_{xy}}{\partial \bar{y}} = 0 \quad (5.14)$$

$$\epsilon^2 \bar{\rho} \left( \frac{\partial \bar{v}}{\partial \bar{t}} + \bar{v} \frac{\partial \bar{v}}{\partial \bar{y}} \right) + \frac{\partial \bar{P}_{yy}}{\partial \bar{y}} = 0 \quad (5.15)$$

$$\begin{aligned} & \frac{3}{4} \bar{n} \left( \frac{\partial \bar{T}}{\partial \bar{t}} + \bar{v} \frac{\partial \bar{T}}{\partial \bar{y}} \right) + \frac{\partial \bar{q}_y}{\partial \bar{y}} + \bar{P}_{xy} \frac{\partial \bar{u}}{\partial \bar{y}} + \bar{P}_{yy} \frac{\partial \bar{v}}{\partial \bar{y}} + R_2 \bar{w} \left( \bar{E} + \frac{3}{2} \bar{T} \right) \\ &= \frac{3}{4} \bar{T} \frac{\partial}{\partial \bar{y}} \left\{ \sum_s \bar{n}_s \bar{V}_s \right\} \end{aligned} \quad (5.16)$$

where the dimensionless source term  $\bar{w}$  is from ( 3.43),

$$\bar{w} = \frac{\bar{n}_1 \bar{n}_2}{R_2 \bar{n}} \frac{P}{\bar{\tau}_{av}} \quad (5.17)$$

and,

$$R_s = \frac{\rho_\infty}{2n_\infty m_s} \quad (s = 1, 2). \quad (5.18)$$

According to the procedures of the matched asymptotic expansion theory, we formally expand the dimensionless dependent variables in powers of  $\epsilon$ ,

$$\begin{aligned} \bar{\rho} &= \rho^{(0)} + \epsilon \rho^{(1)} + \epsilon^2 \rho^{(2)} + \dots \\ \bar{T} &= T^{(0)} + \epsilon T^{(1)} + \epsilon^2 T^{(2)} + \dots \\ \bar{u} &= u^{(0)} + \epsilon u^{(1)} + \epsilon^2 u^{(2)} + \dots \\ \bar{v} &= v^{(0)} + \epsilon v^{(1)} + \epsilon^2 v^{(2)} + \dots \\ \bar{P}_{xy} &= P_{xy}^{(0)} + \epsilon P_{xy}^{(1)} + \epsilon^2 P_{xy}^{(2)} + \dots \\ \bar{P}_{yy} &= P_{yy}^{(0)} + \epsilon P_{yy}^{(1)} + \epsilon^2 P_{yy}^{(2)} + \dots \\ \bar{q}_y &= q_y^{(0)} + \epsilon q_y^{(1)} + \epsilon^2 q_y^{(2)} + \dots \end{aligned} \quad (5.19)$$

Other similar variables with a suffix such as  $\bar{\rho}_1, \bar{T}_1$ , etc. can be expanded in the same way.

Likewise, the distribution functions  $\bar{f}_s$  and the Maxwell distribution functions  $\bar{\Psi}_{sr}$  can be expanded in powers of  $\epsilon$ ,

$$\begin{aligned} \bar{f}_s &= f_s^{(0)} + \epsilon f_s^{(1)} + \epsilon^2 f_s^{(2)} + \dots \\ \bar{\Psi}_{sr} &= \Psi_{sr}^{(0)} + \epsilon \Psi_{sr}^{(1)} + \epsilon^2 \Psi_{sr}^{(2)} + \dots \quad (s, r = 1, 2) \end{aligned} \quad (5.20)$$

The expansion of the Maxwell distribution functions can be expressed with averaged properties defined in ( 5.19).

If we substitute (5.19) and ( 5.20) into the dimensionless equations of motion ( 5.12)  $\sim$  ( 5.16), we obtain a hierarchy of partial differential equations. And, if additional unknowns;  $\bar{v}_1, \bar{v}_2, \bar{P}_{xy}, \bar{P}_{yy}$  and  $\bar{q}_y$  can be expressed in terms of main unknowns, these equations are fully determinate and give solutions for each order of  $\epsilon$ . This can be done by solving the dimensionless Boltzmann-Krook equations ( 5.10) and ( 5.11) and by calculating additional unknown variables with the definitions given in Section

## 5.2 Determination of the expansion parameter

In the dimensionless Boltzmann-Krook equations ( 5.10) and ( 5.11), the characteristic times  $\bar{\tau}_{11}$ ,  $\bar{\tau}_{22}$  and  $\bar{\tau}_{av}$  also appear. In the continuum flow, these characteristic times are also small. Therefore, it is necessary to relate  $\epsilon$  to these physical parameters in order to obtain solutions of distribution functions in each order of  $\epsilon$ .

Trilling [8] made the order estimation of a characteristic time of a monoatomic gas by considering the slip conditions on the wall for the tangential velocity  $u$  and temperature  $T$ . In this section, a similar concept is applied to the case of the mixture of gases in our problem.

From the expressions for  $u_1(0)$ ,  $u_2(0)$ ,  $T_1(0)$  and  $T_2(0)$  in ( 4.11), ( 4.12), ( 4.18) and ( 4.19) respectively, we get the following equations after non-dimensionalization,

$$(\theta_1 - \gamma)(\bar{u}_w - \bar{u}_1(0)) = (2 - \theta_1)(\bar{u}_1(0) - \bar{u}_1(\bar{\lambda}_1, \bar{t} - \bar{\tau}_1)) \quad (5.21)$$

$$\begin{aligned} & \{(\theta_2(\bar{\rho}_{2in}\bar{v}_{2in}) + \gamma(\bar{\rho}_{1in}\bar{v}_{1in}))\}(\bar{u}_w - \bar{u}_2(0)) \\ &= (2 - \theta_2)(\bar{\rho}_{2in}\bar{v}_{2in})(\bar{u}_2(0) - \bar{u}_2(\bar{\lambda}_2, \bar{t} - \bar{\tau}_2)) \end{aligned} \quad (5.22)$$

$$(\theta_1 - \gamma)(\bar{T}_w - \bar{T}_1(0)) = (2 - \theta_1)(\bar{T}_1(0) - \bar{T}_1(\bar{\lambda}_1, \bar{t} - \bar{\tau}_1)) \quad (5.23)$$

$$\begin{aligned} & \left\{(\theta_2(\bar{n}_{2in}\bar{v}_{2in}) + \frac{\gamma}{2}(\bar{n}_{1in}\bar{v}_{1in}))\right\}(\bar{T}_w - \bar{T}_2(0)) \\ &= (2 - \theta_2)(\bar{n}_{2in}\bar{v}_{2in})(\bar{T}_2(0) - \bar{T}_2(\bar{\lambda}_2, \bar{t} - \bar{\tau}_2)). \end{aligned} \quad (5.24)$$

These equations represent the slip conditions for the species tangential velocities and temperatures on the wall. If the slip values should be small compared with the wall velocity and the wall temperature, we must select the magnitudes of  $\bar{\lambda}_1$ ,  $\bar{\lambda}_2$ ,  $\bar{\tau}_1$

and  $\bar{\tau}_2$  as,

$$\bar{\lambda}_1, \bar{\lambda}_2 \ll 1, \quad \bar{\tau}_1, \bar{\tau}_2 \ll 1. \quad (5.25)$$

As introduced in Chapter 3, the total characteristic time is defined as,

$$\frac{1}{\tau_s} = \sum_{r=1,2} \frac{1}{\tau_{sr}} = \nu_s \quad (5.26)$$

and the mean free path of species  $s$ ,  $\lambda_s$ , is defined as,

$$\lambda_s = \frac{c_s}{\nu_s} = c_s \tau_s \quad (5.27)$$

where  $c_s$  is the average molecular speed of species  $s$ .

Next, we consider the dimensionless forms of these values. The dimensionless mean free path in the  $y$ -direction of species  $s$  is defined as,

$$\bar{\lambda}_s = \frac{\lambda_s}{\epsilon L} \quad (5.28)$$

and the dimensionless characteristic time is,

$$\bar{\tau}_s = \frac{\tau_s c_\infty}{L}. \quad (5.29)$$

From ( 5.27)  $\sim$  ( 5.29), we get,

$$\bar{\lambda}_s = \frac{\bar{c}_s \bar{\tau}_s}{\epsilon} \quad (5.30)$$

where  $\bar{c}_s$  is the dimensionless molecular speed of species  $s$  and its magnitude is order of unity.

In our problem, we assumed the following condition for the order of magnitude of each characteristic times in ( 3.8) in chapter 3,

$$\bar{\tau}_{12}, \bar{\tau}_{21} \ll \bar{\tau}_{11}, \bar{\tau}_{22}. \quad (5.31)$$

Therefore, we can assume for  $\bar{\tau}_1$  and  $\bar{\tau}_2$  from ( 5.26),

$$\frac{1}{\bar{\tau}_1} \approx \frac{1}{\bar{\tau}_{12}}, \quad \frac{1}{\bar{\tau}_2} \approx \frac{1}{\bar{\tau}_{21}}. \quad (5.32)$$

From ( 5.30) and ( 5.32), we get,

$$\bar{\lambda}_1 \approx \frac{\bar{c}_1 \bar{\tau}_{12}}{\epsilon}, \quad \bar{\lambda}_2 \approx \frac{\bar{c}_2 \bar{\tau}_{21}}{\epsilon}. \quad (5.33)$$

For Perot's model, i.e.  $\bar{\tau}_{12} = \bar{\tau}_{21} = \bar{\tau}_{av}$ , introduced in Section 3.4 which should be applied to non-reacting terms in ( 3.55) and ( 3.56),

$$\bar{\lambda}_1 \approx \frac{\bar{c}_1 \bar{\tau}_{av}}{\epsilon}, \quad \bar{\lambda}_2 \approx \frac{\bar{c}_2 \bar{\tau}_{av}}{\epsilon}. \quad (5.34)$$

Recalling the condition  $\bar{\lambda}_1, \bar{\lambda}_2 \ll 1$ , we should select  $\bar{\tau}_{av}$  as,

$$\bar{\tau}_{av} = \epsilon^2. \quad (5.35)$$

Once we get ( 5.35), the other condition  $\bar{\tau}_1, \bar{\tau}_2 \ll 1$  in ( 5.25) is automatically satisfied.

Furthermore, if we approximate the dimensionless molecular speed of species  $s$  as,

$$\bar{c}_1 \approx \bar{c}_2 \approx 1, \quad (5.36)$$

we get from ( 5.34),

$$\bar{\lambda}_1 \approx \bar{\lambda}_2 \approx \frac{\bar{\tau}_{av}}{\epsilon} = \epsilon = \bar{\lambda}. \quad (5.37)$$

And, in order to get systematic expansions for our problem, from ( 5.31), we should select  $\bar{\tau}_{11}$  and  $\bar{\tau}_{22}$  simply as,

$$\bar{\tau}_{11} = \bar{\tau}_{22} = \epsilon. \quad (5.38)$$

The expansion parameter  $\epsilon$  can be related to a familiar non-dimensional parameter. From ( 5.32) and ( 5.37), we can write,

$$\bar{\tau}_{av} \approx \epsilon \bar{\lambda} = \frac{\lambda}{L} = K_n \quad (5.39)$$

where  $K_n$  is the Knudsen number. Then, we get,

$$\epsilon = \sqrt{K_n}. \tag{5.40}$$

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

# Chapter 6

## Construction of the distribution functions

In this chapter, the distribution functions of each order of the expansion parameter  $\epsilon$  is constructed from the dimensionless Boltzmann-Krook equations introduced in Chapter 5. Before proceeding with this, another small parameter  $P$  which still exists in the Boltzmann-Krook equations is modeled and expressed in powers of  $\epsilon$  in the first section. In the last section, the procedures to obtain the closed system of equations of motion are discussed, which is a preparation for the later analysis.

### 6.1 Modeling of the parameter $P$

In the dimensionless Boltzmann-Krook equations ( 5.10) and ( 5.11), there still exists another small parameter  $P$  which is the fraction of collisions involving energy greater than the activation energy that is required to cause dissociation. In the nonequilibrium flow, this is expected to be a complicated function of several variables such as temperature, species densities, etc.

However, as Perot [14] pointed out in the case when  $P \rightarrow 0$ , the first order of distribution functions are the Maxwell distribution functions and species temperatures  $T_1, T_2$  are the same as the temperature of the gas mixture at least up to the second

order,

$$T_1^{(0)} = T_2^{(0)} = T^{(0)} \quad T_1^{(1)} = T_2^{(1)} = T^{(1)}. \quad (6.1)$$

These results give the reasonable motivation to select the model of  $P$  for the equilibrium case as an approximation for our problem.

The form of  $P$  for the equilibrium flow, if only the relative translational energy in the direction of the line of centers is specified (see, e.g. Vincenti & Kruger [12]), is given as,

$$P = \exp\left\{-\frac{\Theta}{T}\right\} = \exp\left\{-\frac{\bar{\Theta}}{\bar{T}}\right\}. \quad (6.2)$$

Substituting ( 5.19) into ( 6.2) and expanding in powers of  $\epsilon$ , we get,

$$P = \exp\left\{-\frac{\bar{\Theta}}{\bar{T}^{(0)}}\right\} \left[ 1 - \frac{T^{(1)}}{T^{(0)}}\epsilon + \left\{ \frac{3}{2} \left( \frac{T^{(1)}}{T^{(0)}} \right)^2 - \frac{T^{(2)}}{T^{(0)}} \right\} \epsilon^2 + \dots \right]. \quad (6.3)$$

The term  $P/\bar{\tau}_{av}$  in the right-hand side of ( 5.10) and ( 5.11) can be interpreted as a reciprocal of the dimensionless characteristic time for the chemical reaction,

$$\frac{1}{\bar{\tau}_{chem}} = \frac{P}{\bar{\tau}_{av}} = \frac{1}{\bar{\tau}_{av}/P}. \quad (6.4)$$

Since  $\bar{\tau}_{av} = \epsilon^2$ , we get from ( 6.3) and ( 6.4),

$$\bar{\tau}_{chem} = \frac{\exp\left\{-\frac{\bar{\Theta}}{\bar{T}^{(0)}}\right\}}{\epsilon^2} \left[ 1 - \frac{T^{(1)}}{T^{(0)}}\epsilon + \left\{ \frac{3}{2} \left( \frac{T^{(1)}}{T^{(0)}} \right)^2 - \frac{T^{(2)}}{T^{(0)}} \right\} \epsilon^2 + \dots \right]. \quad (6.5)$$

If we introduce a new parameter  $\alpha$  which is the first order dimensionless chemical characteristic time,

$$\alpha = \frac{\exp\left\{-\frac{\bar{\Theta}}{\bar{T}^{(0)}}\right\}}{\epsilon^2}, \quad (6.6)$$

we can define the model of  $P$  which should be applied in our problem, from ( 6.3) and ( 6.6),

$$P = \alpha\epsilon^2 - \alpha\frac{T^{(1)}}{T^{(0)}}\epsilon^3 + \alpha\left\{ \frac{3}{2} \left( \frac{T^{(1)}}{T^{(0)}} \right)^2 - \frac{T^{(2)}}{T^{(0)}} \right\} \epsilon^4 + \dots \quad (6.7)$$



## 6.2 Construction of the distribution functions

Once all of the physical small parameters can be related to the expansion parameter  $\epsilon$ , we can construct the distribution functions  $\bar{f}_1, \bar{f}_2$  as the solutions of the dimensionless Boltzmann-Krook equations. By substituting the expansion forms of the distribution functions ( 5.20) and the model of  $P$  ( 6.7) into ( 5.10) and ( 5.11) and by replacing the characteristic times  $\bar{\tau}_{av}$  and  $\bar{\tau}_{11}$  ( $= \bar{\tau}_{22}$ ) by  $\epsilon^2$  and  $\epsilon$  respectively, we obtain the following equations,

$$\begin{aligned}
& \epsilon^2 \left[ \frac{\partial f_1^{(0)}}{\partial t} + \epsilon \frac{\partial f_1^{(1)}}{\partial t} + \epsilon^2 \frac{\partial f_1^{(2)}}{\partial t} + \dots \right] + \epsilon \eta_1 \left[ \frac{\partial f_1^{(0)}}{\partial y} + \epsilon \frac{\partial f_1^{(1)}}{\partial y} + \epsilon^2 \frac{\partial f_1^{(2)}}{\partial y} + \dots \right] \\
= & \epsilon \left[ (\Psi_{11}^{(0)} - f_1^{(0)}) + \epsilon (\Psi_{11}^{(1)} - f_1^{(1)}) + \dots \right] \\
& + \left[ (\Psi_{12}^{(0)} - f_1^{(0)}) + \epsilon (\Psi_{12}^{(1)} - f_1^{(1)}) + \dots \right] \\
& + \epsilon^2 \left[ 4 \frac{n_2}{n} \alpha (\Psi_{12}^{(0)} + \epsilon \Psi_{12}^{(1)} + \dots) \left( 1 - \frac{T^{(1)}}{T^{(0)}} \epsilon + \dots \right) \right] \tag{6.8}
\end{aligned}$$

$$\begin{aligned}
& \epsilon^2 \left[ \frac{\partial f_2^{(0)}}{\partial t} + \epsilon \frac{\partial f_2^{(1)}}{\partial t} + \epsilon^2 \frac{\partial f_2^{(2)}}{\partial t} + \dots \right] + \epsilon \eta_2 \left[ \frac{\partial f_2^{(0)}}{\partial y} + \epsilon \frac{\partial f_2^{(1)}}{\partial y} + \epsilon^2 \frac{\partial f_2^{(2)}}{\partial y} + \dots \right] \\
= & \epsilon \left[ (\Psi_{22}^{(0)} - f_2^{(0)}) + \epsilon (\Psi_{22}^{(1)} - f_2^{(1)}) + \dots \right] \\
& + \left[ (\Psi_{21}^{(0)} - f_2^{(0)}) + \epsilon (\Psi_{21}^{(1)} - f_2^{(1)}) + \dots \right] \\
& - \epsilon^2 \left[ 2 \frac{n_1}{n} \alpha (\Psi_{21}^{(0)} + \epsilon \Psi_{21}^{(1)} + \dots) \left( 1 - \frac{T^{(1)}}{T^{(0)}} \epsilon + \dots \right) \right] \tag{6.9}
\end{aligned}$$

where the bars are omitted, but all quantities are dimensionless. The solutions of these equations are obtained by regrouping the terms of the same order of  $\epsilon$ ,

$$f_1^{(0)} = \Psi_{12}^{(0)} \tag{6.10}$$

$$f_1^{(1)} = \Psi_{11}^{(0)} - f_1^{(0)} + \Psi_{12}^{(1)} - \eta_1 \frac{\partial f_1^{(0)}}{\partial y} \tag{6.11}$$

$$f_1^{(2)} = \Psi_{11}^{(1)} - f_1^{(1)} + \Psi_{12}^{(2)} - \eta_1 \frac{\partial f_1^{(1)}}{\partial y} - \frac{\partial f_1^{(0)}}{\partial t} + 4 \frac{n_2^{(0)}}{n^{(0)}} \alpha \Psi_{12}^{(0)} \tag{6.12}$$

$$\begin{aligned}
f_1^{(n)} &= \Psi_{11}^{(n-1)} - f_1^{(n-1)} + \Psi_{12}^{(n)} - \eta_1 \frac{\partial f_1^{(n-1)}}{\partial y} - \frac{\partial f_1^{(n-2)}}{\partial t} \\
&\quad + (\text{terms of } n, n_1, n_2, T, \Psi_{12}, \alpha)
\end{aligned} \tag{6.13}$$

$$f_2^{(0)} = \Psi_{21}^{(0)} \tag{6.14}$$

$$f_2^{(1)} = \Psi_{22}^{(0)} - f_2^{(0)} + \Psi_{21}^{(1)} - \eta_2 \frac{\partial f_2^{(0)}}{\partial y} \tag{6.15}$$

$$f_2^{(2)} = \Psi_{22}^{(1)} - f_2^{(1)} + \Psi_{21}^{(2)} - \eta_2 \frac{\partial f_2^{(1)}}{\partial y} - \frac{\partial f_2^{(0)}}{\partial t} - 2 \frac{n_1^{(0)}}{n^{(0)}} \alpha \Psi_{21}^{(0)} \tag{6.16}$$

$$\begin{aligned}
f_2^{(n)} &= \Psi_{22}^{(n-1)} - f_2^{(n-1)} + \Psi_{21}^{(n)} - \eta_2 \frac{\partial f_2^{(n-1)}}{\partial y} - \frac{\partial f_2^{(n-2)}}{\partial t} \\
&\quad + (\text{terms of } n, n_1, n_2, T, \Psi_{21}, \alpha).
\end{aligned} \tag{6.17}$$

We should note that the  $n$ -th order solutions of the distribution functions  $f_s^{(n)}$  are explicitly expressed by  $f_s$  of the order of less than  $n$  and the Maxwell distribution functions  $\Psi_{sr}$  of the  $n$ -th order. Therefore, if we can obtain  $\Psi_{sr}^{(n)}$  at each step, we can construct the solutions iteratively from the first order system.

### 6.3 Procedures to obtain the closed system of equations of motion

In the previous section, we showed that the  $n$ -th order of distribution functions  $f_s^{(n)}$  are expressed as,

$$f_s^{(n)} = f_s^{(n)} \left( f_s^{(0)}, f_s^{(1)}, \dots, f_s^{(n-1)}; \Psi_{ss}^{(0)}, \Psi_{ss}^{(1)}, \dots, \Psi_{ss}^{(n-1)}; \Psi_{sr}^{(0)}, \Psi_{sr}^{(1)}, \dots, \Psi_{sr}^{(n)} \right). \tag{6.18}$$

Assuming that the solutions of  $f_s$  are obtained until  $(n-1)$ -th order, all the distribution functions within the parenthesis in ( 6.18) are functions of five main unknowns

of the  $n$ -th order, i.e.  $\rho_1^{(n)}, \rho_2^{(n)}, u^{(n)}, v^{(n)}, T^{(n)}$ . Therefore,

$$f_s^{(n)} = f_s^{(n)} (\rho_1^{(n)}, \rho_2^{(n)}, u^{(n)}, v^{(n)}, T^{(n)}) . \quad (6.19)$$

These main unknowns must satisfy the dimensionless equations of motion ( 5.12)  $\sim$  ( 5.16) which should be also expanded in powers of  $\epsilon$ . These main unknowns of the  $n$ -th order are solutions of the system of order  $n$  and the quantities of order of less than  $n$  should have already been determined as solutions of the system of order less than  $n$ .

We should note that there still exist additional five unknowns of order  $n$ , i.e.  $v_1^{(n)}, v_2^{(n)}, P_{xy}^{(n)}, P_{yy}^{(n)}, q_y^{(n)}$  in each order system. These variables must be expressed in terms of the main unknowns. For this purpose, we can use the definitions of these hydrodynamic quantities in terms of the distribution functions which are introduced in Section 2.2 because these distribution functions have already been expressed by the main unknowns.

Once these procedures are completed in each steps of the  $n$ -th order, we can obtain the closed system of equations of motion of order  $n$  expressed with five unknown variables only. This system constructs a closed set of problem of order  $n$  if suitable boundary conditions which should be also expanded in powers of  $\epsilon$  are specified. The boundary conditions on the wall are given in Chapter 4. The outer boundary conditions should be determined by the matching process according to the asymptotic expansion theory, i.e. the outer limit of the inner expansion should coincide with the inner limit of the outer expansion. A brief discussion will be made in Chapter 8.

# Chapter 7

## First and second order systems of governing equations

In this chapter, we get the explicit expressions of the first and second order systems of governing equations by following the procedures mentioned in the previous chapter. In the first section, we get the first and second order distribution functions  $f_s^{(0)}$  and  $f_s^{(1)}$  and use them to eliminate the first order additional unknowns. Finally, we obtain the closed system of the first order equations of motion. In the next section, we iterate similar procedures and get the third order distribution function  $f_s^{(2)}$  and eliminate the second order additional unknowns. And finally, we obtain the closed system of the second order equations of motion.

In this and next chapters, the bars which denote dimensionless variables are omitted but all quantities are dimensionless unless we specify otherwise.

### 7.1 First order system

In order to obtain the solutions of the distribution function  $f_s^{(n)}$ , first of all, we should consider the dimensionless forms of each Maxwell distribution function defined in ( 3.57) ~ ( 3.60) and expand them in powers of  $\epsilon$  since each  $f_s^{(n)}$  contains components of  $\Psi_{s,s}$  up to the  $(n - 1)$ -st order and  $\Psi_{s,r}$  up to the  $n$ -th order.

The dimensionless forms of the Maxwell distribution functions are,

$$\Psi_{ss} = \frac{\rho_s}{(2\pi R_s T_{ss})^{3/2}} \exp \left\{ -\frac{1}{2R_s T_{ss}} [(\xi_s - u)^2 + (\eta_s - \epsilon v)^2 + \zeta_s^2] \right\} \quad (s = 1, 2) \quad (7.1)$$

$$\Psi_{sr} = \frac{\rho_s}{(2\pi R_s T_{12})^{3/2}} \exp \left\{ -\frac{1}{2R_s T_{12}} [(\xi_s - u)^2 + (\eta_s - \epsilon v)^2 + \zeta_s^2] \right\} \quad (s, r = 1, 2; \quad s \neq r) \quad (7.2)$$

where

$$R_s = \frac{\rho_\infty}{2n_\infty m_s} \quad (s = 1, 2) \quad (7.3)$$

as defined in ( 5.18). And,  $n_s$  is related to  $\rho_s$  as,

$$n_s = 2R_s \rho_s \quad (s = 1, 2). \quad (7.4)$$

The dimensionless form of the temperature  $T_{12}$  defined in ( 3.61) can be expanded in powers of  $\epsilon$  with the expression of  $P$  ( 6.7),

$$\begin{aligned} T_{12} &= \frac{3n^2 T - 4n_1 n_2 P E}{3n^2 + 6n_1 n_2 P} \\ &= T^{(0)} + \epsilon T^{(1)} + \epsilon^2 \left\{ -\frac{2n_1^{(0)} n_2^{(0)}}{(n^{(0)})^2} \left( T^{(0)} + \frac{2}{3} E \right) + T^{(2)} \right\} + \dots \end{aligned} \quad (7.5)$$

Then, we get,

$$T_{12}^{(0)} = T^{(0)}. \quad (7.6)$$

By expanding the dimensionless distribution functions  $\Psi_{12}$  and  $\Psi_{21}$  up to the first order, we obtain the forms of  $f_1^{(0)}$  and  $f_2^{(0)}$ ,

$$f_1^{(0)} = \Psi_{12}^{(0)} = \frac{\rho_1^{(0)}}{(2\pi R_1 T^{(0)})^{3/2}} \exp \left\{ -\frac{(\xi_1 - u^{(0)})^2 + \eta_1^2 + \zeta_1^2}{2R_1 T^{(0)}} \right\} \quad (7.7)$$

$$f_2^{(0)} = \Psi_{21}^{(0)} = \frac{\rho_2^{(0)}}{(2\pi R_2 T^{(0)})^{3/2}} \exp \left\{ -\frac{(\xi_2 - u^{(0)})^2 + \eta_2^2 + \zeta_2^2}{2R_2 T^{(0)}} \right\}. \quad (7.8)$$

As mentioned in Chapter 6, the first order main unknown variables which appear in ( 7.7) and ( 7.8) must satisfy the first order system of equations motion which are obtained by expanding ( 5.12)  $\sim$  ( 5.16) in powers of  $\epsilon$ . However, this system contains additional unknowns. Therefore, it is necessary to eliminate them by using the definitions introduced in Chapter 2 to get a closed system. From ( 2.7), ( 2.11) and ( 2.16), the dimensionless forms of  $u_s$ ,  $v_s$ ,  $(P_s)_{xy}$ ,  $(P_s)_{yy}$  and  $(q_s)_y$  are,

$$\rho_s u_s = \int_{\mathbb{R}^3} \xi_s f_s d\vec{\xi}_s \quad (7.9)$$

$$\rho_s v_s = \frac{1}{\epsilon} \int_{\mathbb{R}^3} \eta_s f_s d\vec{\xi}_s \quad (7.10)$$

$$(P_s)_{xy} = \frac{1}{\epsilon} \int_{\mathbb{R}^3} (\xi_s - u) (\eta_s - \epsilon v) f_s d\vec{\xi}_s \quad (7.11)$$

$$(P_s)_{yy} = \int_{\mathbb{R}^3} (\eta_s - \epsilon v)^2 f_s d\vec{\xi}_s \quad (7.12)$$

$$(q_s)_y = \frac{1}{2\epsilon} \int_{\mathbb{R}^3} (\eta_s - \epsilon v) \left\{ (\xi_s - u)^2 + (\eta_s - \epsilon v)^2 + \zeta_s^2 \right\} f_s d\vec{\xi}_s. \quad (7.13)$$

By expanding them in powers of  $\epsilon$ , we get the first order forms,

$$(\rho_s u_s)^{(0)} = \int_{\mathbb{R}^3} \xi_s f_s^{(0)} d\vec{\xi}_s \quad (7.14)$$

$$(\rho_s v_s)^{(0)} = \int_{\mathbb{R}^3} \eta_s f_s^{(1)} d\vec{\xi}_s \quad (7.15)$$

$$(P_s)_{xy}^{(0)} = \int_{\mathbb{R}^3} (\xi_s - u^{(0)}) \eta_s f_s^{(1)} d\vec{\xi}_s \quad (7.16)$$

$$(P_s)_{yy}^{(0)} = \int_{\mathbb{R}^3} \eta_s^2 f_s^{(0)} d\vec{\xi}_s \quad (7.17)$$

$$\begin{aligned} (q_s)_y^{(0)} &= \frac{1}{2} \int_{\mathbb{R}^3} \eta_s \left\{ (\xi_s - u^{(0)})^2 + \eta_s^2 + \zeta_s^2 \right\} f_s^{(1)} d\vec{\xi}_s \\ &\quad - \frac{1}{2} v^{(0)} \int_{\mathbb{R}^3} \left\{ (\xi_s - u^{(0)})^2 + \eta_s^2 + \zeta_s^2 \right\} f_s^{(0)} d\vec{\xi}_s \end{aligned}$$

$$- \int_{\mathbb{R}^3} \eta_s \left\{ (\xi_s - u^{(0)}) u^{(1)} + \eta_s v^{(0)} \right\} f_s^{(0)} d\vec{\xi}_s. \quad (7.18)$$

Since ( 7.14) and ( 7.17) contain the first order distribution function  $f_s^{(0)}$  only, these can be calculated immediately with the expressions ( 7.7) and ( 7.8). A direct substitution gives,

$$u_1^{(0)} = u_2^{(0)} = u^{(0)} \quad (7.19)$$

$$(P_1)_{yy}^{(0)} = \frac{1}{2} n_1^{(0)} T^{(0)}, \quad (P_2)_{yy}^{(0)} = \frac{1}{2} n_2^{(0)} T^{(0)}. \quad (7.20)$$

( 7.19) leads to simpler forms for the various first order temperatures with a simple manipulation (see Appendix C.1),

$$T_1^{(0)} = T_{11}^{(0)} = T_2^{(0)} = T_{22}^{(0)} = T^{(0)}. \quad (7.21)$$

And the definition of the partial stress tensor of the mixture ( 2.12) gives,

$$P_{yy}^{(0)} = \frac{1}{2} n^{(0)} T^{(0)}. \quad (7.22)$$

From the  $y$ -momentum equation ( 5.15),  $P_{yy}$  turns out to be a constant up to the second order,

$$\frac{\partial P_{yy}^{(0)}}{\partial y} = \frac{\partial P_{yy}^{(1)}}{\partial y} = 0. \quad (7.23)$$

From ( 7.22) and ( 7.23), we get,

$$P_{yy}^{(0)} = \frac{1}{2}, \quad n^{(0)} T^{(0)} = 1. \quad (7.24)$$

On the other hand, ( 7.15), ( 7.16) and ( 7.18) contain the second order distribution function  $f_s^{(1)}$ . Therefore, we need to evaluate them with the iterative expressions for  $f_s^{(1)}$  in ( 6.11) and ( 6.15). From ( 7.19) and ( 7.21), the first order Maxwell distribution functions turn out to be,

$$\Psi_{11}^{(0)} = \Psi_{12}^{(0)} = f_1^{(0)} \quad (7.25)$$

$$\Psi_{22}^{(0)} = \Psi_{21}^{(0)} = f_2^{(0)}. \quad (7.26)$$

Substituting ( 7.25) and ( 7.26) into ( 6.11) and ( 6.15) respectively, the second order distribution functions  $f_1^{(1)}$  and  $f_2^{(1)}$  become,

$$f_1^{(1)} = \Psi_{12}^{(1)} - \eta_1 \frac{\partial f_1^{(0)}}{\partial y} \quad (7.27)$$

$$f_2^{(1)} = \Psi_{21}^{(1)} - \eta_2 \frac{\partial f_2^{(0)}}{\partial y}. \quad (7.28)$$

The first terms of the right-hand side of ( 7.27) and ( 7.28) can be obtained by expanding ( 7.2) in powers of  $\epsilon$  and collecting the terms of order  $\epsilon$ ,

$$\Psi_{sr}^{(1)} = \Psi_{sr}^{(0)} \left[ \frac{\rho_s^{(1)}}{\rho_s^{(0)}} + \left( W_{s1}^2 - \frac{3}{2} \right) \frac{T^{(1)}}{T^{(0)}} + W_{s2}^2 \right] \quad (7.29)$$

where

$$W_{s1}^2 = \frac{(\xi_s - u^{(0)})^2 + \eta_s^2 + \zeta_s^2}{2R_s T^{(0)}} \quad (7.30)$$

$$W_{s2}^2 = \frac{(\xi_s - u^{(0)}) u^{(1)} + \eta_s v^{(0)}}{R_s T^{(0)}}. \quad (7.31)$$

The  $y$ -derivative of  $f_s^{(0)}$  in the second terms of the right-hand side of ( 7.27) and ( 7.28) can be easily obtained,

$$\frac{\partial f_s^{(0)}}{\partial y} = f_s^{(0)} \left[ \frac{1}{\rho^{(0)}} \frac{\partial \rho_s^{(0)}}{\partial y} + \left( W_{s1}^2 - \frac{3}{2} \right) \frac{1}{T^{(0)}} \frac{\partial T^{(0)}}{\partial y} + \frac{\xi_s - u^{(0)}}{R_s T^{(0)}} \frac{\partial u^{(0)}}{\partial y} \right]. \quad (7.32)$$

Then, we get the second order distribution function  $f_s^{(1)}$ ,

$$\begin{aligned} \frac{f_s^{(1)}}{f_s^{(0)}} &= \frac{\rho_s^{(1)}}{\rho_s^{(0)}} + \left( W_{s1}^2 - \frac{3}{2} \right) \frac{T^{(1)}}{T^{(0)}} + W_{s2}^2 \\ &\quad - \eta_s \left[ \frac{1}{\rho^{(0)}} \frac{\partial \rho_s^{(0)}}{\partial y} + \left( W_{s1}^2 - \frac{3}{2} \right) \frac{1}{T^{(0)}} \frac{\partial T^{(0)}}{\partial y} + \frac{\xi_s - u^{(0)}}{R_s T^{(0)}} \frac{\partial u^{(0)}}{\partial y} \right]. \end{aligned} \quad (7.33)$$

With this expression, ( 7.15), ( 7.16) and ( 7.18) can be evaluated as,

$$\rho_s^{(0)} v_s^{(0)} = \rho_s^{(0)} v^{(0)} - \frac{1}{2} \frac{\partial (n_s T)^{(0)}}{\partial y} \quad (7.34)$$



$$(P_s)_{xy}^{(0)} = -\frac{1}{2}n_s^{(0)}T^{(0)}\frac{\partial u^{(0)}}{\partial y} \quad (7.35)$$

$$(q_s)_y^{(0)} = -\frac{5}{4}\frac{\partial}{\partial y}\left\{n_1^{(0)}R_s\left(T^{(0)}\right)^2\right\}. \quad (7.36)$$

In these manipulations, we must integrate the moments of  $f_s^{(1)}$ . This can be simplified by using the formula proposed by Perot [14] (see Appendix C.2).

By summing up ( 7.35) and ( 7.36) over both species, we can get the mixture quantities,

$$P_{xy}^{(0)} = -\frac{1}{2}\frac{\partial u^{(0)}}{\partial y} \quad (7.37)$$

$$q_y^{(0)} = -\frac{5}{4}\frac{\partial}{\partial y}\left\{\tilde{n}T^2\right\}^{(0)} \quad (7.38)$$

where

$$\tilde{n} = n_1R_1 + n_2R_2. \quad (7.39)$$

Once the first order additional unknowns;  $v_1^{(0)}$ ,  $v_2^{(0)}$ ,  $P_{xy}^{(0)}$ ,  $P_{yy}^{(0)}$  and  $q_y^{(0)}$  are expressed in terms of the main unknowns in ( 7.24) and ( 7.34) ~ ( 7.36), the closed first order system of equations of motion can be obtained by expanding ( 5.12) ~ ( 5.16) in powers of  $\epsilon$  and collecting the terms independent of  $\epsilon$  (see Appendix C.3 for detail of the derivation of the energy equation),

$$\frac{\partial n_1^{(0)}}{\partial t} + \frac{\partial (n_1^{(0)}v^{(0)})}{\partial y} = \frac{\partial^2 (n_1^{(0)}R_1T^{(0)})}{\partial y^2} + 4\frac{n_1^{(0)}n_2^{(0)}}{n^{(0)}}\alpha \quad (7.40)$$

$$\frac{\partial n_2^{(0)}}{\partial t} + \frac{\partial (n_2^{(0)}v^{(0)})}{\partial y} = \frac{\partial^2 (n_2^{(0)}R_2T^{(0)})}{\partial y^2} - 2\frac{n_1^{(0)}n_2^{(0)}}{n^{(0)}}\alpha \quad (7.41)$$

$$\rho^{(0)}\left(\frac{\partial u^{(0)}}{\partial t} + v^{(0)}\frac{\partial u^{(0)}}{\partial y}\right) - \frac{1}{2}\frac{\partial^2 u^{(0)}}{\partial y^2} = 0 \quad (7.42)$$

$$n^{(0)}T^{(0)} = 1 \quad (7.43)$$

$$\frac{5}{4}\frac{\partial v^{(0)}}{\partial y} - \frac{1}{2}\left(\frac{\partial u^{(0)}}{\partial y}\right)^2 - \frac{5}{4}\frac{\partial^2}{\partial y^2}\left\{(n_1^{(0)}R_1 + n_2^{(0)}R_2)\left(T^{(0)}\right)^2\right\} + \frac{n_1^{(0)}n_2^{(0)}}{n^{(0)}}\alpha E = 0. \quad (7.44)$$

## 7.2 Second order system

The procedures to obtain the second order system of governing equations are similar to those for the first order explained in the previous section although the second order case contains much more complicated manipulations.

The second order distribution function  $f_s^{(1)}$  has already been obtained in ( 7.33) in the previous section. It contains the second order main unknown variables;  $\rho_1^{(1)}$ ,  $\rho_2^{(1)}$ ,  $u^{(1)}$ ,  $v^{(1)}$  and  $T^{(1)}$ . They must satisfy the second order system of equations of motion which are obtained by collecting the terms of order  $\epsilon$  in the expansions ( 5.12)  $\sim$  ( 5.16). This system also contains the additional second order unknowns;  $v_1^{(1)}$ ,  $v_2^{(1)}$ ,  $P_{xy}^{(1)}$ ,  $P_{yy}^{(1)}$  and  $q_y^{(1)}$ . Therefore, in order to get the closed system of second order equations of motion, these additional unknowns should be eliminated.

By expanding ( 7.9)  $\sim$  ( 7.13) and collecting the terms of order  $\epsilon$ , we get the expressions of the second order additional unknown variables,

$$(\rho_s u_s)^{(1)} = \int_{\mathbb{R}^3} \xi_s f_s^{(1)} d\vec{\xi}_s \quad (7.45)$$

$$(\rho_s v_s)^{(1)} = \int_{\mathbb{R}^3} \eta_s f_s^{(2)} d\vec{\xi}_s \quad (7.46)$$

$$\begin{aligned} (P_s)_{xy}^{(1)} &= \int_{\mathbb{R}^3} (\xi_s - u^{(0)}) \eta_s f_s^{(2)} d\vec{\xi}_s + \rho_1^{(0)} u^{(1)} v^{(0)} - u^{(1)} \int_{\mathbb{R}^3} \eta_s f_s^{(1)} d\vec{\xi}_s \\ &\quad - v^{(0)} \int_{\mathbb{R}^3} (\xi_s - u^{(0)}) f_s^{(1)} d\vec{\xi}_s \end{aligned} \quad (7.47)$$

$$(P_s)_{yy}^{(1)} = \int_{\mathbb{R}^3} \eta_s^2 f_s^{(1)} d\vec{\xi}_s \quad (7.48)$$

$$\begin{aligned} (q_s)_y^{(1)} &= \frac{1}{2} \int_{\mathbb{R}^3} \eta_s \left[ (\xi_s - u^{(0)})^2 + \eta_s^2 + \zeta_s^2 \right] f_s^{(2)} d\vec{\xi}_s \\ &\quad - \frac{1}{2} v^{(1)} \int_{\mathbb{R}^3} \left[ (\xi_s - u^{(0)})^2 + 3\eta_s^2 + \zeta_s^2 \right] f_s^{(0)} d\vec{\xi}_s \\ &\quad - \int_{\mathbb{R}^3} \eta_s \left[ (\xi_s - u^{(0)}) u^{(1)} + \eta_s v^{(0)} \right] f_s^{(1)} d\vec{\xi}_s \\ &\quad - \frac{1}{2} v^{(0)} \int_{\mathbb{R}^3} \left[ (\xi_s - u^{(0)})^2 + \eta_s^2 + \zeta_s^2 \right] f_s^{(1)} d\vec{\xi}_s. \end{aligned} \quad (7.49)$$

As in the first order case, ( 7.45) and ( 7.48) can be calculated immediately with the expression of  $f_s^{(1)}$  in ( 7.33), however, to calculate ( 7.46), ( 7.47) and ( 7.49), the third order distribution function  $f_s^{(2)}$  must be evaluated beforehand.

By substituting ( 7.33) into ( 7.45) and ( 7.48), we get,

$$u_1^{(1)} = u_2^{(1)} = u^{(1)} \quad (7.50)$$

$$(P_1)_{yy}^{(1)} = \frac{1}{2} (n_1 T)^{(1)}, \quad (P_1)_{yy}^{(2)} = \frac{1}{2} (n_2 T)^{(1)}. \quad (7.51)$$

Then, the stress tensor of the mixture becomes,

$$(P)_{yy}^{(1)} = \frac{1}{2} (nT)^{(1)} = \frac{1}{2} \left( n^{(1)} T^{(0)} + n^{(0)} T^{(1)} \right). \quad (7.52)$$

And, the various second order temperatures can be obtained in the same way as for the first order case from ( 7.50) (see Appendix D.1),

$$T_1^{(1)} = T_{11}^{(1)} = T_2^{(1)} = T_{22}^{(1)} = T^{(1)}. \quad (7.53)$$

Furthermore, recalling ( 7.23), we get the following expression for the  $y$ -momentum equation,

$$P_{yy}^{(1)} = 0 \quad (7.54)$$

$$\frac{n^{(1)}}{n^{(0)}} + \frac{T^{(1)}}{T^{(0)}} = 0. \quad (7.55)$$

The third order distribution function  $f_s^{(2)}$  can be obtained by evaluating each terms in ( 6.12) and ( 6.16). The second order Maxwell distribution function  $\Psi_{ss}^{(1)}$  has the similar form to  $\Psi_{sr}^{(1)}$ ,

$$\Psi_{ss}^{(1)} = \Psi_{ss}^{(0)} \left[ \frac{\rho_s^{(1)}}{\rho_s^{(0)}} + \left( W_{s1}^2 - \frac{3}{2} \right) \frac{T^{(1)}}{T^{(0)}} + \frac{(\xi_s - u^{(0)}) u^{(1)} + \eta_s v_s^{(0)}}{R_s T^{(0)}} \right]. \quad (7.56)$$

By replacing  $v_s^{(0)}$  in ( 7.56) by using the expression ( 7.34) and subtracting  $f_s^{(1)}$ , we

get,

$$\Psi_{ss}^{(1)} - f_s^{(1)} = \eta_s f_s^{(0)} \left[ \left( W_{s1}^2 - \frac{5}{2} \right) \frac{1}{T^{(0)}} \frac{\partial T^{(0)}}{\partial y} + \frac{\xi_s - u^{(0)}}{R_s T^{(0)}} \frac{\partial u^{(0)}}{\partial y} \right]. \quad (7.57)$$

The third order Maxwell distribution function  $\Psi_{sr}^{(2)}$  can be obtained by expanding ( 7.2) in powers of  $\epsilon$  and collecting the terms of order  $\epsilon^2$ ,

$$\begin{aligned} \frac{\Psi_{sr}^{(2)}}{f_s^{(0)}} &= \frac{\rho_s^{(2)}}{\rho_s^{(0)}} + \left( W_{s1}^2 - \frac{3}{2} \right) \frac{T_{12}^{(2)}}{T^{(0)}} \\ &+ \left[ \left( \frac{1}{2} W_{s1}^4 - \frac{5}{2} W_{s1}^2 + \frac{15}{8} \right) \frac{T^{(1)}}{T^{(0)}} + \left( W_{s1}^2 - \frac{3}{2} \right) \frac{\rho_s^{(1)}}{\rho_s^{(0)}} + \left( W_{s1}^2 - \frac{5}{2} \right) W_{s2}^2 \right] \frac{T^{(1)}}{T^{(0)}} \\ &+ W_{s2}^2 \frac{\rho_s^{(1)}}{\rho_s^{(0)}} + \frac{1}{2} W_{s2}^4 - W_{s3}^2 \end{aligned} \quad (7.58)$$

where

$$W_{s3}^2 = \frac{(u^{(1)})^2 + (v^{(0)})^2 - 2 \left[ (\xi_s - u^{(0)}) u^{(2)} + \eta_1 v^{(1)} \right]}{2R_s T^{(0)}} \quad (7.59)$$

$$T_{12}^{(2)} = T^{(2)} - 2 \frac{n_1^{(0)} n_2^{(0)}}{(n^{(0)})^2} \left( T^{(0)} + \frac{2}{3} E \right). \quad (7.60)$$

From ( 7.33), the  $y$ -derivative of  $f_s^{(1)}$  is given as,

$$\begin{aligned} \frac{\partial f_s^{(1)}}{\partial y} &= f_s^{(0)} \left\{ \frac{\partial}{\partial y} \left[ \frac{\rho_s^{(1)}}{\rho_s^{(0)}} + \left( W_{s1}^2 - \frac{3}{2} \right) \frac{T^{(1)}}{T^{(0)}} + W_{s2}^2 \right] \right. \\ &- \eta_s \frac{\partial}{\partial y} \left[ \frac{1}{\rho^{(0)}} \frac{\partial \rho_s^{(0)}}{\partial t} + \left( W_{s1}^2 - \frac{3}{2} \right) \frac{1}{T^{(0)}} \frac{\partial T^{(0)}}{\partial y} + \frac{\xi_s - u^{(0)}}{R_s T^{(0)}} \frac{\partial u^{(0)}}{\partial y} \right] \\ &+ \left[ \frac{\rho_s^{(1)}}{\rho_s^{(0)}} + \left( W_{s1}^2 - \frac{3}{2} \right) \frac{T^{(1)}}{T^{(0)}} + W_{s2}^2 \right] \\ &\quad \left[ \frac{1}{\rho^{(0)}} \frac{\partial \rho_s^{(0)}}{\partial t} + \left( W_{s1}^2 - \frac{3}{2} \right) \frac{1}{T^{(0)}} \frac{\partial T^{(0)}}{\partial y} + \frac{\xi_s - u^{(0)}}{R_s T^{(0)}} \frac{\partial u^{(0)}}{\partial y} \right] \\ &\left. - \eta_s \left[ \frac{1}{\rho^{(0)}} \frac{\partial \rho_s^{(0)}}{\partial t} + \left( W_{s1}^2 - \frac{3}{2} \right) \frac{1}{T^{(0)}} \frac{\partial T^{(0)}}{\partial y} + \frac{\xi_s - u^{(0)}}{R_s T^{(0)}} \frac{\partial u^{(0)}}{\partial y} \right]^2 \right\}. \quad (7.61) \end{aligned}$$

And, the time derivative of  $f_s^{(0)}$  is given as,

$$\frac{f_s^{(0)}}{\partial t} = f_s^{(0)} \left[ \frac{1}{\rho^{(0)}} \frac{\partial \rho_s^{(0)}}{\partial t} + \left( W_{s1}^2 - \frac{3}{2} \right) \frac{1}{T^{(0)}} \frac{\partial T^{(0)}}{\partial t} + \frac{\xi_s - u^{(0)}}{R_s T^{(0)}} \frac{\partial u^{(0)}}{\partial t} \right]. \quad (7.62)$$

Substituting these expressions ( 7.57)  $\sim$  ( 7.62) into ( 6.12) and ( 6.16), we get

the third order distribution function  $f_s^{(2)}$ ,

$$\begin{aligned}
\frac{f_s^{(2)}}{f_s^{(0)}} &= \frac{\rho_s^{(2)}}{\rho_s^{(0)}} + \left(W_{s1}^2 - \frac{3}{2}\right) \frac{T_{12}^{(2)}}{T^{(0)}} \\
&+ \left[ \left(\frac{1}{2}W_{s1}^4 - \frac{5}{2}W_{s1}^2 + \frac{15}{8}\right) \frac{T^{(1)}}{T^{(0)}} + \left(W_{s1}^2 - \frac{3}{2}\right) \frac{\rho_s^{(1)}}{\rho_s^{(0)}} + \left(W_{s1}^2 - \frac{5}{2}\right) W_{s2}^2 \right] \frac{T^{(1)}}{T^{(0)}} \\
&+ W_{s2}^2 \frac{\rho_s^{(1)}}{\rho_s^{(0)}} + \frac{1}{2}W_{s2}^4 - W_{s3}^2 \\
&- \left[ \frac{1}{\rho_s^{(0)}} \frac{\partial \rho_s^{(0)}}{\partial t} + \left(W_{s1}^2 - \frac{3}{2}\right) \frac{1}{T^{(0)}} \frac{\partial T^{(0)}}{\partial t} + \frac{\xi_s - u^{(0)}}{R_s T^{(0)}} \frac{\partial u^{(0)}}{\partial t} \right] \\
&+ \eta_s \left[ \left(W_{s1}^2 - \frac{5}{2}\right) \frac{1}{T^{(0)}} \frac{\partial T^{(0)}}{\partial y} + \frac{\xi_s - u^{(0)}}{R_s T^{(0)}} \frac{\partial u^{(0)}}{\partial y} \right] \\
&- \eta_s \frac{\partial}{\partial y} \left[ \frac{\rho_s^{(1)}}{\rho_s^{(0)}} + \left(W_{s1}^2 - \frac{3}{2}\right) \frac{T^{(1)}}{T^{(0)}} + W_{s2}^2 \right] \\
&+ \eta_s^2 \frac{\partial}{\partial y} \left[ \frac{1}{\rho_s^{(0)}} \frac{\partial \rho_s^{(0)}}{\partial y} + \left(W_{s1}^2 - \frac{3}{2}\right) \frac{1}{T^{(0)}} \frac{\partial T^{(0)}}{\partial y} + \frac{\xi_s - u^{(0)}}{R_s T^{(0)}} \frac{\partial u^{(0)}}{\partial y} \right] \\
&- \eta_s \left[ \frac{\rho_s^{(1)}}{\rho_s^{(0)}} + \left(W_{s1}^2 - \frac{3}{2}\right) \frac{T^{(1)}}{T^{(0)}} + W_{s2}^2 \right] \\
&\quad \left[ \frac{1}{\rho_s^{(0)}} \frac{\partial \rho_s^{(0)}}{\partial y} + \left(W_{s1}^2 - \frac{3}{2}\right) \frac{1}{T^{(0)}} \frac{\partial T^{(0)}}{\partial y} + \frac{\xi_s - u^{(0)}}{R_s T^{(0)}} \frac{\partial u^{(0)}}{\partial y} \right] \\
&+ \eta_s^2 \left[ \frac{1}{\rho_s^{(0)}} \frac{\partial \rho_s^{(0)}}{\partial y} + \left(W_{s1}^2 - \frac{3}{2}\right) \frac{1}{T^{(0)}} \frac{\partial T^{(0)}}{\partial y} + \frac{\xi_s - u^{(0)}}{R_s T^{(0)}} \frac{\partial u^{(0)}}{\partial y} \right]^2 \\
&+ F_R
\end{aligned} \tag{7.63}$$

where

$$\begin{aligned}
F_R &= +4 \frac{n^{(2)}}{n^{(0)}} \alpha \quad (\text{for } s = 1) \\
F_R &= -2 \frac{n^{(1)}}{n^{(0)}} \alpha \quad (\text{for } s = 2).
\end{aligned} \tag{7.64}$$

$f_1^{(2)}$  and  $f_2^{(2)}$  have different forms because the chemical reaction terms appear in them differently.

With this expression of  $f_s^{(2)}$ , we can calculate ( 7.46), ( 7.47) and ( 7.49) which

are the moments of  $f_s^{(2)}$ . After cumbersome manipulations, we obtain,

$$(\rho_s v_s)^{(1)} = (\rho_s v)^{(1)} - \frac{1}{2} \frac{\partial (n_s T)^{(1)}}{\partial y} \quad (7.65)$$

$$(P_s)_{xy}^{(1)} = \frac{1}{2} n_s^{(0)} T^{(0)} \frac{\partial u^{(0)}}{\partial y} - \frac{1}{2} (n_s T)^{(1)} \frac{\partial u^{(0)}}{\partial y} - \frac{1}{2} n_s^{(0)} T^{(0)} \frac{\partial u^{(1)}}{\partial y} \quad (7.66)$$

$$(q_s)_y^{(1)} = -\frac{5}{4} \frac{\partial}{\partial y} \left\{ R_s (n_s T^2)^{(1)} \right\} + \frac{5}{4} R_s n_s^{(0)} T^{(0)} \frac{\partial T^{(0)}}{\partial y}. \quad (7.67)$$

As in the first order case, these calculations of the moments of  $f_s^{(2)}$  can be simplified drastically by using the formula proposed by Perot [14] (see Appendix D.2). By summing up ( 7.66) and ( 7.67) over both species, we can get the second order partial stress tensor and heat flux vector of the mixture of gases,

$$(P)_{xy}^{(1)} = \frac{1}{2} \frac{\partial u^{(0)}}{\partial y} - \frac{1}{2} \frac{\partial u^{(1)}}{\partial y} \quad (7.68)$$

$$(q)_y^{(1)} = -\frac{5}{4} \frac{\partial (\bar{n} T^2)^{(1)}}{\partial y} + \frac{5}{4} \bar{n}^{(0)} T^{(0)} \frac{\partial T^{(0)}}{\partial y}. \quad (7.69)$$

Having determined the second order additional unknowns expressed in terms of the second order main unknowns in ( 7.50), ( 7.54), ( 7.68) and ( 7.69), we can obtain the second order system of equations of motion by expanding ( 5.12)  $\sim$  ( 5.16) in powers of  $\epsilon$ , and collecting the terms of order  $\epsilon$  (see Appendix D.3 for detail of the derivation of the energy equation),

$$\frac{\partial n_1^{(1)}}{\partial t} + \frac{\partial (n_1 v)^{(1)}}{\partial y} = \frac{\partial^2 (n_1 R_1 T)^{(1)}}{\partial y^2} + 4 \frac{(n_1 n_2)^{(1)}}{n^{(0)}} \alpha \quad (7.70)$$

$$\frac{\partial n_2^{(1)}}{\partial t} + \frac{\partial (n_2 v)^{(1)}}{\partial y} = \frac{\partial^2 (n_2 R_2 T)^{(1)}}{\partial y^2} - 2 \frac{(n_1 n_2)^{(1)}}{n^{(0)}} \alpha \quad (7.71)$$

$$\rho^{(0)} \left( \frac{\partial u^{(1)}}{\partial t} + v^{(0)} \frac{\partial u^{(1)}}{\partial y} \right) - \frac{1}{2} \frac{\partial^2 u^{(1)}}{\partial y^2} = -\rho^{(0)} v^{(1)} \frac{\partial u^{(0)}}{\partial y} - \frac{1}{2} \left( 1 + \frac{\rho^{(1)}}{\rho^{(0)}} \right) \frac{\partial^2 u^{(0)}}{\partial y^2} \quad (7.72)$$

$$\frac{n^{(1)}}{n^{(0)}} + \frac{T^{(1)}}{T^{(0)}} = 0 \quad (7.73)$$

$$\begin{aligned}
& \frac{5}{4} \frac{\partial v^{(1)}}{\partial y} - \frac{\partial u^{(0)}}{\partial y} \frac{\partial u^{(1)}}{\partial y} - \frac{5}{4} \frac{\partial^2 (\tilde{n} T^2)^{(1)}}{\partial y^2} \\
= & -\frac{1}{2} \left( \frac{\partial u^{(0)}}{\partial y} \right)^2 - \frac{5}{4} \frac{\partial}{\partial y} \left( \tilde{n} T \frac{\partial T}{\partial y} \right)^{(0)} - \frac{(n_1 n_2)^{(1)}}{n^{(0)}} \alpha E - \frac{3}{2} \frac{n_1^{(0)} n_2^{(0)}}{n^{(0)}} T^{(1)} \alpha. \quad (7.74)
\end{aligned}$$

The second order main unknown variables;  $\rho_1^{(1)}$ ,  $\rho_2^{(1)}$ ,  $u^{(1)}$ ,  $v^{(1)}$  and  $T^{(1)}$  must satisfy this system and the third order distribution function  $f_s^{(2)}$  in ( 7.63) can be fully determined by them.

# Chapter 8

## First and second order boundary conditions

In this chapter, we get the explicit expressions of the first and second order boundary conditions derived in Chapter 4. In the first and second sections, we obtain the boundary conditions for the velocity in the  $y$ -direction  $v$  and the atom density  $\rho_1$  respectively. In the next section, we obtain the slip conditions for the tangential velocity  $u$  and the temperature  $T$ . In the last section, we consider the energy balance on the wall when the adiabatic wall condition is given.

These boundary conditions define a closed set of problems of the first and second order with the equations of motion derived in Chapter 7.

### 8.1 First and second order boundary conditions for the velocity $v$

The dimensionless boundary condition for  $v$  is given as, from ( 4.2),

$$v(0) = 0. \tag{8.1}$$



Therefore, we get the  $n$ -th order boundary condition for the velocity  $v$  simply,

$$v^{(0)}(0) = v^{(1)}(0) = \dots = v^{(n)}(0) = 0. \quad (8.2)$$

## 8.2 First and second order boundary conditions for the atom density

The dimensional boundary condition for the atom density  $\rho_1$  is given in (4.4). As pointed out in Section 4.3, when  $\gamma$  is order of unity,  $k_w$  in (4.4) is of the same order as the speed of sound. Then, if we define the dimensionless form of  $k_w$  as,

$$\bar{k}_w = \frac{k_w}{c_\infty}, \quad (8.3)$$

the dimensionless boundary condition for  $\rho_1$  becomes,

$$\epsilon(\rho_1 v_1)(0) = -k_w \rho_1(0) \quad (8.4)$$

where the bar was omitted. The dimensionless form of  $k_w$  in (8.4) can be obtained by non-dimensionalizing (4.9),

$$k_w = -\frac{\gamma}{\rho_1(0)} \int_{-\infty}^{\infty} \int_{-\infty}^0 \int_{-\infty}^{\infty} \eta_1 f_1(-\eta_1 \epsilon^2, t - \epsilon^2) d\xi_1 d\eta_1 d\zeta_1 \quad (8.5)$$

where we used the relation  $\tau_1 = \epsilon^2 (= \tau_{av})$ .

By expanding (8.4) in powers of  $\epsilon$  and collecting the terms independent of  $\epsilon$  and of order  $\epsilon$  respectively, we can get the following first and second order boundary conditions for  $\rho_1$ ,

$$\rho_1^{(0)}(0) = 0 \quad (8.6)$$

$$(\rho_1 v_1)^{(0)}(0) = -k_w^{(0)} \rho_1^{(1)}(0). \quad (8.7)$$

From the result of (8.6),

$$\rho_1(0) = \epsilon \rho_1^{(1)}(0) + O(\epsilon^2) \quad (8.8)$$

$$\begin{aligned}
f_1(-\eta_1 \epsilon^2, t - \epsilon^2) &= f_1^{(0)}(0, t) + \epsilon f_1^{(1)}(0, t) + \epsilon^2 \left( f_1^{(2)}(0, t) + \frac{1}{2} \eta_1^2 \left( \frac{\partial^2 f_1^{(0)}}{\partial y^2} \right)_{y=0, t=t} \right) \\
&= \epsilon f_1^{(1)}(0) + O(\epsilon^2).
\end{aligned} \tag{8.9}$$

Then,  $k_w^{(0)}$  becomes,

$$k_w^{(0)} = -\frac{\gamma}{\rho_1^{(0)}(0)} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \eta_1 f_1^{(1)}(0) d\xi_1 d\eta_1 d\zeta_1. \tag{8.10}$$

When  $\rho_1^{(0)} = 0$ , the expression for  $f_1^{(1)}$  in ( 7.33) is simplified as,

$$f_1^{(1)}(0) = \left[ \rho_1^{(1)}(0) - \eta_1 \left( \frac{\partial \rho_1^{(0)}}{\partial y} \right)_{y=0} \right] \frac{1}{(2\pi R_1 T^{(0)})^{3/2}} \exp \left\{ -\frac{1}{2R_1 T^{(0)}} [(\xi_1 - u)^2 + \eta_1^2 + \zeta_1^2] \right\}. \tag{8.11}$$

Substituting ( 8.11) into ( 8.10), we get,

$$k_w^{(0)} = \gamma \sqrt{\frac{R_1 T^{(0)}}{2\pi}} + \frac{\gamma}{2} R_1 T^{(0)} \frac{1}{\rho_1^{(1)}(0)} \left( \frac{\partial \rho_1^{(0)}}{\partial y} \right)_{y=0} \tag{8.12}$$

Substituting ( 8.12) and the expression ( 7.34) with  $v^{(0)} = 0$  into ( 8.7) and recalling the relations  $R_1 = \rho_\infty / 2m_1 n_\infty$  and  $\rho_1 = n_1 / 2R_1$ , the second order boundary condition for  $\rho_1$  becomes,

$$\rho_1^{(1)}(0) = \frac{2 - \gamma}{4\gamma} \sqrt{\frac{2\pi T^{(0)}}{R_1}} \left( \frac{\partial n_1^{(0)}}{\partial y} \right)_{y=0}. \tag{8.13}$$

In ( 8.13), we assume that  $\gamma$  is order of unity since the surface is highly catalytic as mentioned in Chapter 1 and 4. When the order of  $\gamma$  is less than unity, a ordering of terms in ( 8.4) should be changed.

### 8.3 First and second order slip conditions on the wall

The dimensionless slip conditions which can be derived from ( 4.26)  $\sim$  ( 4.31) are,

$$\rho u(0) = \frac{2 - \theta_1}{2 - \gamma} \rho_1(0) u_1(\epsilon, t - \epsilon^2) + \frac{\theta_1 - \gamma}{2 - \gamma} \rho_1(0) u_w + \rho_2(0) \left( \frac{F_2}{F_1} \right) \quad (8.14)$$

where

$$F_1 = 2 + \gamma \left( \frac{\rho_{1in} v_{1in}}{\rho_{2in} v_{2in}} \right) \quad (8.15)$$

$$F_2 = (2 - \theta_2) u_2(\epsilon, t - \epsilon^2) + \theta_2 u_w + \gamma \left( \frac{\rho_{1in} v_{1in}}{\rho_{2in} v_{2in}} \right) u_w. \quad (8.16)$$

And,

$$nT(0) = \frac{2 - \theta_1}{2 - \gamma} n_1(0) T_1(\epsilon, t - \epsilon^2) + \frac{\theta_1 - \gamma}{2 - \gamma} n_1(0) T_w + n_2(0) \left( \frac{G_2}{G_1} \right) \quad (8.17)$$

where

$$G_1 = 2 + \frac{\gamma}{2} \left( \frac{n_{1in} v_{1in}}{n_{2in} v_{2in}} \right). \quad (8.18)$$

$$G_2 = (2 - \theta_2) T_2(\epsilon, t - \epsilon^2) + \theta_2 T_w + \frac{\gamma}{2} \left( \frac{n_{1in} v_{1in}}{n_{2in} v_{2in}} \right) T_w. \quad (8.19)$$

With the relation  $\rho_1^{(0)} = 0$ , we can write, from ( 4.16) and ( 4.17),

$$\left( \frac{\rho_{1in} v_{1in}}{\rho_{2in} v_{2in}} \right) = \epsilon \left( \frac{\rho_{1in} v_{1in}}{\rho_{2in} v_{2in}} \right)^{(1)} + O(\epsilon^2) \quad (8.20)$$

and,

$$\left( \frac{n_{1in} v_{1in}}{n_{2in} v_{2in}} \right) = \epsilon \left( \frac{n_{1in} v_{1in}}{n_{2in} v_{2in}} \right)^{(1)} + O(\epsilon^2). \quad (8.21)$$

Then, from ( 4.27), ( 4.28), ( 4.30) and ( 4.31),

$$F_1^{(0)} = 2 \quad (8.22)$$

$$F_2^{(0)} = (2 - \theta_2) u_2^{(0)} + \theta_2 u_w \quad (8.23)$$

$$G_1^{(0)} = 2 \quad (8.24)$$

$$G_2^{(0)} = (2 - \theta_2)T_2^{(0)} + \theta_2 T_w \quad (8.25)$$

The first order form of  $\rho u(0)$ ,  $nT(0)$  are given from ( 4.26) and ( 4.29),

$$(\rho u)^{(0)}(0) = \rho_2^{(0)}(0) \left( \frac{F_2}{F_1} \right)^{(0)} \quad (8.26)$$

$$(nT)^{(0)}(0) = n_2^{(0)}(0) \left( \frac{G_2}{G_1} \right)^{(0)}. \quad (8.27)$$

Substituting ( 8.22)  $\sim$  ( 8.25) into ( 8.26) and ( 8.27) and using the relation  $\rho^{(0)}(0) = \rho_2^{(0)}(0)$ ,  $n^{(0)}(0) = n_2^{(0)}(0)$ ,  $u_2^{(0)} = u^{(0)}$  and  $T_2^{(0)} = T^{(0)}$ , we get the first order slip conditions,

$$u^{(0)} = u_w^{(0)} \quad (8.28)$$

$$T^{(0)} = T_w^{(0)}. \quad (8.29)$$

Therefore, it turns out that the first order tangential velocity and temperature are the wall velocity and the wall temperature respectively.

The second order form of  $\rho u(0)$ ,  $nT(0)$  are given from ( 8.14) and ( 8.17),

$$(\rho u)^{(1)}(0) = \frac{2 - \theta}{2 - \gamma} \rho_1^{(1)} u_1^{(0)}(0) + \frac{\theta - \gamma}{2 - \gamma} \rho_1^{(1)} u_w^{(0)} + \rho_2^{(1)}(0) \left( \frac{F_2}{F_1} \right)^{(0)} + \rho_2^{(0)}(0) \left( \frac{F_2}{F_1} \right)^{(1)} \quad (8.30)$$

$$(nT)^{(1)}(0) = \frac{2 - \theta}{2 - \gamma} n_1^{(1)} T_1^{(0)}(0) + \frac{\theta - \gamma}{2 - \gamma} n_1^{(1)} T_w^{(0)} + n_2^{(1)}(0) \left( \frac{G_2}{G_1} \right)^{(0)} + n_2^{(0)}(0) \left( \frac{G_2}{G_1} \right)^{(1)}. \quad (8.31)$$

From ( 8.22) and ( 8.23),

$$\left( \frac{F_2}{F_1} \right)^{(0)} = u_w^{(0)} \quad (8.32)$$

and,

$$\left( \frac{F_2}{F_1} \right)^{(1)} = \frac{F_2^{(1)}}{F_1^{(0)}} - \left( \frac{F_2}{F_1} \right)^{(0)} \frac{F_1^{(1)}}{F_1^{(0)}}. \quad (8.33)$$

Substituting ( 8.32) and ( 8.33) into ( 8.30), we get

$$\rho^{(0)}u^{(1)} = \rho_2^{(0)} \frac{1}{F_1^{(0)}} \left( F_2^{(1)} - u_w^{(0)} F_1^{(1)} \right). \quad (8.34)$$

In the same way for  $(nT)^{(1)}(0)$ , we get,

$$n^{(0)}T^{(1)} = n_2^{(0)} \frac{1}{G_1^{(0)}} \left( G_2^{(1)} - T_w^{(0)} G_1^{(1)} \right). \quad (8.35)$$

The second order  $F_1^{(1)}$  and  $F_2^{(1)}$  are, from ( 8.15) and ( 8.16),

$$F_1^{(1)} = \gamma \left( \frac{\rho_{1in} v_{1in}}{\rho_{2in} v_{2in}} \right)^{(1)} \quad (8.36)$$

$$F_2^{(1)} = (2 - \theta_2) \left( u_2^{(1)}(0) + \left( \frac{\partial u_2^{(0)}}{\partial y} \right)_{y=0} \right) + \gamma \left( \frac{\rho_{1in} v_{1in}}{\rho_{2in} v_{2in}} \right)^{(1)} u_w^{(0)}. \quad (8.37)$$

In the same way, we get for  $G_1^{(1)}$  and  $G_2^{(1)}$ ,

$$G_1^{(1)} = \gamma \left( \frac{n_{1in} T_{1in}}{n_{2in} T_{2in}} \right)^{(1)} \quad (8.38)$$

$$G_2^{(1)} = (2 - \theta_2) \left( T_2^{(1)}(0) + \left( \frac{\partial T_2^{(0)}}{\partial y} \right)_{y=0} \right) + \theta_2 T_w^{(1)} + \gamma \left( \frac{n_{1in} T_{1in}}{n_{2in} T_{2in}} \right)^{(1)} T_w^{(0)} \quad (8.39)$$

where we assumed,

$$u_w = u_w^{(0)} \quad (8.40)$$

$$T_w = T_w^{(0)} + \epsilon T_w^{(1)} + \dots \quad (8.41)$$

$u_w^{(1)}$  is assumed to be zero since  $u_w$  is given a priori.

Substituting ( 8.36) and ( 8.37) into ( 8.34) and considering the relations  $\rho_2^{(0)} = \rho^{(0)}$ ,  $u_2^{(0)} = u^{(0)}$  and  $u_2^{(1)} = u^{(1)}$ , we get the second order slip condition for  $u$ ,

$$u^{(1)}(0) = \frac{2 - \theta_2}{\theta_2} \left( \frac{\partial u^{(0)}}{\partial y} \right)_{y=0}. \quad (8.42)$$

In the same way, substituting ( 8.38) and ( 8.39) into ( 8.35) and considering the relations  $n_2^{(0)} = n^{(0)}$ ,  $T_2^{(0)} = T^{(0)}$  and  $T_2^{(1)} = T^{(1)}$ , we get the second order slip condition for  $T$ ,

$$T^{(1)}(0) = \frac{2 - \theta_2}{\theta_2} \left( \frac{\partial T^{(0)}}{\partial y} \right)_{y=0} + T_w^{(1)}. \quad (8.43)$$

As pointed out in Section 4.1, when  $T_w(t)$  is given a priori, the second order temperature of the mixture  $T^{(1)}(0)$  should be determined from ( 8.43) with  $T_w^{(1)} = 0$ . And, when the adiabatic boundary condition is given,  $T^{(1)}(0)$  should be specified at first from the energy balance on the wall and, afterwards,  $T_w^{(1)}$  can be determined from ( 8.43).

## 8.4 First and second order temperature of the mixture when the wall is adiabatic

The dimensional expression of the energy balance on the wall is given ( 4.33). By expanding this in powers of  $\epsilon$ , the first order and second order expressions become,

$$q_y^{(0)}(0) + \frac{E}{4}(n_1 v_1)^{(0)}(0) = 0 \quad (8.44)$$

$$q_y^{(1)}(0) + \frac{E}{4}(n_1 v_1)^{(1)}(0) = 0. \quad (8.45)$$

From ( C.13),

$$(n_1 v_1)^{(0)}(0) = -R_1 \left( \frac{\partial (n_1 T)^{(0)}}{\partial y} \right)_{y=0}. \quad (8.46)$$

Substituting ( 7.38) and ( 8.46) into ( 8.44), we get the first order equation of the energy balance on the wall,

$$\frac{5}{4} \left( \frac{\partial}{\partial y} \{ \tilde{n} T^2 \}^{(0)} \right)_{y=0} + \frac{E}{4} R_1 \left( \frac{\partial (n_1 T)^{(0)}}{\partial y} \right)_{y=0} = 0. \quad (8.47)$$

In the same way, from ( 7.65),

$$(n_1 v_1)^{(1)}(0) = -\frac{1}{2} R_1 \left( \frac{\partial (n_1 T)^{(1)}}{\partial y} \right)_{y=0} \quad (8.48)$$

Substituting ( 7.69) and ( 8.48) into ( 8.45), we get the second order equation of the energy balance on the wall,

$$\frac{5}{4} \left( \frac{\partial (\tilde{n} T^2)^{(1)}}{\partial y} \right)_{y=0} - \frac{5}{4} \tilde{n}^{(0)}(0) T^{(0)}(0) \left( \frac{\partial T^{(0)}}{\partial y} \right)_{y=0} + \frac{E}{8} R_1 \left( \frac{\partial (n_1 T)^{(1)}}{\partial y} \right)_{y=0} = 0 \quad (8.49)$$

# Chapter 9

## Discussions

### 9.1 Structures of the first and second order systems

We obtained the first order equations of motion ( 7.40)  $\sim$  (7.44) with the boundary conditions ( 8.2), ( 8.6), ( 8.28), ( 8.29) (when the wall temperature is specified) and ( 8.46) (when the wall is adiabatic). As pointed out by Trilling [8] and Perot [14], the first order system is similar to the Navier-Stokes system with no slip boundary conditions for the tangential velocity and the temperature.

However, other than the simpler cases of previous analyses, this system has chemical reaction terms. They already appear in the first order system because we treat the first order dimensionless chemical characteristic time  $\alpha$  defined in ( 6.6) as a different parameter from the expansion parameter  $\epsilon$ . The main reason for this treatment is that it is difficult to estimate the order of the exponential term contained in the chemical characteristic time and that the reaction process is distinct from the mechanics of the flow. Consequently, we treat two processes; i.e. the kinetic and the chemical relaxation processes, separately.

Another important characteristic of this system is that, for a highly catalytic surface, the first order species density of O molecules  $\rho_1(0)$  is zero and the  $y$ -derivative of  $\rho_1^{(0)}$  is contained in the second order of  $\rho_1(0)$ . Therefore, the actual value of  $\rho_1(0)$



is mainly expressed in the second order terms.

The second order equations of motion ( 7.70)  $\sim$  ( 7.74) refine the first order system with the second order boundary conditions ( 8.2), ( 8.13), ( 8.42), ( 8.43) with  $T_w^{(1)} = 0$  (when the wall temperature is specified) and ( 8.49) (when the wall is adiabatic). The system has a finite value of  $\rho_1(0)$  and slip boundary conditions for the tangential velocity and temperature.

The slip conditions ( 8.42) and ( 8.43) are functions of an accommodation coefficient  $\theta_2$  for  $O_2$  molecules and have the same forms as those for the case of a monatomic gas in [8]. This follows from the result that  $\rho_1^{(0)}(0)$  is zero and, therefore, an accommodation coefficient  $\theta_1$  for  $O$  molecules does not have any contribution to the second order slip values. In the third order, however,  $\theta_1$  and the catalytic efficiency  $\gamma$  appear for the first time. The second order species density  $\rho_1^{(1)}(0)$  in ( 8.13) is the function of the catalytic efficiency  $\gamma$  and, for the same temperature, it decreases as  $\gamma$  increases. The influence of  $\gamma$  on the heat transfer rate on the surface will be discussed in Section 9.3.

The equations of the second order system have the same structure as the first order system. They contain the higher order derivatives than the first order system; however, these are derivatives of quantities of a lower expansion term and have already been obtained in the first order system and are known functions. Furthermore, the second order system is a sequence of linear equations as pointed out by Perot [14]. The same characteristics mentioned above hold if we iterate the same procedure for a higher order system.

## 9.2 Outer boundary conditions

We did not discuss the outer boundary conditions when we derived the first and second order systems. In the formalism of the asymptotic expansion theory, the outer boundary conditions should be specified by the matching process mentioned in Chapter 6. In this section, we consider the relationship between the order of the Knudsen number on which the expansion parameter  $\epsilon$  in this study is based and the

Reynolds number on which the ordinary boundary layer theory is based and briefly discuss the treatment of the outer boundary conditions.

At first, we consider a monatomic gas. The Reynolds number is defined, for example, by  $\rho_\infty, u_\infty, L$  and a viscosity coefficient  $\mu_\infty$ ,

$$Re = \frac{\rho_\infty u_\infty L}{\mu_\infty}. \quad (9.1)$$

From elementary kinetic theory (see, e.g. Vincenti & Kruger [12]),

$$\mu_\infty \approx \rho_\infty c_\infty \lambda \quad (9.2)$$

where  $\lambda$  is a mean free path of the gas. Then, the order of the Reynolds number becomes,

$$Re \approx M_\infty \frac{L}{\lambda} \approx \frac{M_\infty}{Kn} \quad (9.3)$$

where  $M_\infty$  is the Mach number. Consequently, the order of the square root of the Knudsen number is,

$$\sqrt{Kn} \approx \frac{\sqrt{M_\infty}}{\sqrt{Re}}. \quad (9.4)$$

Therefore, the order of the expansion parameter  $\epsilon$  in [8] is the inverse of the square root of the Reynolds number if the Mach number is of order unity. This means that the region where the inner expansion for the case of a monatomic gas is valid is the same as the boundary layer. In this sense, Trilling [8] specified values in the uniform region; i.e.  $u_\infty = v_\infty = 0$  and  $T_\infty$  as the outer boundary conditions for a monatomic gas.

For the mixture of gases in this study, the same discussion can be applied. For example, the viscosity coefficient for the mixture  $\mu$  can be expressed in terms of the viscosity for each species  $\mu_i$  according to Wilke's rule (see, e.g. Anderson [20]),

$$\mu = \sum_i \frac{X_i \mu_i}{\sum_j X_j \Phi_{ij}} \quad (9.5)$$

where

$$\Phi_{ij} = \frac{1}{\sqrt{8}} \left(1 + \frac{m_i}{m_j}\right)^{-1/2} \left[1 + \left(\frac{\mu_i}{\mu_j}\right)^{1/2} \left(\frac{m_j}{m_i}\right)^{1/4}\right]^2. \quad (9.6)$$

In ( 9.5),  $X_i$  is the mole fraction of species  $i$ . Considering that the orders of mean free paths of both O and O<sub>2</sub> molecules are the same (see ( 5.37)), the order of  $\mu$  is also the order of  $\rho_\infty c_\infty \lambda$  and the relation,

$$\epsilon = \sqrt{Kn} \approx \frac{\sqrt{M_\infty}}{\sqrt{Re}} \quad (9.7)$$

holds.

Therefore, we can specify the outer boundary conditions as,

$$\lim_{y \rightarrow \infty} \rho_s = \rho_{s\infty} \quad (9.8)$$

$$\lim_{y \rightarrow \infty} T = T_\infty \quad (9.9)$$

$$\lim_{y \rightarrow \infty} u, v = 0. \quad (9.10)$$

We have already used these relations in Chapter 7 to derive ( 7.24) and ( 7.55).

### 9.3 Effect of the wall catalysis on the heat transfer rate

It is well known that the catalytic efficiency  $\gamma$  influences the heat transfer rate on the wall (see, e.g. Fay & Riddell [1], Goulard [2], Park [17]). The main reason why the thermal protection system of Space Shuttle uses a low catalytic surface is based on the results of these analyses which show that the heat transfer rate on the surface is greatly reduced at re-entry if the surface is near non-catalytic. In reality, the catalytic efficiency  $\gamma$  is in itself a function of temperature (see, e.g. Anderson [21], Scott [22, 23], Rakich et al. [24], Stewart et al [25, 26],) and this fact greatly complicates this problem. In this section, we briefly discuss the order of magnitude of the heat transfer rate in the case of a highly catalytic surface. Here, the terminology

'highly catalytic surface' is used in the sense that the order of  $\gamma$  is unity.

From the results in Section 8.4, the dimensionless heat transfer rate on the wall  $q_w$  can be expressed up to the second order as,

$$\begin{aligned}
q_w &= q_w^{(0)} + q_w^{(1)} + O(\epsilon^2) \\
&= \frac{5}{4} \left( \frac{\partial}{\partial y} \{ \tilde{n} T^2 \}^{(0)} \right)_{y=0} + \frac{E}{4} R_1 \left( \frac{\partial (n_1 T)^{(0)}}{\partial y} \right)_{y=0} \\
&\quad + \epsilon \left[ \frac{5}{4} \left( \frac{\partial (\tilde{n} T^2)^{(1)}}{\partial y} \right)_{y=0} - \frac{5}{4} \tilde{n}^{(0)}(0) T^{(0)}(0) \left( \frac{\partial T^{(0)}}{\partial y} \right)_{y=0} + \frac{E}{8} R_1 \left( \frac{\partial (n_1 T)^{(1)}}{\partial y} \right)_{y=0} \right] \\
&\quad + O(\epsilon^2) \tag{9.11}
\end{aligned}$$

where  $q_w$  is positive when the heat flux enters the surface as defined in Section 4.5. As discussed in Chapter 8 and Section 9.1, the influence of the catalytic efficiency  $\gamma$  appears for the first time in the second order of  $\rho_1(0)$  and in the third order of  $u(0)$  and  $T(0)$ . Therefore, the first order heat transfer rate  $q_w^{(0)}$  is independent of  $\gamma$  and has the same value for all  $\gamma$  as long as the order of  $\gamma$  is unity. The influence of  $\gamma$  appears in the second order heat transfer rate  $q_w^{(1)}$  through the terms  $(\partial T^{(1)}/\partial y)_{y=0}$ ,  $n_1^{(1)}(0)$  and  $(\partial n_1^{(1)}/\partial y)_{y=0}$ .

In the following discussion about the effects of the catalytic efficiency on the heat transfer rate on the wall, for simplicity, the wall temperature  $T_w$  is assumed to be constant. By using relations obtained in Chapter 7 and 8, the second order heat flux  $q_w^{(1)}$  becomes,

$$\begin{aligned}
q_w^{(1)} &= \left[ \frac{5}{8} R_1 (T_w^{(0)})^2 + \frac{E}{8} R_1 T_w^{(0)} \right] \left( \frac{\partial n_1^{(1)}}{\partial y} \right)_{y=0} \\
&\quad + \left[ \frac{5}{4} R_1 T_w^{(0)} + \frac{E}{8} R_1 \right] \left( \frac{\partial T^{(0)}}{\partial y} \right)_{y=0} n_1^{(1)}(0) \\
&\quad + \frac{5}{8} R_1 \left( \frac{\partial T^{(1)}}{\partial y} \right)_{y=0} \\
&\quad + \left[ \left( \frac{5}{4} R_1 T_w^{(0)} + \frac{E}{8} R_1 \right) T^{(1)}(0) \left( \frac{\partial n_1^{(0)}}{\partial y} \right)_{y=0} - \frac{5}{8} R_1 \left( \frac{\partial T^{(0)}}{\partial y} \right)_{y=0} \right] \tag{9.12}
\end{aligned}$$

Terms in the last bracket can be expressed by the first order quantities and have nothing to do with  $\gamma$ .  $(\partial T^{(1)}/\partial y)_{y=0}$  in the third term contains the effect of  $\gamma$  through the second order system ( 7.70)  $\sim$  ( 7.74); however, this term is of order unity and is multiplied by  $\epsilon$ ; therefore it can be neglected compared with the first order heat flux  $q_w^{(0)}$ . On the other hand, the first and second terms in the right-hand side of ( 9.12) which contain  $(\partial n_1^{(1)}/\partial y)_{y=0}$  and  $n_1^{(1)}(0)$  respectively may become comparable to  $q_w^{(0)}$  when  $\gamma$  is small of order of  $\epsilon$  since  $n_1^{(1)}(0)$  contains the term  $(2 - \gamma)/4\gamma$ . Also,  $n_1^{(1)}(0)$  is always positive and decreases with  $\gamma$  and  $(\partial n_1^{(1)}/\partial y)_{y=0}$  can be considered to be negative and has the order of magnitude,

$$\left(\frac{\partial n_1^{(1)}}{\partial y}\right)_{y=0} \approx \frac{0 - n_1^{(1)}(0)}{\delta} = -\frac{n_1^{(1)}(0)}{\delta} \quad (9.13)$$

where  $\delta$  is order of unity and has the same order of the thickness of the boundary layer. Therefore, if the following condition,

$$\frac{5}{8} (T_w^{(0)})^2 + \frac{E}{8} T_w^{(0)} \ll \left[ \frac{5}{4} T_w^{(0)} + \frac{E}{8} \right] \left( \frac{\partial T^{(0)}}{\partial y} \right)_{y=0} \quad (9.14)$$

is satisfied,  $q_w$  is a decreasing function of  $\gamma$  up to the second order. This contradicts the results derived from ordinary boundary layer theory in which the heat transfer rate simply increases as the catalytic efficiency increases (e.g. Goulard [2]). One of the possibilities of this result is that we assumed  $\tau_{av} \ll \tau_{11}, \tau_{22}$  although, near the wall, the number density  $n_2$  is much larger than  $n_1$  and, therefore,  $\tau_{22}$  is dominantly small if the surface is highly catalytic. However, in order to judge whether this contradiction comes from an error of the kinetic model used in this study or this model describes the physical phenomena of the catalytic process on the surface more exactly, further investigation will be needed.

# Chapter 10

## Summary and Conclusions

This thesis presents an asymptotic solution of the Boltzmann- Krook equations for the Rayleigh shear flow problem in which the flow consists of a reacting mixture of gases (O and O<sub>2</sub> molecules) and the wall is a highly catalytic surface whose catalytic efficiency is order of unity. The chemical process occurs both in the flow and on the surface and the extended kinetic model which contains the dissociation reaction in the flow and the boundary condition which describes the recombination reaction process on the highly catalytic surface are constructed. The another boundary conditions for the kinetic model are specified on averaged quantities of the distribution functions rather than on the distribution functions themselves.

The equations of motion and the boundary conditions are expanded in powers of the square root of the Knudsen number of the flow. In order to obtain the additional unknowns such as diffusion velocities, the stress tensor and the heat flux vector, each order of distribution functions which are derived from the Boltzmann-Krook equations expanded in powers of the same expansion parameter are used.

The first and second order of equations of motion with the same order of boundary conditions are constructed. The first order system is similar to the Navier-Stokes equations with no-slip boundary conditions for the tangential velocity and the temperature. The second order system represents a slip flow and has the same coefficients as those in the first order system. The expansion procedure presented here guarantees that the systems obtained by the succeeding iterates have the same structures as

the Navier-Stokes equations and that the higher order derivatives which may appear in the subsequent systems involve the lower order terms which have already been determined in the previous steps.

In this study, one of ways to treat with the highly catalytic surface is presented and the relationship among the diffusion velocity of O molecules, the catalytic efficiency  $\gamma$  and the catalytic recombination rate constant  $k_w$  is clarified by using the description of the distribution functions derived from the expansion procedure mentioned in the previous paragraph. And it is shown that, for the highly catalytic surface whose catalytic efficiency is order of unity, the first order of species density of O molecules  $\rho_1(0)$  should be zero and actual value appears in the second order.

Corresponding heat transfer rate on the surface caused by both the heat conduction and the recombination process on the catalytic surface is obtained until the second order. The effect of the catalytic efficiency on the heat transfer rate is discussed and it is shown that it appears in the second order terms for the first time. Our result also suggests that, if the wall temperature is assumed to be constant, the heat transfer rate may decrease as the catalytic efficiency increases under some conditions. It contradicts with the results of analyses derived from the ordinary boundary layer theory and it is necessary to investigate further in order to judge whether it is because of an error which comes from the kinetic model used in this study or this model describes the physical phenomena on the highly catalytic surface more exactly.

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# Appendix A

## Equations of motion

### A.1 Relation between $T_s$ and $T_{ss}$

From the definition ( 2.10) and ( 2.13),

$$\begin{aligned}\frac{3}{2}n_1kT_1 &= \frac{1}{2}\int_{\mathbb{R}^3}|\vec{\xi}_1 - \vec{v}|^2 f_1 d\vec{\xi}_1 \\ &= \frac{1}{2}\int_{\mathbb{R}^3}|\vec{\xi}_1 - \vec{v}_1 + \vec{v}_1 - \vec{v}|^2 f_1 d\vec{\xi}_1.\end{aligned}\tag{A.1}$$

( A.1) can be written by using ( 2.19),

$$\begin{aligned}\frac{3}{2}n_1kT_1 &= \frac{3}{2}n_1kT_{11} + \int_{\mathbb{R}^3} \left( (\vec{\xi}_1 - \vec{v}_1) \cdot (\vec{v}_1 - \vec{v}) + \frac{1}{2}|\vec{v}_1 - \vec{v}|^2 \right) f_1 d\vec{\xi}_1 \\ &= \frac{3}{2}n_1kT_{11} + \frac{1}{2}\rho_1|\vec{v}_1 - \vec{v}|^2\end{aligned}\tag{A.2}$$

and,

$$\vec{v}_1 - \vec{v} = \vec{v}_1 - \frac{\rho_1\vec{v}_1 + \rho_2\vec{v}_2}{\rho} = \frac{\rho_2(\vec{v}_1 - \vec{v}_2)}{\rho}.\tag{A.3}$$

By substituting this result into ( A.2), we can get ( 2.20) in Section 2.2,

$$T_1 = T_{11} + \frac{m_1\rho_2^2}{3k\rho^2}|\vec{v}_2 - \vec{v}_1|^2.\tag{2.20}$$

In the same way, we can get the similar result ( 2.21) for species 2,

$$T_2 = T_{22} + \frac{m_2 \rho_1^2}{3k\rho^2} |\vec{v}_2 - \vec{v}_1|^2. \quad (2.21)$$

## A.2 Derivation of the energy conservation equation

The left-hand side of ( 2.29) for species 1 can be written,

$$\frac{\partial}{\partial y} \left\{ \int_{\mathbb{R}^3} \frac{1}{2} |\vec{\xi}_s|^2 f_1 d\vec{\xi}_1 \right\} + \frac{\partial}{\partial y} \left\{ \int_{\mathbb{R}^3} \frac{1}{2} \eta_1 |\vec{\xi}_s|^2 f_1 d\vec{\xi}_1 \right\}. \quad (A.4)$$

The first term of ( A.4) is the time derivative of

$$\begin{aligned} \int_{\mathbb{R}^3} \frac{1}{2} |\vec{\xi}_s|^2 f_1 d\vec{\xi}_1 &= \frac{1}{2} \int_{\mathbb{R}^3} |\vec{c}_1 + \vec{v}|^2 f_1 d\vec{\xi}_1 \\ &= \frac{3}{2} p_1 + \vec{v} \cdot \int_{\mathbb{R}^3} \vec{c}_1 f_1 d\vec{\xi}_1 + \frac{1}{2} \rho_1 |\vec{v}|^2. \end{aligned} \quad (A.5)$$

The second term of ( A.4) is the  $y$ -derivative of

$$\begin{aligned} &\int_{\mathbb{R}^3} \frac{1}{2} \eta_1 |\vec{\xi}_s|^2 f_1 d\vec{\xi}_1 \\ &= \frac{1}{2} \int_{\mathbb{R}^3} ((c_1)_y + v) (|\vec{c}_1|^2 + 2\vec{c}_1 \cdot \vec{v} + |\vec{v}|^2) f_1 d\vec{\xi}_1 \\ &= (q_1)_y + \frac{1}{2} \int_{\mathbb{R}^3} (2(c_1)_y \vec{c}_1 \cdot \vec{v} + (c_1)_y |\vec{v}|^2 + v |\vec{c}_1|^2 + 2v \vec{c}_1 \cdot \vec{v}) f_1 d\vec{\xi}_1 \\ &\quad + \frac{1}{2} \rho_1 v |\vec{v}|^2 \end{aligned} \quad (A.6)$$

where a notation  $\vec{c}_1 = ((c_1)_x, (c_1)_y, (c_1)_z)$  is used. For species 2, we get similar expressions to ( A.5) and ( A.6). After some manipulations,

$$\sum_s \int_{\mathbb{R}^3} \frac{1}{2} |\vec{\xi}_s|^2 f_s d\vec{\xi}_1 = \frac{3}{2} nkT + \frac{1}{2} \rho |\vec{v}|^2 \quad (A.7)$$

$$\sum_s \int_{\mathbb{R}^3} \frac{1}{2} \eta_s |\vec{\xi}_s|^2 f_s d\vec{\xi}_1 = q_y + u P_{xy} + v P_{yy} + \frac{3}{2} nkT v + \frac{1}{2} \rho v |\vec{v}|^2. \quad (A.8)$$

Then, we obtain the energy conservation equation,

$$\begin{aligned} & \frac{\partial}{\partial t} \left\{ \frac{3}{2}nkT + \frac{1}{2}\rho|\vec{v}|^2 \right\} + \frac{\partial}{\partial y} \left\{ q_y + uP_{xy} + vP_{yy} + \frac{3}{2}nkTv + \frac{1}{2}\rho v|\vec{v}|^2 \right\} + \frac{E}{m_2}\dot{w} \\ & = 0. \end{aligned} \quad (\text{A.9})$$

Equation ( A.9) can be rearranged into simpler form. Among terms in ( A.9),

$$\begin{aligned} & \frac{\partial}{\partial t} \left\{ \frac{3}{2}nkT \right\} + \frac{\partial}{\partial y} \left\{ \frac{3}{2}nkTv \right\} \\ & = \frac{3}{2}nk \left( \frac{\partial T}{\partial t} + v \frac{\partial T}{\partial y} \right) + \frac{3}{2}kT \left( \frac{\partial n}{\partial t} + v \frac{\partial(nv)}{\partial y} \right) \\ & = \frac{3}{2}nk \left( \frac{\partial T}{\partial t} + v \frac{\partial T}{\partial y} \right) + \frac{3}{2}kT \sum_s \left( \frac{\partial n_s}{\partial t} + \frac{\partial(n_s v_s)}{\partial y} - \frac{\partial(n_s V_s)}{\partial y} \right) \\ & = \frac{3}{2}nk \left( \frac{\partial T}{\partial t} + v \frac{\partial T}{\partial y} \right) + \frac{3}{2}kT \left( \frac{\dot{w}}{m_1} - \frac{\dot{w}}{m_2} \right) - \frac{3}{2}kT \frac{\partial}{\partial y} \left\{ \sum_s n_s V_s \right\} \\ & = \frac{3}{2}nk \left( \frac{\partial T}{\partial t} + v \frac{\partial T}{\partial y} \right) + \frac{3}{2}kT \frac{\dot{w}}{m_2} - \frac{3}{2}kT \frac{\partial}{\partial y} \left\{ \sum_s n_s V_s \right\} \end{aligned} \quad (\text{A.10})$$

where the species conservation equations ( 2.30), ( 2.31) and a relation  $m_2 = 2m_1$  are used. Furthermore, from the conservation of the total mass,

$$\frac{|\vec{v}|^2}{2} \left( \frac{\partial \rho}{\partial t} + \frac{\partial(\rho v)}{\partial y} \right) = 0 \quad (\text{A.11})$$

and from the momentum conservation equations ( 2.32) and ( 2.33),

$$\begin{aligned} & \frac{\rho}{2} \left( \frac{\partial|\vec{v}|^2}{\partial t} + v \frac{\partial|\vec{v}|^2}{\partial y} \right) + u \frac{\partial P_{xy}}{\partial y} + v \frac{\partial P_{yy}}{\partial y} \\ & = \frac{\rho}{2} \left( \frac{\partial}{\partial t} \{u^2 + v^2\} + v \frac{\partial}{\partial y} \{u^2 + v^2\} \right) - \rho u \left( \frac{\partial u}{\partial t} + v \frac{\partial u}{\partial y} \right) - \rho v \left( \frac{\partial v}{\partial t} + v \frac{\partial v}{\partial y} \right) \\ & = 0. \end{aligned} \quad (\text{A.12})$$

Substituting ( A.10) ~ ( A.12) into ( A.9), we obtain the final form of the energy conservation equation ( 2.34),

$$\frac{3}{2}nk \left( \frac{\partial T}{\partial t} + v \frac{\partial T}{\partial y} \right) + \frac{\partial q_y}{\partial y} + P_{xy} \frac{\partial u}{\partial y} + P_{yy} \frac{\partial v}{\partial y} + \frac{\dot{w}}{m_2} \left( E + \frac{3}{2}kT \right)$$

$$= \frac{3}{2}kT \frac{\partial}{\partial y} \left\{ \sum_s n_s V_s \right\}. \quad (2.34)$$

# Appendix B

## Kinetic Model

### B.1 Conditions of unknown parameters for the conservation of the collision invariants

By substituting ( 3.35) and ( 3.36) into ( 3.38), the terms of ( 3.38) for species 1 corresponding to the conservation of the total momentum is,

$$\begin{aligned}
 & \int_{\mathbb{R}^3} \vec{\xi}_1 J_1(f_1) d\vec{\xi}_1 \\
 = & \int_{\mathbb{R}^3} \vec{\xi}_1 \left[ \frac{\Psi_{11} - f_1}{\tau_{11}} + \frac{\Psi_{12} - f_1}{\tau_{av}} - 2 \frac{n_2}{n} P \frac{\Psi_{12}}{\tau_{av}} + 2 \frac{n_2}{n} P \frac{\Psi_{R1}}{\tau_{av}} + 2 \frac{\rho_2}{\rho_1} \frac{n_1}{n} P \frac{\Psi_{R2}}{\tau_{av}} \right] d\vec{\xi}_1 \\
 = & \frac{\rho_1}{\tau_{av}} (\vec{v}_{12} - \vec{v}_1) - 2 \frac{n_2}{n} P \frac{\rho_1 \vec{v}_{12}}{\tau_{av}} + 2 \frac{n_2}{n} P \frac{\rho_1 \vec{v}_{R1}}{\tau_{av}} + 2 \frac{n_1}{n} P \frac{\rho_2 \vec{v}_{R2}}{\tau_{av}}. \tag{B.1}
 \end{aligned}$$

The terms for species 2 is,

$$\begin{aligned}
 & \int_{\mathbb{R}^3} \vec{\xi}_2 J_2(f_2) d\vec{\xi}_2 \\
 = & \int_{\mathbb{R}^3} \vec{\xi}_2 \left[ \frac{\Psi_{21} - f_2}{\tau_{av}} + \frac{\Psi_{22} - f_2}{\tau_{22}} - 2 \frac{n_1}{n} P \frac{\Psi_{21}}{\tau_{av}} \right] d\vec{\xi}_2 \\
 = & \frac{\rho_2}{\tau_{av}} (\vec{v}_{21} - \vec{v}_2) - 2 \frac{n_1}{n} P \frac{\rho_2 \vec{v}_{21}}{\tau_{av}}. \tag{B.2}
 \end{aligned}$$

By adding ( B.1) to ( B.2), we can get the form ( 3.41).

In the same way, the terms of ( 3.39) for species 1 corresponding to the conservation

of the total energy is,

$$\begin{aligned}
& \int_{\mathbb{R}^3} \frac{1}{2} |\vec{\xi}_1|^2 J_1(f_1) d\vec{\xi}_1 \\
&= \frac{1}{2} \int_{\mathbb{R}^3} |\vec{\xi}_1|^2 \left[ \frac{\Psi_{11} - f_1}{\tau_{11}} + \frac{\Psi_{12} - f_1}{\tau_{av}} - 2 \frac{n_2}{n} P \frac{\Psi_{12}}{\tau_{av}} + 2 \frac{n_2}{n} P \frac{\Psi_{R1}}{\tau_{av}} + 2 \frac{\rho_2}{\rho_1} \frac{n_1}{n} P \frac{\Psi_{R2}}{\tau_{av}} \right] d\vec{\xi}_1 \\
&= \frac{1}{2\tau_{av}} \left\{ \int_{\mathbb{R}^3} \Psi_{12} \left[ |\vec{\xi}_1 - \vec{v}_{12}|^2 + 2\vec{v}_{12} \cdot (\vec{\xi}_1 - \vec{v}_{12}) + |\vec{v}_{12}|^2 \right] d\vec{\xi}_1 \right. \\
&\quad \left. - \int_{\mathbb{R}^3} f_1 \left[ |\vec{\xi}_1 - \vec{v}|^2 + 2\vec{v} \cdot (\vec{\xi}_1 - \vec{v}) + |\vec{v}|^2 \right] d\vec{\xi}_1 \right\} \\
&\quad - 2 \frac{n_2}{n} \frac{P}{\tau_{av}} \left( \frac{3}{2} n_1 k T_{12} + \frac{\rho_1}{2} |\vec{v}_{12}|^2 \right) + 2 \frac{n_2}{n} \frac{P}{\tau_{av}} \left( \frac{3}{2} n_1 k T_{R1} + \frac{\rho_1}{2} |\vec{v}_{R1}|^2 \right) \\
&\quad + 2 \frac{n_1 \rho_2}{n \rho_1} \frac{P}{\tau_{av}} \left( \frac{3}{2} n_1 k T_{R2} + \frac{\rho_1}{2} |\vec{v}_{R2}|^2 \right) \\
&= \frac{1}{\tau_{av}} \left[ \frac{3}{2} n_1 k (T_{12} - T_1) + \frac{\rho_1}{2} (|\vec{v}_{12}|^2 - |\vec{v}|^2) - \rho_1 \vec{v} \cdot (\vec{v}_1 - \vec{v}) \right] \\
&\quad - 2 \frac{n_2}{n} \frac{P}{\tau_{av}} \left( \frac{3}{2} n_1 k T_{12} + \frac{\rho_1}{2} |\vec{v}_{12}|^2 \right) + 2 \frac{n_2}{n} \frac{P}{\tau_{av}} \left( \frac{3}{2} n_1 k T_{R1} + \frac{\rho_1}{2} |\vec{v}_{R1}|^2 \right) \\
&\quad + 2 \frac{n_1}{n} \frac{P}{\tau_{av}} \left( \frac{3}{2} \cdot 2 n_2 k T_{R2} + \frac{\rho_2}{2} |\vec{v}_{R2}|^2 \right). \tag{B.3}
\end{aligned}$$

The terms for species 2 is,

$$\begin{aligned}
& \int_{\mathbb{R}^3} \frac{1}{2} |\vec{\xi}_2|^2 J_2(f_2) d\vec{\xi}_2 \\
&= \frac{1}{2} \int_{\mathbb{R}^3} |\vec{\xi}_2|^2 \left[ \frac{\Psi_{21} - f_2}{\tau_{av}} + \frac{\Psi_{22} - f_2}{\tau_{22}} - 2 \frac{n_1}{n} P \frac{\Psi_{21}}{\tau_{av}} \right] d\vec{\xi}_2 \\
&= \frac{1}{\tau_{av}} \left[ \frac{3}{2} n_2 k (T_{21} - T_2) + \frac{\rho_2}{2} (|\vec{v}_{21}|^2 - |\vec{v}|^2) - \rho_2 \vec{v} \cdot (\vec{v}_2 - \vec{v}) \right] \\
&\quad - 2 \frac{n_1}{n} \frac{P}{\tau_{av}} \left( \frac{3}{2} n_2 k T_{21} + \frac{\rho_2}{2} |\vec{v}_{21}|^2 \right). \tag{B.4}
\end{aligned}$$

With the use of ( 3.43), the right hand-side of ( 3.39) gives,

$$- \frac{E}{m_2} \dot{w} = - \frac{E}{m_2} \cdot 2 \rho_2 \frac{n_1}{n} \frac{P}{\tau_{av}} = - \frac{2 n_1 n_2 P E}{n \tau_{av}}. \tag{B.5}$$

By substituting ( B.3) ~ ( B.5) into ( 3.39), we can get the final form ( 3.42).



## B.2 The H-theorem for the non-reacting flow

In this section, we prove H-theorem for the non-reacting flow, in other words, for the mixture when  $P \rightarrow 0$  by following Perot [14]. In this section, for simplicity for the explanation, we introduce distribution functions which represent the number densities in the phase space other than the mass densities in any other part of this thesis,

$$f_{n1} = \frac{f_1}{m_1}, \quad \Psi_{n11} = \frac{\Psi_{11}}{m_1}, \quad \Psi_{n12} = \frac{\Psi_{12}}{m_1} \quad (\text{B.6})$$

$$f_{n2} = \frac{f_2}{m_2}, \quad \Psi_{n22} = \frac{\Psi_{22}}{m_2}, \quad \Psi_{n21} = \frac{\Psi_{21}}{m_2}. \quad (\text{B.7})$$

When  $P \rightarrow 0$ , with these newly defined distribution functions, ( 3.33) and ( 3.34) become,

$$\frac{Df_{n1}}{Dt} = \frac{\partial f_{n1}}{\partial t} + \eta_1 \frac{\partial f_{n1}}{\partial y} = \frac{\Psi_{n11} - f_{n1}}{\tau_{11}} + \frac{\Psi_{n12} - f_{n1}}{\tau_{av}} \quad (\text{B.8})$$

$$\frac{Df_{n2}}{Dt} = \frac{\partial f_{n2}}{\partial t} + \eta_2 \frac{\partial f_{n2}}{\partial y} = \frac{\Psi_{n21} - f_{n2}}{\tau_{av}} + \frac{\Psi_{n22} - f_{n2}}{\tau_{22}} \quad (\text{B.9})$$

where

$$\Psi_{n11} = n_1 \left( \frac{m_1}{2\pi kT_{11}} \right)^{3/2} \exp \left\{ -\frac{m_1}{2kT_{11}} |\vec{\xi}_1 - \vec{v}_1|^2 \right\}. \quad (\text{B.10})$$

$$\Psi_{n22} = n_2 \left( \frac{m_2}{2\pi kT_{22}} \right)^{3/2} \exp \left\{ -\frac{m_2}{2kT_{22}} |\vec{\xi}_2 - \vec{v}_2|^2 \right\}. \quad (\text{B.11})$$

$$\Psi_{n12} = n_1 \left( \frac{m_1}{2\pi kT_{12}} \right)^{3/2} \exp \left\{ -\frac{m_1}{2kT_{12}} |\vec{\xi}_1 - \vec{v}|^2 \right\} \quad (\text{B.12})$$

$$\Psi_{n21} = n_2 \left( \frac{m_2}{2\pi kT_{12}} \right)^{3/2} \exp \left\{ -\frac{m_2}{2kT_{12}} |\vec{\xi}_2 - \vec{v}|^2 \right\} \quad (\text{B.13})$$

and the H-function for species  $s$  is defined as,

$$H_s = \int_{\mathbb{R}^3} f_{ns} \ln f_{ns} d\vec{\xi}_s \quad (\text{B.14})$$

For species 1, the convective derivative of  $H_1$  is,

$$\begin{aligned}
\frac{H_1}{Dt} &= \int_{\mathfrak{R}^3} \frac{Df_{n1}}{Dt} (1 + \ln f_{n1}) d\vec{\xi}_1 \\
&= \int_{\mathfrak{R}^3} \left( \frac{1}{\tau_{11}} (\Psi_{n11} - f_{n1}) + \frac{1}{\tau_{av}} (\Psi_{n12} - f_{n1}) \right) (1 + \ln f_{n1}) d\vec{\xi}_1 \\
&= \frac{1}{\tau_{11}} \int_{\mathfrak{R}^3} (\Psi_{n11} - f_{n1}) (1 + \ln f_{n1}) d\vec{\xi}_1 \\
&\quad + \frac{1}{\tau_{av}} \int_{\mathfrak{R}^3} (\Psi_{n12} - f_{n1}) (1 + \ln f_{n1}) d\vec{\xi}_1. \tag{B.15}
\end{aligned}$$

The first term of the right-hand side of ( B.15) can be written as,

$$\frac{1}{\tau_{11}} \int_{\mathfrak{R}^3} \left\{ (\Psi_{n11} - f_{n1}) + (\Psi_{n11} - f_{n1}) \ln \left( \frac{f_{n1}}{\Psi_{n11}} \right) + (\Psi_{n11} - f_{n1}) \ln \Psi_{n11} \right\} d\vec{\xi}_1. \tag{B.16}$$

The first term of ( B.16) vanishes and the second term is always negative or zero.

The third term can be expressed with the definition ( B.10),

$$\frac{1}{\tau_{11}} \int_{\mathfrak{R}^3} \left\{ \ln \left[ n_1 \left( \frac{m_1}{2\pi k T_{11}} \right)^{3/2} \right] - \frac{m_1}{2\pi k T_{11}} |\vec{\xi}_1 - \vec{v}_1|^2 \right\} (\Psi_{n11} - f_{n1}) d\vec{\xi}_1. \tag{B.17}$$

With the use of the definition ( 2.19), this term also vanishes. Then, the only remaining term in ( B.16) is the second one which is always negative or zero.

As for the first term, we can write for the second term of the right-hand side of ( B.15) as,

$$\frac{1}{\tau_{av}} \int_{\mathfrak{R}^3} \left\{ (\Psi_{n12} - f_{n1}) + (\Psi_{n12} - f_{n1}) \ln \left( \frac{f_{n1}}{\Psi_{n12}} \right) + (\Psi_{n12} - f_{n1}) \ln \Psi_{n12} \right\} d\vec{\xi}_1. \tag{B.18}$$

The first term of ( B.18) vanishes and the second term is always negative or zero.

The third term can be expressed with the definition ( B.12),

$$\begin{aligned}
&\frac{1}{\tau_{av}} \int_{\mathfrak{R}^3} \left\{ \ln \left[ n_1 \left( \frac{m_1}{2\pi k T_{12}} \right)^{3/2} \right] - \frac{m_1}{2\pi k T_{12}} |\vec{\xi}_1 - \vec{v}_{12}|^2 \right\} (\Psi_{n12} - f_{n1}) d\vec{\xi}_1 \\
&= \frac{1}{2kT_{12}\tau_{av}} \cdot \\
&\quad \left[ 3n_1 k T_{12} - 3n_1 k T_1 - \rho_1 |\vec{v} - \vec{v}_{12}|^2 - 2\rho_1 (\vec{v} - \vec{v}_{12}) \cdot (\vec{v}_1 - \vec{v}) \right] \tag{B.19}
\end{aligned}$$

In the same way, for  $H_2$  we can do the similar analysis.  $H_2$  has two negative terms similar to those for species 1 and the following complementary term corresponding to ( B.19),

$$\frac{1}{2kT_{21}\tau_{av}} \left[ 3n_2kT_{21} - 3n_2kT_2 - \rho_2|\vec{v} - \vec{v}_{21}|^2 - 2\rho_2(\vec{v} - \vec{v}_{21}) \cdot (\vec{v}_2 - \vec{v}) \right]. \quad (\text{B.20})$$

In this stage, it is clear that the sufficient conditions to satisfy the H-theorem are,

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

by the following reason. When  $P \rightarrow 0$ , the condition for the conservation of the total momentum and the total energy ( 3.41) and ( 3.42) become,

$$\rho_1\vec{v}_{12} + \rho_2\vec{v}_{21} = \rho\vec{v} \quad (\text{B.22})$$

$$3n_1k(T_{12} - T_1) + 3n_2k(T_{21} - T_2) + \rho_1 \left( |\vec{v}_{12}|^2 - |\vec{v}|^2 \right) + 2\rho_2 \left( |\vec{v}_{21}|^2 - |\vec{v}|^2 \right) = 0 \quad (\text{B.23})$$

respectively. Applying conditions ( B.21) to ( B.22) and ( B.23), we can get,

$$\vec{v}_{12} = \vec{v}_{21} = \vec{v} \quad (\text{B.24})$$

$$T_{12} = T_{21} = T. \quad (\text{B.25})$$

Then, the summation of ( B.19) and ( B.20) becomes,

$$\frac{3}{2T\tau_{av}} [n_1(T - T_1) + n_2(T - T_2)] = 0. \quad (\text{B.26})$$

Therefore, we get the following inequality,

$$\begin{aligned} \frac{DH}{Dt} &= \frac{DH_1}{Dt} + \frac{DH_2}{Dt} \\ &= \frac{1}{\tau_{11}} \int_{\mathfrak{R}^3} (\Psi_{n11} - f_{n1}) \ln \left( \frac{f_{n1}}{\Psi_{n11}} \right) d\vec{\xi}_1 + \frac{1}{\tau_{av}} \int_{\mathfrak{R}^3} (\Psi_{n12} - f_{n1}) \ln \left( \frac{f_{n1}}{\Psi_{n12}} \right) d\vec{\xi}_1 \\ &\quad + \frac{1}{\tau_{av}} \int_{\mathfrak{R}^3} (\Psi_{n21} - f_{n2}) \ln \left( \frac{f_{n2}}{\Psi_{n21}} \right) d\vec{\xi}_2 + \frac{1}{\tau_{22}} \int_{\mathfrak{R}^3} (\Psi_{n22} - f_{n2}) \ln \left( \frac{f_{n2}}{\Psi_{n22}} \right) d\vec{\xi}_2 \end{aligned}$$

$$\leq 0. \quad (\text{B.27})$$

And,  $DH/Dt$  is zero if and only if each terms in the right-hand side are zero, then,

$$f_{n1} = \Psi_{n11} = \Psi_{n12}, \quad f_{n2} = \Psi_{n21} = \Psi_{n22}. \quad (\text{B.28})$$

( B.28) are equivalent to the following conditions,

$$\vec{v}_1 = \vec{v}_2 = \vec{v}, \quad T_1 = T_2 = T. \quad (\text{B.29})$$

( B.29) implies that  $DH/Dt$  is zero if and only if the mixture is in equilibrium. Therefore, for the non-reacting mixture, the H-theorem are satisfied under the conditions ( B.29).

### B.3 Derivation of reasonable forms of unknown parameters

If we impose the condition ( 3.50) when  $P \rightarrow 0$  (but  $P \neq 0$ ), ( 3.48) can be approximated as,

$$\rho(\vec{v}_{12} - \vec{v}) = \vec{0} \quad (\text{B.30})$$

because  $P(\vec{v}_R - \vec{v}_{12})$  approaches  $\vec{0}$  more rapidly than  $(\vec{v}_{12} - \vec{v})$ . Therefore, when  $P$  is small, we can get,

$$\vec{v}_{12} = \vec{v}. \quad (\text{B.31})$$

Then, ( 3.48) becomes,

$$\frac{2P}{n}(n_2\rho_1 + n_1\rho_2)(\vec{v}_R - \vec{v}_{12}) = \vec{0}. \quad (\text{B.32})$$

Since  $P \neq 0$ ,  $\vec{v}_R$  must be  $\vec{v}_{12}$ . Consequently, we get ( 3.52).

When ( 3.52) are satisfied, ( 3.49) becomes,

$$3nk(T_{12} - T) + 2\frac{n_2}{n}P \cdot 3n_1k(T_R - T_{12}) + 2\frac{n_1}{n}P \cdot 3n_2k(2T_R - T_{12}) + \frac{4n_1n_2}{n}PE = 0. \quad (\text{B.33})$$

In the same way for ( B.30), if we impose the condition ( 3.51) when  $P \rightarrow 0$  (but  $P \neq 0$ ), ( B.33) can be approximated as,

$$3nk(T_{12} - T) + 2\frac{n_1}{n}P \cdot 3n_2kT_{12} + \frac{4n_1n_2}{n}PE = 0 \quad (\text{B.34})$$

because  $P(T_R - T_{12})$  approaches zero more rapidly than  $(T_{12} - T)$ , and  $T_R \rightarrow T_{12}$  when  $P \rightarrow 0$ . Therefore, we can get when  $P$  is small,

$$T_{12} = \frac{3n^2kT - 4n_1n_2PE}{3n^2k + 6n_1n_2kP}. \quad (\text{B.35})$$

By substituting ( B.35) into ( B.34), we get,

$$T_R = T_{12}. \quad (\text{B.36})$$

Consequently, we get ( 3.53).

# Appendix C

## First order system of governing equations

### C.1 Temperatures of the first order

From the definition of species temperature  $T_s$  in ( 2.13), we get the dimensionless form,

$$\frac{3}{2}n_s T_s = \int_{\mathbb{R}^3} [(\xi_s - u)^2 + (\eta_s - \epsilon v)^2 + \zeta_s^2] f_s d\vec{\xi}_s. \quad (\text{C.1})$$

By expanding this in powers of  $\epsilon$  and collecting the terms independent of  $\epsilon$ , we obtain the first order form,

$$\begin{aligned} \frac{3}{2}n_s^{(0)}T_s^{(0)} &= \int_{\mathbb{R}^3} [(\xi_s - u^{(0)})^2 + \eta_s^2 + \zeta_s^2] f_s^{(0)} d\vec{\xi}_s \\ &= 3\rho_s^{(0)}R_s T^{(0)} \\ &= \frac{3}{2}n_s^{(0)}T^{(0)}. \end{aligned} \quad (\text{C.2})$$

Then, we obtain the relation,

$$T_1^{(0)} = T_2^{(0)} = T^{(0)}. \quad (\text{C.3})$$

The dimensional  $T_{s,s}$  is defined in ( 2.19). The dimensionless form of  $T_{s,s}$  can be obtained by replacing  $u, v$  in ( C.1) by  $u_s, v_s$  respectively. However, since  $u_s^{(0)} = u^{(0)}$ ,

the first order  $T_{s's}^{(0)}$  is the same as  $T_s^{(0)}$ . Therefore, we finally get,

$$T_1^{(0)} = T_{11}^{(0)} = T_2^{(0)} = T_{22}^{(0)} = T^{(0)}. \quad (7.21)$$

## C.2 Formula of the moments of the second order distribution functions

As seen from the form of  $f_s^{(1)}$  in (7.33),  $f_s^{(1)}$  is the products of polynomials containing  $\xi_s$ ,  $\eta_s$  and  $\zeta_s$  and main unknown variables by the Maxwell distribution function  $f_s^{(0)}$ . Therefore, in principle, any integrals of the moments of  $f_s^{(1)}$  can be calculated by using the following formula (Perot [14]),

$$\int_{\mathbb{R}^3} (\xi_s - u^{(0)})^n \eta_s^p \zeta_s^q f_s^{(0)} d\vec{\xi}_s = \rho_s^{(0)} (2R_s T^{(0)})^{\frac{n+p+q}{2}} \left(\frac{n-1}{2}\right)! \left(\frac{p-1}{2}\right)! \left(\frac{q-1}{2}\right)! \quad (C.4)$$

where,  $n, p$  and  $q$  are positive integers and,

$$\left(\frac{n-1}{2}\right)! = \frac{n-1}{2} \left(\frac{n-3}{2}\right)!, \quad \left(\frac{1}{2}\right)! = \frac{1}{2}. \quad (C.5)$$

Especially, when one of  $n, p, q$  is odd, (C.4) is zero.

However, applying (C.5) to all terms contained in the moments are, in general, very cumbersome. A simpler way to calculate these integrals is given by the following formula proposed by Perot [14],

$$\int_{\mathbb{R}^3} h_s f_s^{(1)} d\vec{\xi}_s = \int_{\mathbb{R}^3} h_s \Psi_{sr}^{(1)} d\vec{\xi}_s - \frac{\partial}{\partial y} \int_{\mathbb{R}^3} \eta_s h_s f_s^{(0)} d\vec{\xi}_s + \int_{\mathbb{R}^3} \eta_s \frac{\partial h_s}{\partial y} f_s^{(0)} d\vec{\xi}_s \quad (C.6)$$

where  $h_s$  is the any function of velocity components  $\xi_s, \eta_s$  and  $\zeta_s$ .

### C.3 Derivation of the first order energy equation

By expanding ( 5.16), the first order energy equation becomes,

$$\begin{aligned} & \frac{3}{4}n^{(0)} \left( \frac{\partial T^{(0)}}{\partial t} + v^{(0)} \frac{\partial T^{(0)}}{\partial y} \right) + \frac{\partial q_y^{(0)}}{\partial y} + P_{xy}^{(0)} \frac{\partial u^{(0)}}{\partial y} + P_{yy}^{(0)} \frac{\partial v^{(0)}}{\partial y} + R_2 \dot{w}^{(0)} \left( E + \frac{3}{2}T^{(0)} \right) \\ &= \frac{3}{4}T^{(0)} \frac{\partial}{\partial y} \left\{ \sum_s n_s^{(0)} V_s^{(0)} \right\} \end{aligned} \quad (\text{C.7})$$

where, from ( 5.17) and ( 6.7)

$$\dot{w}^{(0)} = \frac{n_1^{(0)} n_2^{(0)}}{n^{(0)}} \frac{\alpha}{R_2}. \quad (\text{C.8})$$

From the first order species continuity equations ( 7.40) and ( 7.41),

$$\frac{\partial n_1^{(0)}}{\partial t} + v^{(0)} \frac{\partial n_1^{(0)}}{\partial y} = \frac{\partial^2 (n_1^{(0)} R_1 T^{(0)})}{\partial y^2} - n_1^{(0)} \frac{\partial v^{(0)}}{\partial y} + 4 \frac{n_1^{(0)} n_2^{(0)}}{n^{(0)}} \alpha \quad (\text{C.9})$$

$$\frac{\partial n_2^{(0)}}{\partial t} + v^{(0)} \frac{\partial n_2^{(0)}}{\partial y} = \frac{\partial^2 (n_2^{(0)} R_2 T^{(0)})}{\partial y^2} - n_2^{(0)} \frac{\partial v^{(0)}}{\partial y} - 2 \frac{n_1^{(0)} n_2^{(0)}}{n^{(0)}} \alpha. \quad (\text{C.10})$$

By summing up them and using the relation  $n^{(0)} T^{(0)} = 1$ , we get,

$$n^{(0)} \left( \frac{\partial T^{(0)}}{\partial t} + v^{(0)} \frac{\partial T^{(0)}}{\partial y} \right) = -T^{(0)} \frac{\partial^2 (\tilde{n}^{(0)} T^{(0)})}{\partial y^2} + \frac{\partial v^{(0)}}{\partial y} - 2T^{(0)} \frac{n_1^{(0)} n_2^{(0)}}{n^{(0)}} \alpha. \quad (\text{C.11})$$

By substituting ( C.11) into ( C.7), the left-hand side of the first order energy equation becomes,

$$-\frac{3}{4}T^{(0)} \frac{\partial^2 (\tilde{n}^{(0)} T^{(0)})}{\partial y^2} + \frac{5}{4} \frac{\partial v^{(0)}}{\partial y} - \frac{1}{2} \left( \frac{\partial u^{(0)}}{\partial y} \right)^2 - \frac{5}{4} \frac{\partial^2}{\partial y^2} \left\{ \tilde{n}^{(0)} (T^{(0)})^2 \right\} + \frac{n_1^{(0)} n_2^{(0)}}{n^{(0)}} \alpha E. \quad (\text{C.12})$$

Since the diffusion velocity of species  $s$  can be transformed from ( 7.34) as,

$$n_s^{(0)} V_s^{(0)} = -R_s \frac{\partial (\tilde{n}_s T)^{(0)}}{\partial y}, \quad (\text{C.13})$$



the right-hand side of the first order energy equation becomes,

$$-\frac{3}{4}T^{(0)}\frac{\partial^2(\tilde{n}T)^{(0)}}{\partial y^2}. \quad (\text{C.14})$$

From ( C.12) and ( C.14), we obtain the final form of the first order energy equation ( 7.44).

# Appendix D

## Second order system of governing equations

### D.1 Temperatures of the second order

By expanding the expression of the dimensionless form of  $T_s$ , ( C.1) and collecting the terms of order  $\epsilon$ , we get,

$$\frac{3}{2} (n_s T_s)^{(1)} = \int_{\mathbb{R}^3} [(\xi_s - u^{(0)})^2 + \eta_s^2 + \zeta_s^2] f_s^{(1)} d\vec{\xi}_s - 2 \int_{\mathbb{R}^3} [u^{(1)}(\xi_s - u^{(0)}) + \eta_s v^{(0)}] f_s^{(0)} d\vec{\xi}_s. \quad (\text{D.1})$$

The second integral vanishes from the formula ( C.4), then, we get,

$$\frac{3}{2} (n_s T_s)^{(1)} = 3\rho^{(1)} R_s T^{(0)} + 3\rho^{(0)} R_s T^{(1)} + \frac{3}{2} (n_s T)^{(1)}. \quad (\text{D.2})$$

Since  $T_s^{(0)} = T^{(0)}$ , we obtain,

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

As for the first order case, the second order form of  $T_{s,s}$  can be obtained by replacing  $u^{(0)}, v^{(0)}$  in ( D.1) by  $u_s^{(0)}, v_s^{(0)}$  respectively. Considering  $u_s^{(1)} = u^{(1)}$ , the second order

$T_{ss}^{(1)}$  is the same as  $T_s^{(1)}$ . Therefore, we finally get,

$$T_1^{(1)} = T_{11}^{(1)} = T_2^{(1)} = T_{22}^{(1)} = T^{(1)}. \quad (7.53)$$

## D.2 Formula of the moments of the second order distribution function

By the same reason explained in Appendix C.2, any integrals of the moments of  $f_s^{(2)}$  can be calculated, in principle, by using the formula (C.4). However, there exists a simpler way to calculate them which are proposed by Perot [14].

From (7.27) and (7.28), we get,

$$\eta_s \frac{\partial f_s^{(1)}}{\partial y} = \eta_s \frac{\partial \Psi_{sr}^{(0)}}{\partial y} - \eta_s^2 \frac{\partial^2 f_s^{(0)}}{\partial y^2}. \quad (D.4)$$

From (6.12), (6.16) and (D.4), we can construct the following formula of the moments of  $f_s^{(2)}$ ,

$$\begin{aligned} \int_{\mathbb{R}^3} h_s f_s^{(2)} d\vec{\xi}_s &= \int_{\mathbb{R}^3} h_s \left( \Psi_{sr}^{(2)} + \Psi_{ss}^{(1)} - f_s^{(1)} + G_R \right) d\vec{\xi}_s - \frac{\partial^2}{\partial y^2} \int_{\mathbb{R}^3} \eta_s^2 h_s f_s^{(0)} d\vec{\xi}_s \\ &+ 2 \frac{\partial}{\partial y} \int_{\mathbb{R}^3} \eta_s^2 \frac{\partial h_s}{\partial y} f_s^{(0)} d\vec{\xi}_s - \int_{\mathbb{R}^3} \eta_s^2 \frac{\partial^2 h_s}{\partial y^2} f_s^{(0)} d\vec{\xi}_s - \frac{\partial}{\partial t} \int_{\mathbb{R}^3} h_s f_s^{(0)} d\vec{\xi}_s \\ &+ \int_{\mathbb{R}^3} \frac{\partial h_s}{\partial t} f_s^{(0)} d\vec{\xi}_s - \frac{\partial}{\partial y} \int_{\mathbb{R}^3} \eta_s h_s \Psi_{sr}^{(1)} d\vec{\xi}_s \\ &+ \int_{\mathbb{R}^3} \eta_s \frac{\partial h_s}{\partial y} \Psi_{sr}^{(1)} d\vec{\xi}_s \end{aligned} \quad (D.5)$$

where

$$\begin{aligned} G_R &= +4 \frac{n^{(2)}}{n^{(0)}} \alpha \Psi_{12}^{(0)} & (for \quad s = 1) \\ G_R &= -2 \frac{n^{(1)}}{n^{(0)}} \alpha \Psi_{21}^{(0)} & (for \quad s = 2). \end{aligned} \quad (D.6)$$

### D.3 Derivation of the second order energy equation

By expanding ( 5.16) in powers of  $\epsilon$  and collecting the terms of  $\epsilon$  order, the second order energy equation becomes,

$$\begin{aligned}
& \frac{3}{4}n^{(0)} \left( \frac{\partial T^{(1)}}{\partial t} + v^{(0)} \frac{\partial T^{(1)}}{\partial y} + v^{(1)} \frac{\partial T^{(0)}}{\partial y} \right) + \frac{3}{4}n^{(1)} \left( \frac{\partial T^{(0)}}{\partial t} + v^{(0)} \frac{\partial T^{(0)}}{\partial y} \right) \\
& + \frac{\partial q_y^{(1)}}{\partial y} + P_{xy}^{(0)} \frac{\partial u^{(1)}}{\partial y} + P_{xy}^{(1)} \frac{\partial u^{(0)}}{\partial y} + P_{yy}^{(0)} \frac{\partial v^{(1)}}{\partial y} + P_{yy}^{(1)} \frac{\partial v^{(0)}}{\partial y} \\
= & \frac{3}{4}T^{(0)} \frac{\partial}{\partial y} \left\{ \sum_s (n_s V_s)^{(1)} \right\} + \frac{3}{4}T^{(1)} \frac{\partial}{\partial y} \left\{ \sum_s (n_s V_s)^{(0)} \right\} \\
& - R_2 \left( E + \frac{3}{2}T^{(0)} \right) \dot{w}^{(1)} - \frac{3}{2}R_2 T^{(1)} \dot{w}^{(0)} \tag{D.7}
\end{aligned}$$

where, from ( 5.17) and ( 6.7),

$$\dot{w}^{(1)} = \frac{(n_1 n_2)^{(1)}}{n^{(0)}} \frac{\alpha}{R_2}. \tag{D.8}$$

From ( 7.43) and ( 7.73),

$$T^{(1)} = -n^{(1)} (T^{(0)})^{(2)}. \tag{D.9}$$

Then, parts of the left-hand side of ( D.7) can be rewritten as,

$$\frac{\partial T^{(1)}}{\partial t} + v^{(0)} \frac{\partial T^{(1)}}{\partial y} = - (T^{(0)})^2 \left( \frac{\partial n^{(1)}}{\partial t} + v^{(0)} \frac{\partial n^{(1)}}{\partial y} \right) - 2n^{(1)} T^{(0)} \left( \frac{\partial T^{(0)}}{\partial t} + v^{(0)} \frac{\partial T^{(0)}}{\partial y} \right). \tag{D.10}$$

In the same way as in Appendix C.3 for the first order case, by summing up both species continuity equations ( 7.70) and ( 7.71), we get,

$$\frac{\partial n^{(1)}}{\partial t} + v^{(0)} \frac{\partial n^{(1)}}{\partial y} = \frac{\partial^2 (\bar{n} T)^{(1)}}{\partial y^2} - n^{(1)} \frac{\partial v^{(0)}}{\partial y} - \frac{\partial (n^{(0)} v^{(1)})}{\partial y} + 2 \frac{(n_1 n_2)^{(1)}}{n^{(0)}} \alpha. \tag{D.11}$$

From ( D.7), ( D.10) and ( D.11), we get the expression of the left-hand side of the

second order energy equation ( D.7)

$$\begin{aligned}
& -\frac{3}{4} \left[ T \frac{\partial^2 (\bar{n}T)}{\partial y^2} \right]^{(1)} + \frac{3}{4} T^{(0)} \frac{\partial (n^{(0)}v^{(1)})}{\partial y} + \frac{3}{4} n^{(0)}v^{(1)} \frac{\partial T^{(0)}}{\partial y} - \frac{5}{4} \frac{\partial^2 (\bar{n}T^2)^{(1)}}{\partial y^2} \\
& + \frac{5}{4} \frac{\partial}{\partial y} \left\{ \bar{n}T \frac{\partial T}{\partial y} \right\}^{(0)} - \frac{\partial u^{(0)}}{\partial y} \frac{\partial u^{(1)}}{\partial y} + \frac{1}{2} \left( \frac{\partial u^{(0)}}{\partial y} \right)^2 + \frac{1}{2} \frac{\partial v^{(1)}}{\partial y} \\
& - \frac{3}{2} \alpha (n_1 n_2)^{(1)} (T^{(0)})^2
\end{aligned} \tag{D.12}$$

where we used various expressions for the partial stress tensor and heat flux vector ( 7.37), ( 7.43), ( 7.68), ( 7.69), ( 7.73) and the relation ( C.11).

From ( 7.34) and ( 7.65), we get the expressions of the diffusion velocities which appear on the right-hand side of ( D.7),

$$(n_1 V_1 + n_2 V_2)^{(0)} = -\frac{\partial (\bar{n}T)^{(0)}}{\partial y} \tag{D.13}$$

$$(n_1 V_1 + n_2 V_2)^{(1)} = -\frac{\partial (\bar{n}T)^{(1)}}{\partial y}. \tag{D.14}$$

Furthermore, from ( C.8) and ( D.8),

$$\begin{aligned}
& R_2 \left( E + \frac{3}{2} T^{(0)} \right) \dot{w}^{(1)} + \frac{3}{2} R_2 T^{(1)} \dot{w}^{(0)} \\
& = \alpha \left( E + \frac{3}{2} T^{(0)} \right) \frac{(n_1 n_2)^{(1)}}{n^{(0)}} + \frac{3}{2} \frac{(n_1 n_2)^{(0)}}{n^{(0)}} T^{(1)} \alpha.
\end{aligned} \tag{D.15}$$

Substituting ( D.13) ~ ( D.15) into the right-hand side of ( D.7), we get,

$$-\frac{3}{4} \left[ T \frac{\partial^2 (\bar{n}T)}{\partial y^2} \right]^{(1)} - \alpha \left( E + \frac{3}{2} T^{(0)} \right) \frac{(n_1 n_2)^{(1)}}{n^{(0)}} - \frac{3}{2} \frac{(n_1 n_2)^{(0)}}{n^{(0)}} T^{(1)} \alpha. \tag{D.16}$$

Then, from ( D.12) and ( D.16), we can get the final form of the second order energy equation ( 7.74).