ON THE GAS DYNAMICS OF BINARY GAS MIXTURES WITH LARGE MASS DISPARITY

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ABSTRACT

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The standard Chapman-Enskog (CE) theory for binary mixtures applies when $Kn_1 \ll M$, where $M \equiv m_1/m_2 < 1$ is the molecular mass ratio and Kn_1 is the light gas Knudsen number. For disparate-mass mixtures ($M \ll 1$), the Knudsen number range of applicability of that theory is, therefore, very restricted. In this dissertation, a variety of hydrodynamic and reduced kinetic equations covering the broader range $Kn_1 \ll 1$ are given for neutral, monatomic, disparate-mass mixtures. Thus, the theories given here cover the same range of Knudsen numbers as the CE theory for pure gases, or mixtures whose constituents have comparable molecular weights.

We start with a systematic mass-ratio expansion of the cross-collision integrals in the Boltzmann equations (BE), leading to the Lorentz-Bernstein (LB) and Fokker-Planck (FP) collision operators. A further Knudsen number expansion of the BE of the light gas (which after the mass-ratio expansion becomes kinetically decoupled from the heavy gas) yields near-equilibrium hydrodynamic equations for the light gas valid for $Kn_1 \ll 1$, independently of whether the heavy gas is also in near-equilibrium conditions. The resulting distribution function of the light gas is used to obtain an explicit expression for the FP collision operator in terms of the hydrodynamic quantities and their gradients. In the case in which $n_2/n_1 \gg Kn_1$ (where n_i is the number density of species i), a Knudsen number expansion of the heavy gas kinetic equation is also possible, and the problem is reduced to its near-equilibrium hydrodynamic (two-fluid) level. These two-fluid equations are also generalized to arbitrary mass ratios. The transport coefficients are obtained via variational principles, using expansions in Sonine polynomials as trial functions. Explicit expressions for these transport coefficients are given at the first order of these Sonine polynomials expansions. In contrast to previous two-fluid theories, the present derivation makes no heuristic assumption to simplify the Boltzmann equations, and is not limited to a particular molecular model.

When $n_2/n_1 \leq O(M)$ ($M \sim Kn_1 \ll 1$), the heavy gas is far removed from equilibrium and its full BE has to be used, with only the simplification of the FP cross-collision operator. This equation is substantially reduced to an equation of the FP type in the limit $n_2/n_1 \ll M$, where the self-collision term is negligible. Further simplification arises in the hypersonic limit of the heavy gas, which for disparate-mass mixtures can be attained even for subsonic conditions of the light gas. A hypersonic expansion of the FP equation yields closed sets of hydrodynamic (hypersonic) equations at each level of the expansion.

To test the validity of these theories, we apply them to some specific problems. Thus, the two fluid theory is applied to the accoustic problem and compared with experimental data in He-Xe mixtures of Fuentes Losa (1972) and Bowler (1984), showing a good agreement. This example also corroborates our predictions on the Knudsen number range of validity of both the two-fluid and the standard CE theories. On the other hand, the hypersonic approximation for the heavy gas and the near-equilibrium hydrodynamic equations for the light gas are applied to the shock wave problem and to the flow through a converging nozzle. In the first case, the results are compared with shock tube experiments in He-Xe mixtures made by Herczynski *et al.* (1986), and in the nozzle example they are compared with our own discharge coefficient measurements in CCl_4-He mixtures. A simplified version of the shock wave problem is solved using the kinetic FP equation for the heavy gas, corroborating our predictions on the errors of the hypersonic approximation.

A mis padres

...criticism is the prime *duty* of the scientist and of anyone who wants to advance knowledge.

Seeing new problems and having new ideas, on the other hand, are *not* one's duty: originality is,

rather, a gift of the gods.   Popper (1982).

Acknowledgments

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List of abbreviations

BE	=	Boltzmann equation
CE	=	Chapman-Enskog
DMM	=	Disparate-mass mixtures
FP	=	Fokker-Planck
HEA	=	Hypersonic expansion A
HEB	=	Hypersonic expansion B
LB	=	Lorentz-Bernstein
NSEs	=	Navier-Stokes equations

Chapter 1
INTRODUCTION

1.1 Objectives and structure of the thesis

This dissertation is devoted to the study of some gasdynamic problems arising in binary mixtures made up of species with very different molecular masses.

The two principal features that make such mixtures substantially different from mixtures whose components have comparable molecular masses are the partial decoupling between both species (due to the slower interspecies relaxation of momentum and energy compared to the relaxation between identical molecules), and the almost deterministic behavior of the heavy molecules (owing to their large mean speed compared to their thermal velocity). As a consequence, we shall see in the next chapter that the standard hydrodynamic equations for binary mixtures are not appropriate for this class of problems with the same degree of validity as in ordinary mixtures whose components have similar molecular weights. Moreover, we shall also see that the attempts made in the past to formulate suitable basic theories for describing the behavior of these disparate-mass mixtures (DMM) either lack rigor or are severely restricted in their region of validity. Therefore, the field is in need of more systematic and rigorous theories to guide the increasingly important technological applications of DMM. One of the principal objectives of this dissertation will be to furnish such a framework for a large class of industrially relevant problems.

Another important objective of this work will be to test the validity of the theories developed in the earliest part of it. This task will be accomplished in two ways: (i) by testing the theories against existing and new experimental data, and (ii) by comparing among themselves the results from the various hydrodynamic and kinetic theories developed here. The specific problems selected include the propagation of sound, the structure of shock waves and the quasi-one-dimensional flow through a converging nozzle.

Our starting point will be the kinetic Boltzmann equations (BEs). The presence of a small parameter, namely, the ratio of molecular weights $M \equiv m_1/m_2 \ll 1$, provides a perturbation scheme to simplify the rather involved mathematics of these equations. This perturbation attack of the BEs was in fact started long ago by Lorentz (1905). We shall have opportunity in Sec. 2.3 of giving some remarks on the historical development and the details of these perturbation techniques. A very desirable result would be to obtain, from the perturbatively simplified BEs, a near-equilibrium hydrodynamic formulation with the same range of

applicability as that of the hydrodynamic equations for a pure gas, obtained by means of the Chapman-Enskog (CE) method for small Knudsen numbers (defined as the ratio between a microscopic and a macroscopic time or lenght of the problem; see Sec. 2.1 for a more precise definition). Unfortunately, we shall see in the next chapter that the richness of parameters in the binary problem makes the unified near-equilibrium hydrodynamic picture of the pure gas unrepeatable for mixtures, even for small Knudsen numbers.

One of the most important features of the expansion of the BEs in powers of the small mass ratio M is the decoupling of the BE of the light gas from that of the heavy gas: we shall see in Sec. 2.3 that, after the expansion, the heavy species distribution function enters into the light gas BE only through its moments. Consequently, one can solve the light gas BE independently of the heavy gas BE. In particular, we shall apply the *CE method*[*] to solve the former equation in Sec. 2.4, obtaining near-equilibrium hydrodynamic equations for the light gas valid to first order in M, in the light gas Knudsen number Kn_1, and in the ratio v between the difference of mean velocities among species and the light gas thermal speed. On the other hand, the heavy gas BE does depend on the light gas distribution function, which must be specified before solving that equation. To this end, we shall use in Sec.2.5 the near equilibrium light gas distribution function obtained in Sec.2.4 and show that the CE method can only be applied to the heavy gas BE in two situations: (i) when $Kn_1 <<$ M, in which the standard CE theory for binary mixtures may be applied to both species as a single fluid, and (ii) when the ratio between heavy and light gas number densities n_2/n_1 is much larger than Kn_1 [with $Kn_1 << 1$, $Kn_1 \geq O(M)$], in which case a two-fluid CE theory may be used. Therefore, the class of problems that obey a single set of near-equilibrium hydrodynamic equations for a pure gas or for a binary mixture with components of comparable molecular weights must, for DMM, be described by a mixture of hydrodynamic and kinetic equations, depending on the relative values of M, Kn_1 and n_2/n_1. In the particular limit $Kn_1 << 1$ and $n_2/n_1 >> Kn_1$, both species are governed by near-equilibrium hydrodynamic equations. These are two-fluid hydrodynamic equations rather than

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[*] Although the method of Secs.2.4 and 2.5.2 shares with the Chapman-Enskog (CE) method for pure gases (i.e., Chapman and Cowling, 1970, Ch.7) the expansion in the Knudsen number and the elimination of time derivatives from the Euler-level conservation equations (at the first order of the expansion), it differs in the conservation equations from which the time derivatives are eliminated, which in Secs.2.4 and 2.5.2 contain additional terms of transfer of momentum and energy between species. As we shall see, these new terms are essential in the theory. However, since the main features or both methods are the same, and for simplicity sake, we shall mantain the name *CE method.* On the other hand, the (single-fluid) CE theory for binary mixtures given by Chapman and Cowling (1970), Ch.8, will be referred as the *classical* or *standard* CE theory for binary mixtures, while the method of Chapter 3, and that of Secs.2.4 and 2.5.2 taken together, will be termed *two-fluid* CE theory.

the single-fluid hydrodynamic equations obtained from the standard CE theory for binary mixtures, valid for $Kn_1 \ll M$. On the other hand, for $n_2/n_1 \ll M- Kn_1$, as a consecuence of the negligible role played by heavy-heavy collisions, the kinetic equation governing the heavy gas distribution function is substantially simplified to a partial differential equation of the Fokker-Planck (FP) form (Secs.2.5.3-4).

Based in the fact that, for $M \ll 1$, the lowest order distribution functions in the CE method are Maxwellians with independent mean velocities and temperatures, a more general derivation of the two-fluid hydrodynamic equations is given in Chapter 3, valid for any value of the mass ratio M. These hydrodynamic equations contain those derived in Chapter 2 in the limit $M \ll 1$ though, of course, the equations corresponding to the heavy gas are not valid when $n_2/n_1 \leq O(Kn_1)$ (in this limit $M- Kn_1 \ll 1$). For $M=O(1)$, the hydrodynamic equations derived in Chapter 3 coincide with the standard Navier-Stokes equations (NSEs) for binary mixtures when both temperatures and mean velocities are equated. The conditions under which the two-fluid hydrodynamic equations are equivalent to the standard NSEs for binary mixtures are discussed in the last section of Chapter 3.

In Chapter 4 we discuss the heavy gas hypersonic limit. This limit is relevant because, as a consequence of the mass disparity, the heavy gas may be in hypersonic conditions even for subsonic conditions of the light gas. For instance, in a He-Xe mixture ($M \approx 0.03$) with a Mach number of one for the light gas [$Ma_1 \equiv U_1/(\gamma_1 kT_1/m_1)^{1/2} = 1$, where U_1 and T_1 are the light gas mean velocity and temperature, γ_1 is its specific heat ratio and k is Boltzmann's constant], and the same mean velocity for both components, the heavy gas Mach number Ma_2 is equal to $M^{-1/2} \approx$ 5.75. We shall consider the limit $n_2/n_1 \ll M \ll 1$, $Kn_1 \ll 1$, for which the heavy gas is governed by a FP equation and perform an expansion of this equation in powers of Ma_2^{-1}. More precisely, we shall expand in powers of $M^{1/2}$, assuming that the light gas Mach number is $O(1)$ and that v (the ratio between the difference of mean velocities among species and the light gas thermal speed) is small. In particular, two different hypersonic expansions of the FP equation will be considered. In the first of them, the pressure tensor will be neglected in the momentum equation corresponding to the lowest order of the expansion, while, in the second hypersonic expansion, the pressure tensor will be retained in that equation. At the lowest order of both expansions we shall obtain an anisotropic Gaussian distribution as the normal solution, whose first and third moments, density and pressure tensor respectively, obey the standard continuity equation and the pressure tensor equation without the heat flux term (that is, a hypersonic closure of the moment equations). One of the most important results of Chapter 4 is about the order of magnitude of the errors in the above hypersonic hydrodynamic equations. We shall show that the errors in the pressure tensor are $O(M)$ [when $Ma_1=O(1)$ and provided that

the normal Gaussian distribution applies], instead of $O(M^{1/2})$ as one might have expected from the ordinary scaling of the hypersonic closure. Therefore, in the limit $n_2/n_1 \ll M$, $Kn_1 \ll 1$ (for which the near-equilibrium hydrodynamic equations for the heavy gas are not valid), and provided that the heavy gas is in hypersonic conditions, one can still have a hydrodynamic description for both components of the mixture with errors $O(Kn_1, M)$.

The hydrodynamic equations at the lowest order of the expansion (hypersonic closure) will also be obtained without the restrictions $v \ll 1$ and $n_2/n_1 \ll M$ in the last section of Chapter 4. To this end we shall use a generalized form of the FP equation valid for arbitrary values of v (given in Ch.2), and include a self-collision term in the pressure tensor equation.

In the second part of this dissertation, Chapters 5 to 8, we shall apply the theories given in chapters 2, 3 and 4 to some specific problems with the objective of testing them. Thus, the two-fluid CE theory of Chapter 3 (which contains the limit $M \ll 1$ considered in Chapter 2), is applied to the propagation of sound in Chapter 5. In particular, it is applied to the sound propagation in He-Xe mixtures for which experimental data on absorption and dispersion of sound can be found in the literature (Fuentes Losa, 1972, and Bowler, 1984). It is shown that, at low frequencies, the resulting expression for the absorption of sound coincides with Kohler's expression derived from the classical CE theory for binary mixtures, and the agreement with the experiments is excellent. As the frequency increases, the predictions of the standard CE theory become poor, while the two-fluid theory agrees reasonably well with experimental data on absorption. These results are in accordance with the discussion given in Section 2.1 on the frequency (Knudsen number) range of validity of both the standard CE theory for binary mixtures and the two-fluid CE theory.

In Chapter 6 we consider the structure of normal shock waves for DMM in the limit $\rho_2/\rho_1 \leq O(1)$, where ρ_i is the mass density of species i. This is an example where the near-equilibrium hydrodynamic equations for the heavy gas are not valid, even when the light gas is in near equlibrium conditions over most of the flow field. That the heavy gas is far from equilibrium has been clear since the work of Sherman (1960), who applied the standard NSEs for binary mixtures to solve this problem. For He-Ar mixtures ($M \approx 0.1$) and small concentrations of the heavy gas (Ar), Sherman obtained an unphysical overshoot in the heavy gas velocity profile, which was obviously not found in subsequent experiments made by Center (1967). To solve this problem we shall use the hypersonic approximation discussed in Chapter 4 for the heavy component, and the near-equilibrium equations of Chapter 2 for the light gas. In particular, we shall use the lowest hypersonic order of the momentum equation in which the pressure tensor is neglected, since it will permit an algebraic solution in phase space for the

heavy gas velocity. This solution is valid throughout the shock wave (with errors of order M) when the light gas Mach number Ma_1 is less than one [but larger than the minimum admisible value $(1+ \rho_2/\rho_1)^{-1/2}$], corresponding to a so-called fully dispersed wave. When $Ma_1 > 1$, the behavior is similar to that of a *dusty gas*, with the algebraic solution valid in the relaxation or outer layer that follows a narrow boundary layer, corresponding, in first approximation, to the shock wave of the light component as a pure gas. This sharp distinction between inner shock of the light gas and relaxation zone governed by a phase space algebraic solution, becomes blurred as Ma_1 approaches unity, and the shock structure must be obtained by integration of a numerically unstable system of three differential equations. However, we shall take advantage of the near conservation of the light gas entropy at the head of the shock to reduce the order of the system of equations and make it stable. Our results, for both strong [$Ma_1 -1 = O(1)$] and weak shocks [$Ma_1 \approx 1$], are in excellent agreement with shock-tube experiments in He-Xe mixtures made at the Polish Accademy of Sciences by Herczynski, Tarczynski and Walenta (1986).

Another test of the hypersonic approximation is made in Chapter 7 where, again, we make use of the shock wave problem. However, this new test is not against experiments as in Chapter 6, but with respect to an exact solution of the kinetic FP equation governing the heavy gas velocity distribution function. In order to find an exact solution of the FP equation, we use a simplified form of the shock wave problem: we assume that the heavy gas is extremely dilute and that the width of the internal light gas shock is negligible. The predictions made in Chapter 4 on the order of magnitude of the errors in the lowest order hypersonic approximation are corroborated by direct comparison of the velocity distribution functions. We also compare the next order of the hypersonic expansion with the exact FP results.

Finally, in Chapter 8, the Euler-level of the light gas equations (ideal flow), and the hypersonic closure of the heavy gas moment equations, but without the assumptions $n_2/n_1 << M$ and $v << 1$, are applied to the flow through a converging nozzle. We assume quasi-one-dimensional flow and the resulting values for the discharge coefficient are compared with experimental measurements made with CCl_4-He mixtures exhausting through a conical-shaped converging nozzle. The discharge coefficient C_d is defined as the ratio between the actual mass flow through the nozzle and the ideal mass flow predicted by the Euler-level of the standard CE theory for binary mixtures. For a binary mixture whose components have similar molecular weights, the maximum value of C_d is unity. However, for DMM, the discharge coefficient may be larger than one because the species are not in equilibrium at the exit of the nozzle. We have measured discharge coefficients for CCl_4-He mixtures larger than one in spite of the fact that the viscous effects were important. When these measured values are corrected to account for

the viscous effects (using discharge coefficients for pure He measured at the same Reynolds number), they agree quite well with the values predicted by the theory.

Chapters 2 to 7 outlined above are based on the following papers:

Ch.2, Fernández de la Mora and Fernández Feria, 1987a (II),

Ch.3, Fernández de la Mora and Fernández Feria, 1987b (III),

Ch.4, Fernández Feria and Fernández de la Mora, 1987c (IV),

Ch.5, Fernández Feria and Fernández de la Mora, 1986 (V),

Ch.6, Fernández Feria and Fernández de la Mora, 1987a (VI),

Ch.7, Fernández Feria and Fernández de la Mora, 1987b (VII).

Reference will be made to them (using roman numerals in brackets) for the most involved derivations.

1.2 Brief review of the technological applications of DMM and their historical development

Because potential industrial applications have been a major driving force on the evolution of this field, before undertaking the program outlined above we will sketch here some of the developments in applied aspects of DMM.

The technological exploitation of the two main features of DMM that were mentioned at the begining of the preceding section is relatively recent. The oldest and most important industrial application of DMM was in the separation of isotopes of uranium, which followed the early work of Becker *et al.* (1954, 1955,1957,1960). These authors observed species separation effects in supersonic jets exhausting from a nozzle into a vacuum chamber. Similar phenomena were subsequently observed by other investigators like Waterman and Stern (1959,1960), Chow (1959) and Reis and Fenn (1963). Reis and Fenn also gave the first plausible explanation of these separation effects on the basis of the deceleration in the bow shock in front of the meassuring probe immersed in the jet: the light gas is deflected but the heavy gas is not, because of its larger molecular mass and, therefore, larger inertia. Reis and Fenn made an analogy between this problem and the similar situation occurring in the separation of aerosols and fine particles from a high-velocity air stream by impaction. This analogy of heavy molecules and particles has proven to be very fruitful in the field of DMM (see, e.g., Fernández de la Mora, 1984). Subsequent to these findings, Becker's group designed different types of nozzles (based on this principle of separation by deflection) for the industrial separation of uranium isotopes from uranium hexafluoride and a lighter gas (see, for instance, Becker *et al.*, 1979, and Bley and Ehrfeld, 1981).

New technological applications of DMM result from the possibility of producing molecular beams with kinetic energies in the interesting energy range of tens of electron volts by seeding heavy molecules in a supersonic jet of He or H_2 [Anderson, Andres and Fenn (1966)]. Basically, the method is based on converting the thermal energy of the seeded gas into kinetic energy by expanding it through a nozzle. Due to the mass disparity among species, the kinetic energy acquired by the heavy gas, when it is dilute, may be about M^{-1} times larger than the kinetic energy of the host gas. Thus, in a He-Xe mixture, the energy of the xenon molecules would be of the order of 3 eV if the nozzle temperature were 300K, and 30 eV if the nozzle temperature were 3000K. Molecules with kinetic energies between 1 and 100 eV are able to break chemical bounds and, therefore, to activate chemical reactions, to clean surfaces of adsorbed species, *etc*. These beam energies cannot be reached with the conventional oven beam by vacuum evaporation. Moreover, although much higher energies may be achieved through electrostatic acceleration of ions, neutral beams have considerable advantages over ion beams in the range of energies between 1 and 100 eV.

A number of studies have utilized seeded beams to achieve energetic molecule-surface interactions. Fenn and his colleagues [e.g. Prada-Silva *et al.* (1979) and Tsou *et al.* (1987)] studied the effect of the translational energy on the kinetics of chemical reactions, such as the isomerization of cyclopropane. Connoly *et al.* (1981) decomposed $W(CO)_6$ molecules seeded in a supersonic H_2 jet by impact on glass surfaces. Some of the fragments of the $W(CO)_6$ condense upon dissociation allowing to visualize the progress of the reaction. Similar experiments were made by Kolodney and Amirav (1983) who studied the effect of the translational energy on the dissociation of iodine molecules by collision with a solid surface. By exploiting the large inertia of the $W(CO)_6$ molecules, Fernández de la Mora (1985) reproduced the surface reactions of Connolly *et al.* at much larger background pressures (smaller Knudsen number), thus achieving far higher fluxes with rather modest pumps.

One of the most promising applications of seeded molecular beams operating at large background densities is in the production of thin and high quality deposits and coatings on solid surfaces by impaction of heavy molecules. The industrialization of these techniques is being attempted by the newly established company Schmitt Technologies Associates. As a consequence of the *chemical* range of the impaction energy, the surface is chemically modified, with the possibility of achieving very remarkable material properties, as it has been observed by Takagi's group (e.g. Yamada *et al.*,1983) using ionized cluster beams. The principal advantages of seeded neutral molecules beams in contrast to ionized cluster beams or ion beams reside in the higher fluxes attainable and in the better controllability of the impact energy, which are fundamental parameters affecting the deposit properties. Progress in the

characterization of seeded jets impacting on surfaces at large densities has been made by Fernández de la Mora et al. (1986), who determined impact energies of $W(CO)_6$ molecules seeded in H_2 jets as a function of the source pressure and the distance between the nozzle and the impact surface, by measuring the amount of carbonyl deposited on the surface at different conditions.

Chapter 2
KINETIC THEORY OF BINARY MIXTURES WITH LARGE MASS DISPARITY

In this chapter, the cross-collision integrals in the kinetic Boltzmann equations for DMM are expanded in powers of the small mass ratio M. The simplified Boltzmann equations are used to derive a variety of hydrodynamic and reduced kinetic equations for DMM which will cover a broad Knudsen number region in which the standard CE theory for binary mixtures (Chapman and Cowling, 1970, Ch.8; referred as I from now on) is not applicable (see Sec.2.1). In particular, a further expansion in the light gas Knudsen number is used to solve the reduced BE of the light gas by the CE method* for any heavy gas distribution function (Sec.2.4). In the case in which the molar fractions of both species are comparable (specifically, $n_2/n_1 >> Kn_1$), a Knudsen number expansion is also possible for the heavy gas kinetic equation (Sec. 2.5.2), and the problem is reduced to its near-equilibrium hydrodynamic (two-fluid) level. When the CE method is not valid, the simplified BEs (particularly the heavy gas BE which is simplified to a Fokker-Planck equation) will permit one to solve some kinetic problems whose solution from the full BEs is extremely difficult (e.g. Ch.7). Furthermore, the kinetic Fokker-Planck equation given in Secs. 2.5.3-4 will be the basis of the hypersonic approach of Chapter 4, subsequently used in Chapters 6 and 8. Almost all the previous works on the subject have been limited to the derivation of two-fluid near-equilibrium hydrodynamic equations. A brief review of them is given in Sec.2.2.

2.1   Insufficiency of the standard CE theory for DMM

As is well known, the failure of the classical Chapman-Enskog theory (Ref.I, Ch.8) for gas mixtures with large mass disparity is a consequence of the presence of very different relaxation times in the problem. On the one hand, there are two self-relaxation times of equilibration, one for each species due to collisions with themselves, which are of order $\mu_i/p_i = \tau_i$ (μ_i and p_i are the viscosity and partial pressure of the species i, respectively). When the molar fractions of both species are comparable ($n_1 \sim n_2$ or $p_1 \sim p_2$), because the experimental values of the viscosity for noble gases are roughly mass independent (see, e.g., Vargaftik, 1975), both self-relaxation times are of the same order. On the other hand, there is a slower relaxation time that characterizes the process of interspecies equilibration. For instance, the

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* See footnote on page 2.

order of the interspecies energy relaxation time τ_e is M^{-1} times larger than the self-relaxation time. Therefore, for $n_1 \sim n_2$, the problem is characterized by two Knudsen numbers: $Kn_i = \omega\tau_i$ and $\omega\tau_e \sim Kn_i/M \ll Kn_i$, where ω is a characteristic frequency of the system (similar Knudsen numbers may be written in terms of a mean free path between collisions and a characteristic length of the system).

The classical CE theory for binary mixtures assumes that the two relaxation times are comparable. Therefore, it can be applied to ordinary (similar-masses) binary mixtures, in which both Knudsen numbers are comparable, when the characteristic frequency of the system is much smaller than the frequency of self-collision τ_i^{-1}, that is, when $Kn_i \ll 1$. For disparate-mass mixtures, because of the presence of the slower relaxation time τ_e, the range of validity of the classical CE theory is reduced to the more restrictive condition $\omega\tau_e \ll 1$, or $Kn_i \ll M \ll 1$. In order to enlarge the Knudsen number range of validity of the CE method for DMM to $Kn_i \ll 1$ (but $\omega\tau_e \sim 1$ or even larger) as in mixtures with similar molecular masses, two temperatures and two velocities must be allowed in the method. In other words, a hydrodynamic description for DMM with the same Knudsen number range of validity as the classical CE theory for similar-masses mixtures has to be a two-fluid description. However, as we shall see, the two-fluid hydrodynamic theory is not so general as the equivalent hydrodynamic description for mixtures with similar masses. In particular, it is not valid when $n_2/n_1 = O(M)$ or smaller, so that one cannot avoid a kinetic formualtion of the problem, even if the mixture Knudsen number is small.

2.2 Review of previous works

Except for a number of works on the mass ratio expansion of the cross-collision integrals in the BEs and on the FP equation (which will be commented along sections 2.3 and 2.5), most previous theoretical works on DMM are focused on the derivation of two-fluid hydrodynamic equations. Some of them are reviewed next.

Two-fluid hydrodynamic theories for neutral monoatomic gases have been attempted since the work of Grad (1960). This author noticed that the ordering of the different terms of the BE implicit in the classical CE method is not appropriate for DMM, proposing three (in some way heuristic) alternative orderings. Grad assumed that the light species relaxes by self-collisions on the order of $M^{-1/2}$ faster than the heavy species. This assumption, which for $p_1 \sim p_2$ implies the unusual scaling $\mu_1/\mu_2 = O(M^{1/2})$ (the coefficient of viscosity is practically mass independent at room temperature for the noble gases) has been followed by many subsequent works in the field.

Sirovich (1962) and Hamel (1966) used relaxation-type models to replace the

Boltzmann collision integrals. Both authors made use of Maxwell molecules in order to derive the model for the cross-collision integrals. These models were extended to other types of molecules by Morse (1963). From Morse's models, Hamel (1966) estimated the order of magnitude of the different relaxation times appearing in the problem obtaining that, for $n_1 \sim n_2$, $\tau_e \gg \tau_1, \tau_v$, where τ_v is the interspecies momentum relaxation time. For $n_2 \ll n_1$ Hamel obtained $\tau_e, \tau_v, \tau_2 \gg \tau_1$ which implies that, even when the light gas is close to equilibrium ($Kn_1 = \omega \tau_1 \ll 1$), the heavy species need not be close to a Maxwellian distribution in the limit $n_2 \ll n_1$ (we shall arrive at a similar result in Sec. 2.5.2). Using the CE method to solve the model equations for $n_1 \sim n_2$, Hamel also gave the first set of DMM two-fluid hydrodynamic equations, to our knowledge. These equations, in accordance with the orders of magnitude referred above, contain two temperatures but only one mixture mean velocity (which coincides with that of the heavy gas), in addition to a diffusion-like equation for the velocity difference, as in the standard NSEs. Thermal diffusion is missing in Hamel's equations as a consequence of the use of the Maxwell molecules model, and the light gas stress tensor does not enter into the momentum equations as a result of following Grad's assumption $\tau_1/\tau_2 = O(M^{1/2})$.

Chmielski and Ferziger (1967) used an ordering of the collision terms different from those suggested by Grad (1960) as the basis of their modified CE method. They assumed that the cross-collision term in the heavy species BE is of order $M^{1/2}$ with respect to the self-collision term, and that both collision integrals in the light gas BE are comparable. The resulting hydrodynamic equations from this *ad hoc* ordering contain two temperatures and only one mean velocity. The transport coefficients calculated by these authors coincide, when both temperatures are made equal, with those of the standard CE theory in the limit $M \rightarrow 0$. A similar procedure was carried out by Johnson (1973), using one of the heuristic orderings suggested by Grad with $M^{1/2}$ as the small parameter.

Goldman and Sirovich (1967,1969a) developed a rigorous two-fluid CE theory for Maxwell molecules. Since the collision integrals can be evaluated explicitly with this molecular model, they calculated the pressure tensors and the heat fluxes to first order in the CE expansion without the need of the velocity distribution functions. The transport coefficients for the mixture calculated by Goldman and Sirovich are identical to those given by the standard CE method for Maxwell molecules.

Goebel *et al.* (1976), followed quite a different approach based on Grad's (1949) thirteen moments approximation for a binary mixture of Maxwell molecules. The two-fluid hydrodynamic equations of these authors (valid for $n_1 \sim n_2$) consist of two sets of equations for the first 13 moments of each species. A somewhat similar treatment, allowing for arbitrary interaction potentials, was followed by Tiem (1984), who made an expansion of the distribution

functions in Hermite polynomials, a technique also introduced by Grad (1949). Tiem estimated the order of magnitude of the collision terms making use of the Hermite expansion of the collision integrals and the hard sphere model. Then, according to this ordering, he applied the CE method, with the additional restriction $Kn=O(M^{1/2})$. To derive his scaling, Tiem also assumed similar molecular diameters for light and heavy species [$\sigma_1/\sigma_2=O(1)$] which is equivalent to the already mentioned hypothesis $\mu_1/\mu_2=O(M^{1/2})$. As a consequence, the two-fluid hydrodynamic equations derived by Tiem lack the light gas stress tensor, which is not correct even in the case n_1-n_2 he considered.

The above two-fluid theories either are for a specific molecular model (Maxwell molecules) or are derived from a not very rigorous method such as the use of model equations, the ordering of the collision terms in a rather unsystematic way, or the expansion in Hermite polynomials whose truncation is somewhat arbitrary. In sections 2.4 and 2.5.2 we shall derive a two-fluid near-equilibrium theory valid for arbitrary potentials of molecular interaction based on the systematic mass ratio expansion of the cross-collision integrals given in the next section. The two-fluid theory will be extended to arbitrary mass ratios in Chapter 3.

2.3   Lorentz-Bernstein and Fokker-Planck collision operators

The objective of this section is to provide reduced forms for the Boltzmann cross-collision integrals by systematic exploitation of the smallness of the parameter M.

Consider the Boltzmann equations for a binary mixture,

$$Df_1 \equiv \frac{\partial f_1}{\partial t} + u \cdot \nabla f_1 = J_{11}(f_1,f_1) + J_{12}(f_1,f_2), \qquad (2.3.1)$$

$$Df_2 \equiv \frac{\partial f_2}{\partial t} + u \cdot \nabla f_2 = J_{21}(f_2,f_1) + J_{22}(f_2,f_2), \qquad (2.3.2)$$

where $f_1(t,x,u)$ and $f_2(t,x,u)$ are the velocity distribution functions for species 1 (light) and 2 (heavy), and u is the molecular velocity. The collision terms J_{ij} are given by the Boltzmann collision integrals

$$J_{ij}(f_i,f_j) = \int d^3u_j \, d\Omega \, g \, \sigma_{ij}(g,\theta) \, [\, f_1(u'_1) \, f_2(u'_2) - f_1(u_1) \, f_2(u_2)], \qquad (2.3.3)$$

where u'_i and u_i, i, = 1,2, are the molecular velocity of the component i before and after the molecular encounter; $g \equiv u_2-u_1$; $g'\equiv u'_2-u'_1$; $g \equiv |g| = |g'|$; $d\Omega = \sin\theta \, d\theta \, d\phi$, where (g, θ, φ) are the spherical coordinates of g' in a reference frame in which g is along the polar axis, and

$\sigma_{ij}(g,\theta)$ is the differential scattering cross section.

The expansion of the light gas cross-collision integral $J_{12}(f_1, f_2)$ in powers of M is based on the small recoil velocity of the heavy gas upon collision (u'_2-u_2 is of order M relatively to u'_2 or u_2), and on the small width of the heavy gas distribution function compared to that of the light gas (of order $M^{1/2}$). This expansion was carried out by Bernstein (1969a) to first order in M, using a reference frame in which the heavy gas is at rest. A similar expansion, but allowing for an arbitrary reference frame (with the only limitation that the heavy gas mean velocity U_2 must be small compared to the light gas thermal speed in that reference frame) is made in Ref. II, Sec. II. The usefulness of this new reference frame follows from the following arguments: in the subsequent CE derivation of f_1, it will be assumed that the difference between light and heavy gas mean velocities is small compared to the light gas thermal speed $(2kT_1/m_1)^{1/2}$, where T_1 is the light gas temperature and k is Boltzmann's constant; that is, it will be assumed that the magnitude v of the vector

$$v \equiv \frac{U_1 - U_2}{(2kT_1/m_1)^{1/2}} \quad , \tag{2.3.4}$$

is a small number, where U_i is the mean velocity of the component i. Thus, with the reference frame used in Ref. II, it will be possible to choose a frame in which $U_1=0$, where the computations are much simpler than in a frame in which $U_2=0$ (see below).

To first order in M, $J_{12}(f_1,f_2)$ can be written as $\big($Ref.II, Eqs.(14) and (15)$\big)$:

$$J_{12}(f_1,f_2) = N(f_1) + U_2 \cdot [L(f_1) - \nabla_\kappa N(f_1)]$$
$$+ [\frac{kT_2}{m_2} + U_2 U_2] : [\nabla_u \{- L(f_1) + \tfrac{1}{2}\nabla_u N(f_1)\} - \tfrac{1}{2}Y(f_1)]$$
$$+ M \nabla_u \cdot R(f_1) + \ldots$$
$$\equiv L(f_1), \tag{2.3..5}$$

$$N(f_1) \equiv \int d\Omega \ v \ [f_1(\kappa) - f_1(u)], \tag{2.3.6}$$
$$L(f_1) \equiv \int d\Omega \ v \ [\nabla_\kappa f_1(\kappa) - \nabla_u f_1(u)], \tag{2.3.7}$$
$$R(f_1) \equiv \int d\Omega \ v \ (u - \kappa) \ f_1(\kappa), \tag{2.3.8}$$
$$Y(f_1) \equiv \int d\Omega \ v \ [\nabla_\kappa \nabla_\kappa f_1(\kappa) - \nabla_u \nabla_u f_1(u)]. \tag{2.3.9}$$

In the above expressions, κ is the vector into which u transforms after a (θ,ϕ) rotation and $v = n_2 u \sigma_{12}(u,\theta)$ is the frequency for heavy-light collisions. The most remarkable feature of the

cross-collision operator (2.3.5) is that f_2 appears in it only through its moments n_2, U_2, P_2, $T_2 \equiv P_2/n_2k$, ..., defined in Appendix A. Therefore, the light gas BE is kinetically decoupled from that of the heavy gas, and can be solved independently. The lowest order term $N(f_1)$ coincides with the cross-collision integral derived by Lorentz (1905) using the physical arguments that are behind the above mass-ratio expansion (basically, at the lowest order, $u_2'=u_2$, f_2 is a delta-function and $u'=\kappa$). For this reason, the cross-collision operator (2.3.5) will be called the Lorentz-Bernstein (LB) operator (as in Ref.II).

A similar mass-ratio expansion based on the small recoil velocity of the heavy gas upon collision with a light molecule can be made in the cross-collision term $J_{21}(f_2,f_1)$ appearing in the heavy gas BE, resulting (Fernández de la Mora and Mercer, 1982):

$$J_{21}(f_2,f_1) = \nabla_u \cdot [b(f_1;u) \, f_2 + \tfrac{1}{2} \nabla_u \cdot \{\Pi \, (f_1;u) \, f_2\}] + \ldots , \qquad (2.3.10)$$

where

$$b(f_1;u) \equiv M_1 \int d^3g \, g \, g \, Q_{12}^1(g) \, f_1(u - g), \qquad (2.3.11)$$

$$\Pi \, (f_1;u) \equiv M_1^2 \int d^3g \, g \, [\tfrac{1}{2}(g^2 I \, -3gg) \, Q_{12}^2(g) + 2gg \, Q_{12}^1(g)] \, f_1(u - g), \qquad (2.3.12)$$

$$M_i \equiv \frac{m_i}{m_1 + m_2} . \qquad (2.3.13)$$

The functions Q_{12}^i are defined in Appendix C, Eq.(C10), and I is the unit tensor. Equation (2.3.10) is the general form of the Fokker-Planck (FP) collision operator. Further progress can be made once the light gas distribution function f_1 is known. For example, Wang Chang and Uhlenbeck (1970) used a Maxwellian distributon for f_1, so that their expression for J_{21} is valid when the light gas is in equilibrium (their expression coincides with the standard form of the FP operator). Fernández de la Mora and Mercer (1982) extended the previous result to a non-equilibrium light gas by using the first order of the CE expansion for f_1 (with the light gas considered as a pure gas). Since the light gas BE is decoupled from the heavy gas, the right procedure is to solve first the light gas BE and, then, substitute the resulting f_1 into Eq.(2.3.10). This is done in Sec. 2.5 using the expression for f_1 obtained in Sec. 2.4 from a Knudsen number expansion of the light gas BE.

2.4 Near-equilibrium hydrodynamic equations for the light gas

A near-equilibrium closure of the light gas moment equations, which are given in the

Appendix A [Eqs.(A26-28)] with

$$M = m_1 [L(f_1), c_1] ,$$ (2.4.1)

$$E_1 = m_1 [L(f_1), \frac{c_1^2}{2}] ,$$ (2.4.2)

[the inner product is defined in Eq.(A5) of Appendix A], can be obtained in the limit $Kn_1 \ll 1$ by means of an expansion of f_1 in powers of Kn_1. Since only the moments of f_2 enter into Eqs.(2.4.1-2), the resulting hydrodynamic equations for the light gas will be valid regardless of whether the heavy gas is also in near-equilibrium conditions; that is, regardless of whether a similar Knudsen number expansion for the heavy gas is also possible. Moreover, in contrast to some previous works cited in Sec.2.2, there will be no limitation in the relative values of Kn_1 and M; that is to say, the small parameter Kn_1 will be independent of the small parameter M in the respective expansions in powers of M and Kn_1. We shall retain terms up to the first order in both Kn_1 and M.

For the computation of the integrals in the LB operator, we shall use a reference frame in which $U_1=0$, so that U_2 must be substituted by U_2-U_1 in Eq.(2.3.5). At the first order, only the terms of order v will be retained. Thus, we make an expansion of f_1,

$$f_1 = f_{10}(1 + \phi_1 + \cdots) ,$$ (2.4.3)

in such a way that ϕ_1 will contain the first order corrections in Kn_1, M and v. Relatively to $J_{11}(f_1,f_1)$, the streaming term in Eq.(2.3.1) is $O(Kn_1)$, and all the terms of $L(f_1)$, except the first one N (f_1), are either $O(M)$ or $O(v)$, or smaller. Hence, at the lowest order we have

$$J_{11} (f_{10},f_{10}) + N(f_{10}) = 0 ,$$ (2.4.4)

whose unique solution is the Maxwellian[*]

$$f_{10} = n_1 (\frac{m_1}{2\pi kT_1})^{3/2} exp \{- m_1 \frac{|u - U_1|^2}{2kT_1} \}.$$ (2.4.5)

The term $N(f_{10})$ is $O(n_2/n_1)$ relatively to $J_{11}(f_{10},f_{10})$, so that it is not important when $n_2 \ll n_1$

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[*] Notice that $N(f)=0$ for any spherically symmetric function f, that the unique solution of $J_{11}(f_{10},f_{10})=0$ is (2.4.5) and that, as it is shown in Ref.II, Appendix A, $N(f)$ is a nonpositive operator, and so is J_{11} (see Ref.I, Ch.4).

[that this is so can be seen in Appendix C, where the calculated transport coefficients of the light gas contains corrections $O(n_2/n_1)$ with respect to the pure gas values].

To first order in M, Kn_1 and v, we have the following equation for ϕ_1:

$$Df_{10} - L(f_{10}) = K_1(\phi_1) + N(f_{10}\phi_1) ,$$

(2.4.6)

where $K_1(\phi_1) \equiv J_{11}(f_{10},f_{10}\phi_1) + J_{11}(f_{10}\phi_1,f_{10})$ is the linear integral operator $-n_1^2 I(\phi_1)$ of Ref.I, Eq.(4.4,3). Proceeding as in the CE theory for a pure gas (Ref.I, Ch.7),[*] it is shown in Ref.II, Secs. IIIB-D, that the solution of Eq.(2.4.6) can be written as

$$\phi_1 = B_1(\xi_1)\xi_1 \xi_1 : \nabla^\circ U_1 + D_1(\xi_1)\xi_1 \cdot v + A_1(\xi_1)c_1 \cdot \nabla \ln T_1 + k_1 + k_2 \cdot \xi_1 \alpha(\xi_1) + k_3\xi_1^2 ,$$

(2.4.7)

where

$$K_1(B_1\xi_1 \,^\circ\xi_1) + N(f_{10} B_1\xi_1 \,^\circ\xi_1) = 2 f_{10}\xi_1 \,^\circ\xi_1 \equiv \psi_b ,$$

(2.4.8)

$$K_1(D_1\xi_1) + N(f_{10} D_1\xi_1) = 2 f_{10}v_1 \xi_1 \equiv \psi_d ,$$

(2.4.9)

$$K_1(A_1c_1) + N(f_{10} A_1c_1) = f_{10}(\xi_1^2 - \frac{5}{2})c_1 \equiv \psi_a ,$$

(2.4.10)

$$K_1(\alpha\xi_1) + N(f_{10} \alpha\xi_1) = 2 f_{10}\xi_1 \equiv \psi_\alpha ,$$

(2.4.11)

$$\xi_1 \equiv \frac{c_1}{(2kT_1/m_1)^{1/2}} ,$$

(2.4.12)

$$v_1 \equiv n_2 c_1 \overset{1}{Q}_{11}(c_1) ,$$

(2.4.13)

while $\overset{1}{Q}_{11}(c_1)$ is defined in Eq.(C10) and $\nabla^\circ U_1$ is the symmetric traceless velocity gradient tensor. The functions 1, $\xi_1\alpha(\xi_1)$ and ξ_1^2 are the solutions of the homogeneous equation corresponding to (2.4.6).[†] In a pure gas, the solutions of the corresponding homogeneous equation are the collision invariants 1, ξ_1 and ξ_1^2, so that the function $\xi_1\alpha(\xi_1)$ plays here the same role as ξ_1 in the CE theory for a pure gas. k_1, k_2 and k_3 are arbitrary constants which are chosen in such a way that ϕ_1 does not contribute to n_1, U_1 and T_1; that is, $[f_{10}\phi_1,1] = [f_{10}\phi_1,\xi_1]$

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[*] See footnote on page 2.

[†] Notice that, once the time derivatives are eliminated in Df_{10} by means of the Euler-level of the conservation equations (A26-28), this term contributes to the homogeneous equation as a consequence of the momentum and energy transfer between species, M and E_1.

$= [f_{10}\phi_1,\xi_1{}^2]=0$, $j=1,2,3$. Clearly, $k_1=k_2=0$, while $k_2=\lambda_T\nabla\ln T_1 + \lambda_u v$, where the coefficients λ_T and λ_u satisfy the constraints

$$[A_1(\xi_1)c_1 + \lambda_T\xi_1\alpha(\xi_1), f_{10}\xi_1] = 0, \tag{2.4.14}$$

$$[D_1(\xi_1)\xi_1 + \lambda_u\xi_1\alpha(\xi_1), f_{10}\xi_1] = 0, \tag{2.4.15}$$

and are related to the transport coefficients k_{T1} and λ_b given below.

The functions $A_1(\xi_1)$, $B_1(\xi_1)$, $D_1(\xi_1)$ and $\alpha(\xi_1)$ cannot be obtained analytically for a general potential of molecular interaction (only for Maxwell molecules, that is, molecules repelling each other with a fifth-power law, can these functions be obtained in a closed form). Following Bernstein (1969b), we compute these functions from variational principles (based on the symmetry and nonpositivity of the operators K_1 and N), in such a way that the transport coefficients are optimally determined.*

Substituting $f_1=f_{10}(1+\phi_{10})$ into the definitions of P_1, Q_1, M_1 and E_1 (Appendix A), we obtain the following near-equilibrium ($Kn_1 << 1$) closure of the conservation equations (A26-28) for the light gas:

$$P_1 = n_1kT_1 I - 2\mu_1\nabla^\circ U_1, \tag{2.4.16}$$

$$Q_1 = -\lambda_1\nabla T_1 + nkT\,k_{T1}(U_1 - U_2), \tag{2.4.17}$$

$$M_1 \equiv M = -m_1 n_1 n_2 \lambda_b (U_1 - U_2) - nkT\,k_{T1}\nabla\ln T_1, \tag{2.4.18}$$

$$E_1 \equiv E = -n^2\sigma_t(T_1 - T_2), \tag{2.4.19}$$

where

$$n \equiv n_1 + n_2 \tag{2.4.20}$$

and

$$T \equiv \frac{n_1 T_1 + n_2 T_2}{n} \tag{2.4.21}$$

are the number density and temperature of the mixture. For a given class of trial functions $\chi_B(\xi_1)$, $\chi_A(\xi_1)$ and $\chi_\alpha(\xi_1)$, the optimum transport coefficients μ_1, λ_1, k_{T1} and λ_b may be expressed in terms of the functions $\chi_B{}^*(\xi_1)$, $\chi_A{}^*(\xi_1)$ and $\chi_\alpha{}^*(\xi_1)$ that maximize the functionals

$$\Lambda_B(\chi_B) \equiv [\chi_B\xi_1\xi_1 :, K_1(\chi_B\xi_1\xi_1) + N(f_{10}\chi_B\xi_1\xi_1) - 2\psi_b], \tag{2.4.22}$$

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* See appendix B for the basic ideas on these variational principles.

$$\Lambda_A(\chi_A) \equiv [\chi_A \xi_1 \cdot, K_1(\chi_A \xi_1) + N(f_{10} \chi_A \xi_1) - 2\psi_a],$$ (2.4.23)

$$\Lambda_\alpha(\chi_\alpha) \equiv [\chi_\alpha \xi_1 \cdot, K_1(\chi_\alpha \xi_1) + N(f_{10} \chi_\alpha \xi_1) - 2\psi_\alpha],$$ (2.4.24)

respectively, as (see Sec.IIID of Ref.II and Appendix B)

$$\frac{2\mu_1}{kT_1} = \Lambda_B(\chi_B^*)$$ (2.4.25)

$$\frac{\lambda_1}{k} = \Lambda_A(\chi_A^*) - [\chi_\alpha^* \xi_1 \cdot, \psi_a] [\chi_A^* \xi_1 \cdot, \psi_\alpha]/\Lambda_\alpha(\chi_\alpha^*),$$ (2.4.26)

$$k_{T1} = -\frac{m_1 n_1}{2nkT} \left(\frac{2kT_1}{m_1}\right)^{1/2} [\chi_\alpha^* \xi_1 \cdot, \psi_a]/\Lambda_\alpha(\chi_\alpha^*),$$ (2.4.27)

$$\frac{n_2 \lambda_b}{3n} = \{\Lambda_\alpha(\chi_\alpha^*)\}^{-1}.$$ (2.4.28)

The contracted inner products are defined as

$$[f\cdot, g] \equiv \int d^3u\, f(u) \cdot g(u),$$ (2.4.29)

and similarly $[F :, G]$. Notice that the coefficient λ_b of Ref.II corresponds to $-\lambda_b n_2$ defined above (this change is to unify with the notation of the next chapter where all the transport coefficients depend on the number densities only through the molar fractions). A common choice for the trial functions χ_A, χ_B and χ_α are Sonine polynomial expansions. The transport coefficients obtained at the first and second order of these expansions for arbitrary molecular interactions with a central force law are given in Appendix C. Obviously, if the complete Sonine expansions are used, the maxima of the functionals (2.4.22-24) are exactly the functions B_1, A_1 and α_1.

The transport coefficient σ_t is given by [Ref.II, Eqs.(E1) and (B5)]

$$\sigma_t = \frac{3kn_2}{\tau_e\, n^2},$$ (2.4.30)

where

$$\tau_e \equiv \frac{3}{16\, n_1 M\Omega_{12}^{(1,1)}(T_1)}.$$ (2.4.31)*

Notice that, in first approximation in Kn_1, M and v, the function ϕ_1 is not needed for the evaluation of σ_t.

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* See Appendix C for the definition of the Ω-integrals.

2.5 Equations for the heavy gas when $Kn_1 \ll 1$

2.5.1 *Fokker-Planck Collision operator*

When the near-equilibrium light gas distribution functions of the preceding section, $f_1 = f_{10}(1 + \phi_1)$ [Eqs.(2.4.5) and (2.4.7)], is substituted into Eqs.(2.3.10-12), and the quantities b and Π [Eqs.(2.3.11-12)] are expanded in powers of v, the following expression for the FP collision operator results to first order in M, Kn_1 and v [Ref.II,Eq.(92)]:

$$F(f_2) \equiv \nabla_u \cdot \left\{ \left[\frac{M}{m_2 n_2} + \frac{u - U_2}{\tau_e} \right] f_2 + \frac{kT_1}{m_2 \tau_e} \nabla_u f_2 \right\} , \tag{2.5.1}$$

with M and τ_e given by Eqs.(2.4.18) and (2.4.31), respectively. If use is made of the first approximation in the Sonine polynomial expansion for λ_b [Appendix C, Eq.(C4)], the above expression reduces to

$$F(f_2) = \tau_e^{-1} \nabla_u \cdot \left\{ (u - W) f_2 + \frac{kT_1}{m_2} \nabla_u f_2 \right\} , \tag{2.5.2}$$

where

$$W \equiv U_1 + \frac{nkT \, k_{T_1} \tau_e}{m_2 n_2} \nabla \ln T_1 , \tag{2.5.3}$$

which coincides with the FP operator obtained by Fernández de la Mora and Mercer(1982), using the function f_1 given by the first order of the CE theory for a pure gas (without taking into account the effect of the heavy gas on the light gas distribution function). Equation (2.5.2) is not correct when a higher order expression for λ_b is used except in the limit $n_2/n_1 \to 0$, in which $\lambda_b \to [\lambda_b]_1$ (see Appendix C). W can be expressed in a more convenient form in terms of the binary diffusion coefficient D_{12} and the thermal diffusion factor $\alpha_{T1} \equiv k_{T1}/x_1 x_2$, where x_i is the molar fraction of component i. In the limit $M \ll 1$, and in first approximation in the Sonine polynomial expansion, D_{12} can be related to τ_e through [Ref.I, Eq.(9.81,1)]

$$[D_{12}]_1 = \frac{k T \, x_1 \tau_e}{m_2} , \tag{2.5.4}$$

so that

$$W = U_1 + \alpha_{T1} D_{12} \nabla \ln T_1 . \tag{2.5.5}$$

2.5.2 Near-equilibrium hydrodynamic equations for the heavy gas

Similarly to the light gas, a near-equilibrium closure of the heavy gas moment equations is possible when $Kn_2 \ll 1$. Since $\mu_1 \sim \mu_2$ (see Sec.2.1), we have

$$Kn_2 \sim \frac{n_1 Kn_1}{n_2} . \tag{2.5.6}$$

Hence, if the FP operator (2.5.1) is to be used (which was derived for $Kn_1 \ll 1$), a near-equilibrium closure of Eqs.(A26-28) for the heavy gas is valid provided that $n_2/n_1 \geq O(1)$. To be more accurate we estimate next the order of magnitude of the different terms entering into the heavy gas BE.

With respect to the free streaming operator Df_2, the self-collision operator $J_{22}(f_2,f_2)$ is of order $Kn_2^{-1} \equiv p_2\omega^{-1}/\mu_2$, and the cross-collision term is of order $(\omega\tau_e)^{-1}$. On the other hand,

$$\frac{p_2\omega^{-1}}{\mu_2} = \frac{T_2\, n_2\mu_1}{T_1\, n_1\mu_2}Kn_1^{-1} \sim \frac{n_2}{n_1}Kn_1^{-1} , \tag{2.5.7}$$

$$(\omega\tau_e)^{-1} = \frac{T}{T_1}\, Sc\, M\, Kn_1^{-1} \sim M\, Kn_1^{-1} , \tag{2.5.8}\dagger$$

where $Sc \equiv \mu_1/m_1 n D_{12}$ is the Schmidt number, and use has been made of Eq.(2.5.4). Hence, the order of magnitude of the different terms in the heavy gas BE may be written as

$$
\begin{array}{ccccc}
Df_2 & = & F(f_2) & + & J_{22}(f_2,f_2) \\[4pt]
Kn_1 & & M & & \dfrac{n_2}{n_1} ,
\end{array}
\tag{2.5.9}
$$

from which an expansion in powers of Kn_1 can be made in the following two cases: (i) when $Kn_1 \ll M \ll 1$ and for any value of n_2/n_1 ; (ii) when $n_2/n_1 \gg Kn_1$, $1 \gg Kn_1 \geq O(M)$ (i.e., $Kn_1 \ll 1$ and $n_2/n_1 \geq O(1)$, basically). In the first case, the standard CE theory for binary mixtures applies, yielding only one temperature and one mean velocity for the mixture (Ref.I, Ch.8). The second possibility, in which we are interested for greater generality in the Knudsen number range of applicability, allows for independent temperatures and mean velocities of the two gases. In fact, expanding f_2,

---

$\dagger$ Notice that Sc is almost constant and $O(1)$ for noble gases, see Srivastava and Rosner, 1979.

From Eq.(A30), $E_1 + E_2 = -M \cdot (U_1 - U_2)$. Hence, in a first order theory in M, Kn_1 and v, we substitute E_2 by $- E_1 \equiv - E$. The expressions for **M** and E are given by Eqs.(2.4.18-19), and the transport coefficients μ_2 and λ_2 are those of a pure gas (see Ref.I, Sec.9.7, for the expressions of μ_2 and λ_2 calculated by means of an expansion in Sonine polynomials of the functions B_2 and A_2).

2.5.3 *Fokker-Planck equation*

When $n_2/n_1 \sim M \ll 1$ and $Kn_1 \sim M$, the heavy gas BE cannot be solved by the CE method. Therefore, the full Boltzmann equation, but with the simplified form of the cross-collision operator given by Eq.(2.5.1), has to be used. Notice that, when $M \sim 1$, the standard CE theory can be applied to both species, regardless of the value of n_2/n_1, provided that the mixture Knudsen number Kn is small [$Kn \sim \omega \mu_1/(p_1+p_2)$ can be small even if Kn_2 is O(1) or larger; for instance, if $n_2/n_1 \ll Kn_1 \ll 1$].

In the limit $n_2/n_1 \ll M \sim Kn_1$, the self-collision term in the heavy gas BE can be neglected, so that the heavy gas BE is simplified to an equation of the Fokker-Planck form:

$$\frac{\partial f_2}{\partial t} + u \cdot \nabla f_2 = \tau_e^{-1} \nabla_u \cdot \{ (u - W) f_2 + \frac{kT_1}{m_2} \nabla_u f_2 \} . \tag{2.5.20}$$

This equation had its origin in the theory of Brownian motion of particles inmersed in a host fluid, and was originally derived from the Langevin equation and the theory of stochastic processes (see, e.g., Chandrashekar,1943). The inclussion of the nonequilibrium effects of the host gas, within the stochastic point of view, was made by Mazo (1969) and by Slinn and Shen (1971). The driving force W/τ_e due to the light gas plays in Eq.(2.5.20) the same role as the external acceleration in the theory of stochastic processes.

2.5.4 *Fokker-Planck equation for arbitrary slip velocity*

In deriving the FP collision operator (2.5.1) from Eq.(2.3.10), we assumed small slip velocity (v≪1), retaining only first order terms of the expansions of **b** and Π in powers of v. This assumption is in accordance with the light gas distribution function used to derive Eq.(2.5.1), which was also first order in v. However, one can relax this assumption in the limit $n_2/n_1 \ll M \sim Kn_1$ (in which the FP equation is valid) because the effect of the heavy gas on the light gas distribution function is negligible (see Sec.2.5.1). Moreover, for $n_2/n_1 \ll 1$, the assumption v≪1 is more likely to be violated because the efficiency of the momentum transfer

between species decreasses with n_2/n_1 (see Sec.3.3). Therefore, it is convenient to consider the FP equation with the full dependence on v.

The integrals $\mathbf{b}$ and Π [Eqs.(2.3.11-12)] have been computed by Riesco-Chueca, Fernández-Feria and Fernández de la Mora (1987) (referred as VIII from now on) without the assumption of small slip velocity, and in the particular case in which f_1 is a Maxwellian distribution (that is, at the lowest order in Kn_1). In the notation of Riesco-Chueca et al.(1986),

$$\mathbf{b} = \frac{(\mathbf{u} - \mathbf{U}_1)\nu_B}{\tau_e},$$ (2.5.21)

$$\Pi \equiv \Pi_1 + \Pi_2,$$ (2.5.22a)

$$\Pi_1 = \frac{2kT_1[\nu_B(I - \mathbf{e}_\delta\mathbf{e}_\delta) + \nu_{\Pi1}\mathbf{e}_\delta\mathbf{e}_\delta]}{\tau_e m_2},$$ (2.5.22b)

$$\Pi_2 = \frac{2kT_1\delta^2 G \nu_{\Pi2}(I - 3\mathbf{e}_\delta\mathbf{e}_\delta)}{\tau_e m_2},$$ (2.5.22c)

where $\mathbf{e}_\delta$ is the unit vector in the direction of $\mathbf{u} - \mathbf{U}_1$. Hence, the FP equation becomes

$$\frac{\partial f_2}{\partial t} + \mathbf{u} \cdot \nabla f_2 = \tau_e^{-1} \nabla_u \cdot \{ (\mathbf{u} - \mathbf{U}_1) \nu_B f_2$$

$$+ \frac{kT_1}{m_2} \nabla_u \cdot [\nu_B(I - \mathbf{e}_\delta\mathbf{e}_\delta) + \nu_{\Pi1} \mathbf{e}_\delta \mathbf{e}_\delta + \delta^2 G \nu_{\Pi2}(I - 3\mathbf{e}_\delta \mathbf{e}_\delta)]f_2 \} .$$ (2.5.23)

In the above expressions, ν_B, $\nu_{\Pi1}$ and $\nu_{\Pi2}$ are complicated functions of

$$\delta^2 \equiv \frac{|\mathbf{u} - \mathbf{U}_1|^2}{2kT_1/m_1},$$ (2.5.24)

which tend very rapidly to unity as $\delta \to 0$, so that Eq.(2.5.23) coincides with Eq.(2.5.20) for $\delta \ll 1$.* Using the integrals I_B, $I_{\Pi1}$ and $I_{\Pi2}$ defined in Ref. VIII [Eqs.(31-33), but noticing that v must be substituted by δ in those equations], and for a Lennard-Jones potential of molecular interaction characterized by the constants ε_{12} and σ_{12} (see Hirschfelder et al., 1954, Sec.8.4), we have

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* $\delta^2 = v^2 + O(M, vM^{1/2})$ (see Eq. 2.3.4); hence, to first order in M, $\delta \to 0$ is equivalent to $v \to 0$. Notice also that, at the lowest order in Kn_1, $W=U_1$.

$$v_B = \frac{K_B T_1^{*} (2kT_1/m_1)^{-1/2} \tau_e}{\delta M_2} I_B , \qquad (2.5.25a)$$

$$v_{\Pi 1} = \frac{K_\Pi T_1^{*3/2} m_2 \tau_e}{2kT_1 M_2^{2}} I_{\Pi 1} , \qquad (2.5.25b)$$

$$v_{\Pi 2} = \frac{K_\Pi T_1^{*3/2} m_2 \tau_e}{12 kT_1 \delta^2 G M_2^{2}} I_{\Pi 2} , \qquad (2.5.25c)$$

where

$$T_1^{*} \equiv \frac{kT_1 M_2}{\epsilon_{12}} , \qquad (2.5.25d)$$

$$G \equiv \frac{\Omega_{12}^{(2,2)}(T_1)}{5\, \Omega_{12}^{(1,1)}(T_1)} , \qquad (2.5.25e)$$

while the integrals $\Omega_{12}^{(i,j)}$ are defined in Appendix C, Eq.(C9), and M_2 is given by Eq.(2.3.13). The constants K_B and K_Π are defined in Ref.VIII, Eq.(30). Analytic asymptotic expressions for the integrals I_B, $I_{\Pi 1}$ and $I_{\Pi 2}$ are given in the same reference for $\delta \ll 1$, $\delta \gg 1$, $T_1^{*} \ll 1$ and $T_1^{*} \gg 1$. Notice that, in order to use the expressions of Ref.VIII, v must be substituted by δ. Although $\delta = v + O(M^{1/2})$ [see Eq.(2.3.4)], the above substitution contains errors of order M in Ref.VIII (as in sec.4.4 below) because the integrals b and Π are used to compute the momentum and energy transfer between species M and E_2 (b, M and $2E_2$ are denoted, respectively, by B, $\rho_p b$ and - $\rho_p E$ in Ref.VIII). In fact, we shall see in Sec.4.4 that, to obtain the moment equations for the heavy gas correct to first order in M from the FP equation (2.5.23), δ may be substituted by v in the expressions for v_B, $v_{\Pi 1}$ and $v_{\Pi 2}$.

If the non-equilibrium effects (first order terms in Kn_1) are included in the light gas distribution function f_1, the resulting FP equation will contain additional terms proportional to $\nabla^{\circ} U_1$ and $\nabla \ln T_1$. (It must be noticed that the FP equation (2.5.20) does not have a term proportional to $\nabla^{\circ} U_1$ because this term is $O(Kn_1 v)$, and it is neglected in a first order theory in Kn_1 and v.) However, the inclussion of these new terms in the FP equation (2.5.23) is not very important in most situations [in fact, the term proportional to $\nabla \ln T_1$ in Eq.(2.5.20) is usually negligible compared to the term U_1, except when this one vanishes, see Eq.(2.5.5)].

2.6 Summary of the basic equations for DMM

A. General kinetic equations: Eqs.(2.3.1) and (2.3.2) with the cross-collision integrals J_{12} and J_{21} evaluated using the expansions (2.3.5) and (2.3.10) (LB and FP operators, respectively).

B. Limit $Kn_1 \ll 1$: Equations (A26-28) with the near-equilibrium closure (2.4.16-19) for the light gas; the FP collision operator is simplified to the form (2.5.1). Further simplifications of the heavy gas description are possible when, in addition to $Kn_1 \ll 1$, we have:

B1. $n_2/n_1 \gg Kn_1$. The near-equilibrium two-fluid hydrodynamic equations (A26-28) with (2.5.16-19) can be applied to the heavy gas (it behaves, in first approximation, as a pure gas). Therefore, in this limit $Kn_1 \ll 1$ and $n_2/n_1 \gg Kn_1$, we have a near-equilibrium two-fluid hydrodynamic description of the mixture. A more general two-fluid near-equilibrium description valid for arbitrary values of M will be derived in the next chapter.

B2. $n_2/n_1 \ll M$. The FP equation (2.5.20) [or (2.5.23) if v is not small] applies for the heavy gas. No hydrodynamic description for the heavy gas is possible, except in the hypersonic limit discussed in Chapter 4 (which is also valid for $n_2/n_1 \sim M$).

C. Limit $Kn_1 \ll M$. The classical CE theory is valid (Ref.I, Ch.8), so that the standard NSEs can be used.

Chapter 3
TWO-FLUID HYDRODYNAMIC EQUATIONS FOR ARBITRARY MASS RATIO

In the preceding chapter we discussed the different regimes occuring in binary mixtures with $M \ll 1$. In particular, we showed that a near-equilibrium two-fluid hydrodynamic description for both species was possible in the limit $Kn_1 \ll 1$, $n_2/n_1 \ll Kn_1$ [$M \leq O(Kn_1)$]. The present chapter will extend these two-fluid hydrodynamic equations to any value of M. These equations will be a generalization of the single-fluid equations obtained from the standard CE theory for binary mixtures (Ref.I, Ch.8). Thus, in the limit $M=O(1)$, the two-fluid equations developed in the present chapter will coincide with the standard NSEs for binary mixtures when both temperatures and both mean velocities are equated (but allowing for a mean velocity difference in a diffusion-like equation). In the limit $M \rightarrow 0$ they will tend to the near-equilibrium hydrodynamic equations developed in the preceding chapter. In accordance with the orders of magnitude estimated in Sec.2.5, the two-fluid equations will be valid for any value of n_2/n_1 provided that $Kn_1 \ll M$. If M is of the same order or smaller than $Kn_1 \ll 1$, the equations will be restricted to $n_2/n_1 \gg Kn_1$.

As in the preceding chapter, only the general ideas and all the main results will be given here. For many details we shall refer to III.

3.1 Two-fluid Chapman-Enskog theory

Mathematically, the classical CE theory for binary gas mixtures is a single-fluid theory because its lowest order equations are of the form

$$J_{11}(f_1, f_1) + J_{12}(f_1, f_2) = 0, \qquad (3.1.1a)$$
$$J_{21}(f_2, f_1) + J_{22}(f_2, f_2) = 0, \qquad (3.1.1b)$$

whose unique solutions are two Maxwellian distributions with the same temperature T and mean velocity U (coupled Maxwellians, Ref.I, Sec.4.3):

$$f_{i0}^C = n_i (\frac{m_i}{2\pi kT})^{3/2} \exp \{- \frac{m_i |u - U|^2}{2kT} \}, \quad i=1,2. \qquad (3.1.2)$$

It was seen in the preceding chapter that the relative orders of magnitude of the collision terms depend on M in such a way that the lowest order equations (3.1.1) are only valid for $Kn_1 \ll M$.

For M<<1 this is a strong limitation in the validity range of the classical CE theory. However, we showed that, when $Kn_1 \geq O(M)$, the lowest order distribution functions in an expansion in powers of Kn_1 and M are uncoupleld Maxwellians [Eqs.(2.4.5) and (2.5.12)], enabling an extension of the CE method from $Kn_1<<M$ to $Kn_1<<1$. To make this extension uniformly valid in M, we shall force uncoupled Maxwellians f_{i0} as the lowest order solutions for $Kn_1<<1$, regardless of the value of M. If we are contented with a theory valid for small values of the parameters

$$v_i \equiv \frac{|U_i - U|}{(2kT/m_i)^{1/2}}$$

(3.1.3)

and

$$\sigma_i \equiv \frac{T_i - T}{T} ,$$

(3.1.4)

the substitution of $f_{i0}{}^C$ by f_{i0} at the lowest order will be in accordance with a first order theory in these small parameters, since f_{i0}-$f_{i0}{}^C$ is first order in both, v_i and σ_i.* The substitution of the expansion

$$f_i = f_{i0} (1 + \phi_i + \cdots)$$

into the BEs (2.3.1-2) will yield integral equations for the perturbation ϕ_i. An additional difficulty of the resulting equations with respect to the standard CE theory comes from the fact that the uncoupled Maxwellians are not solutions to the Eqs.(3.1.1), so that new terms of the form $J_{ij}(f_{i0},f_{j0})$, $i \neq j$, appear in the equations for ϕ_i. This difficulty was solved by Goldman and Sirovich (1967) by confining their two-fluid theory to Maxwell molecules, for which the new collision integrals can be computed analytically. However, one may solve this problem for arbitrary molecular interaction by relying on the assumption of small v_i and σ_i, and using the same expansion

$$f_i = f_{i0}{}^C(1 + \phi_i{}^C + \cdots)$$

of the standard CE theory. Proceeding in this fashion, the existing computational tools of the standard CE theory can still be used. But, in order to retain the two-fluid features in the problem (errors of order Kn_1 rather than Kn_1/M), two important innovations are made with

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* The near-equilibrium hydrodynamic equations derived in Chapter 2 were valid to first order in the parameter v, Eq.(2.3.4), but there was no restriction with respect to the temperature difference. The parameters v_i are of the same order as v, except in the limit M<<1, $n_2/n_1 \leq O(M)$, in which $v_2>>v$. However, we already know that the near-equilibrium hydrodynamic equations for the heavy gas are not valid in that limit.

respect to the standard CE theory. First, the streaming operators in the left-hand sides of the equations for $\phi_i{}^C$ are evaluated with the uncoupled Maxwellians f_{i0}, instead of the coupled Maxwellians $f_{i0}{}^C$, leading to the first order integral equations

$$Df_{10} = K_{11}(\phi_1{}^C) + K_{12}(\phi_1{}^C + \phi_2{}^C) ,$$ (3.1.5a)

$$Df_{20} = K_{21}(\phi_1{}^C + \phi_2{}^C) + K_{22}(\phi_2{}^C) ,$$ (3.1.5b)

where the K_{ij}'s are the linearized Boltzmann collision operators (the operators K_{11}, K_{12}, K_{21} and K_{22} correspond, respectively, to the operators - $n_1{}^2 I_1$, $-n_1 n_2 I_{12}$, $-n_1 n_2 I_{21}$ and $-n_2{}^2 I_2$, of Ref.I, Sec.4.4). The second substantial difference is about the constraints on the function ϕ_i. We shall require that the functions ϕ_i do not contribute to the number densities, mean velocities and temperatures, n_i, U_i and T_i, of each species, instead of using the constraints of the standard CE theory for binary mixtures according to which the functions $\phi_i{}^C$ have null n_i, U and T. That is to say, in terms of the inner product defined in Appendix A, Eq.(A5), we shall impose the constraints

$$[1, f_{i0} \phi_i] = 0, \quad i=1,2,$$ (3.1.6a)

$$[u, f_{i0} \phi_i] = 0, \quad i=1,2,$$ (3.1.6b)

$$[u^2, f_{i0} \phi_i] = 0, \quad i=1,2,$$ (3.1.6c)

which, since $f_{i0}\phi_i = f_{i0}{}^C - f_{i0} + f_{i0}{}^C \phi_i{}^C + ...$, may be written as

$$[1, f_{i0}{}^C \phi_i{}^C] = 0, \quad i=1,2,$$ (3.1.7a)

$$[c, f_{i0}{}^C \phi_i{}^C] = n_i(U_i - U) , \quad i=1,2,$$ (3.1.7b)

$$[c^2, f_{i0}{}^C \phi_i{}^C] = 3n_i k(T_i - T)/m_i, \quad i=1,2,$$ (3.1.7c)

where $c \equiv u - U$.

Proceeding as in the CE method for pure gases,[*] we eliminate time derivatives in the left side terms Df_{i0} of Eqs.(3.1.5) by means of the conservation equations (A26-28) of Appendix A with $P_i = n_i k T_i I$ and $Q_i = 0$ (two-fluid Euler-level). (Notice that the standard CE theory for binary mixtures eliminates time derivatives from the Euler-level of the *mixture* conservation equations.) In these conservation equations the transfer terms are now given by

$$M = [m_1 c_1, K_{12}(\phi_1{}^C + \phi_2{}^C)] = - [m_2 c_2, K_{21}(\phi_1{}^C + \phi_2{}^C)] ,$$ (3.1.8)

$$E_1 = [m_1 \frac{c_1{}^2}{2}, K_{12}(\phi_1{}^C + \phi_2{}^C)] ,$$ (3.1.9a)

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[*] See footnote on page 2.

$$E_2 = [m_2 \frac{c_2^2}{2}, K_{21}(\phi_1{}^C + \phi_2{}^C)] .$$ (3.1.9b)

The resulting equation for $\phi_i{}^C$ may be written as [Ref.III,Eq.(27)],

$$K_{ii}(\phi_i{}^C) + K_{ij}(\phi_1{}^C + \phi_2{}^C) = \frac{f_{i0}}{2kT_i}[2m_i c_i c_i : \nabla \cdot U_i + c_i \cdot \nabla \ln T_i (m_i c_i{}^2 - 5kT_i)]$$

$$+ \frac{f_{i0}}{p_i} c_i \cdot M_i + \frac{f_{i0}}{p_i} E_i (\frac{m_i c_i{}^2}{3kT} - 1) , \quad (i=1,2; \ j \neq i) ,$$ (3.1.10)

which after substituting c_i, $c_i/(2kT_i/m_i)^{1/2}$ and f_{i0} by c, $c(2kT/m_i)^{1/2}$ and $f_{i0}{}^C$ (this substitution is compatible with our previous change from $f_{i0}{}^C$ to f_{i0}) becomes

$$K_{11}(\phi_1{}^C) + K_{12}(\phi_1{}^C + \phi_2{}^C) = \frac{f_{10}{}^C}{2kT}[2m_1 cc : \nabla \cdot U_1 + c \cdot \nabla \ln T_1 (m_1 c^2 - 5kT)]$$

$$+ \frac{f_{10}{}^C}{n_1 kT}[c \cdot M + E (\frac{m_1 c^2}{3kT} - 1)] ,$$ (3.1.11a)

$$K_{22}(\phi_2{}^C) + K_{21}(\phi_1{}^C + \phi_2{}^C) = \frac{f_{20}{}^C}{2kT}[2m_2 cc : \nabla \cdot U_2 + c \cdot \nabla \ln T_2 (m_2 c^2 - 5kT)]$$

$$- \frac{f_{20}{}^C}{n_2 kT}[c \cdot M + E (\frac{m_2 c^2}{3kT} - 1)] ,$$ (3.1.11b)

where E_2 has been approximated by $-E_1 \equiv -E$, as in Sec.2.5.[†]

It is shown in Ref. III that the functionals M and E are free parameters in the theory; that is, if we consider M and E as constants in Eqs.(3.1.11), the constraints on $\phi_i{}^C$ given by Eqs. (3.1.8) and (3.1.9) are satisfied automatically. These constants M and E are needed as additional free parameters in order to satisfy the constraints (3.1.7) on $\phi_i{}^C$: we need ten scalar parameters in the functions $\phi_i{}^C$ to satisfy these constraints; as in the standard CE theory, six of them come from linear combinations of the collision invariants, which are solutions of the homogeneous equations associated with Eqs.(3.1.11); the remaining four scalar parameters are furnished by E and M.

To be more precise, making use of the vector notation

$$\phi^C = \begin{pmatrix} \phi_1{}^C \\ \phi_2{}^C \end{pmatrix} ,$$

[†] This last approximation is needed in order that the compatibility relations associated to the singular non-homogeneous Eqs.(3.2.11) be satisfied.

the solution to Eqs.(3.2.11) may be written as [Ref.III, Eq.(35)]

$$\underline{\phi}^C = \underline{B}_1 c^\circ c : \nabla U_1 + \underline{B}_2\, c^\circ c : \nabla U_2 + \underline{A}_1 c \cdot \nabla \ln T_1 + \underline{A}_2 c \cdot \nabla \ln T_2 + \frac{Dc \cdot M + \underline{F}\, E}{kT}$$

$$+ k_1 \alpha_1 + k_2 \alpha_2 + k_3 \cdot \alpha_3 + k_4 \alpha_4 \,, \tag{3.1.12}$$

where k_1, k_2, k_3 and k_4 are constants, and the α_i's are the collision invariants:

$$\alpha_1 = \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \quad \alpha_2 = \begin{pmatrix} 0 \\ 1 \end{pmatrix}, \quad \alpha_3 = \begin{pmatrix} m_1 c \\ m_2 c \end{pmatrix}, \quad \alpha_3 = \begin{pmatrix} m_1 c^2 \\ m_2 c^2 \end{pmatrix}. \tag{3.1.13}$$

The vector functions $\underline{B}_i$, $\underline{A}_i$, $\underline{D}$ and $\underline{F}$ satisfy the linear integral equations

$$\underline{K}(\underline{B}_i) c^\circ c = \underline{b}_i c^\circ c \,, \quad i=1,2, \tag{3.1.14a}$$

$$\underline{K}(\underline{A}_i) c = \underline{a}_i c \,, \quad i=1,2, \tag{3.1.14b}$$

$$\underline{K}(\underline{D}) c = \underline{d} c^\circ c \,, \tag{3.1.14c}$$

$$\underline{K}(\underline{F}) c = \underline{e} \,, \tag{3.1.14d}$$

where $\underline{K}$ is the matrix operator defined as

$$\underline{K} = \begin{pmatrix} K_{11} + K_{12} & K_{12} \\ K_{21} & K_{21} + K_{22} \end{pmatrix} \tag{3.1.15}$$

and

$$\underline{b}_1 = \frac{m_1}{kT} \begin{pmatrix} f_{10} c \\ 0 \end{pmatrix}, \quad \underline{b}_2 = \frac{m_2}{kT} \begin{pmatrix} 0 \\ f_{20} c \end{pmatrix}, \tag{3.1.16a}$$

$$\underline{a}_1 = (\frac{m_1 c^2}{2kT} - \frac{5}{2}) \begin{pmatrix} f_{10} c \\ 0 \end{pmatrix}, \quad \underline{a}_2 = (\frac{m_2 c^2}{2kT} - \frac{5}{2}) \begin{pmatrix} 0 \\ f_{20} c \end{pmatrix}, \tag{3.1.16b}$$

$$\underline{d} = \begin{pmatrix} f_{10} c / n_1 \\ -f_{20} c / n_2 \end{pmatrix}, \tag{3.1.16c}$$

$$\underline{e} = \begin{pmatrix} (\frac{m_1 c^2}{3kT} - 1) \frac{f_{10} c}{n_1} \\ -(\frac{m_2 c^2}{3kT} - 1) \frac{f_{20} c}{n_2} \end{pmatrix}. \tag{3.1.16d}$$

The constants k_1, k_2, k_3 and k_4 are fixed by n_1, n_2, U and T, as in the classical CE theory, while $U_1 - U_2$ and $T_1 - T_2$ fix the *constants* M and E, respectively. In fact, substituting Eq.(3.1.12)

into the constraints (3.1.7), we get $k_1 = k_2 = 0$. If, in addition, we make $k_3 = k_4 = 0$, and select **U** as the center-of-mass mean velocity of the mixture and T as the mixture temperature:

$$(\rho_1 + \rho_2)\,\mathbf{U} = \rho_1\mathbf{U}_1 + \rho_2\mathbf{U}_2\,, \tag{3.1.17}$$

$$(n_1 + n_2)T = n_1 T_1 + n_2 T_2\,, \tag{3.1.18}$$

we have the additional constraints on $\phi_i{}^C$

$$\rho_1\,[d_1\mathbf{c},\,\phi_1{}^C] = \rho_2\,[d_2\mathbf{c},\,\phi_2{}^C]\,, \tag{3.1.19a}$$

$$n_1\,[e_1,\,\phi_1{}^C] = n_2\,[e_2,\,\phi_2{}^C]\,, \tag{3.1.19b}$$

where $\underline{d} = \begin{pmatrix} d_1 \\ d_2 \end{pmatrix}$ and $\underline{e} = \begin{pmatrix} e_1 \\ e_2 \end{pmatrix}$. On the other hand, the above choice fix **M** and E as

$$\mathbf{M} = \lambda_1'\nabla\ln T_1 + \lambda_2'\nabla\ln T_2 + \lambda_u(\mathbf{U}_1 - \mathbf{U}_2), \tag{3.1.20}$$

$$E = k(T_1 - T_2)/\{\underline{E},\underline{e}\}\,, \tag{3.1.21}$$

where

$$\lambda_u \equiv 3kT/\{\underline{D}c^2,\underline{d}\}\,, \tag{3.1.22a}$$

$$\lambda_i' \equiv -\lambda_u\,\{\underline{A}_ic^2,\underline{d}\}\,/\,3. \tag{3.1.22b}$$

In the above expressions, the curly brackets inner product is defined as

$$\{\underline{f},\underline{h}\} \equiv [f_1,f_2] + [h_1,h_2]\,, \tag{3.1.23}$$

where $\underline{f} = \begin{pmatrix} f_1 \\ f_2 \end{pmatrix}$, $\underline{h} = \begin{pmatrix} h_1 \\ h_2 \end{pmatrix}$. The coefficients λ_u and λ_i' in Eq.(3.1.20) are related to the transport coefficients k_{Ti} and λ_b given in the next section.

3.2 Two-fluid equations

Making use of the solution (3.1.12) for $\underline{\phi}^C$, it is shown in Ref.III, Sec.III that

$$P_i = n_i kT_i I - 2\mu_{i1}\nabla\cdot\mathbf{U}_1 - 2\mu_{i2}\nabla\cdot\mathbf{U}_2, \quad i=1,2, \tag{3.2.1}$$

$$Q_i = -\lambda_{i1}\nabla T_1 - \lambda_{i2}\nabla T_2 + n\,k\,T\,k_{Ti}\,(\mathbf{U}_1 - \mathbf{U}_2)\,, \quad i=1,2, \tag{3.2.2}$$

$$\mathbf{M} = -n\,k\,T\,(k_{T1}\nabla\ln T_1 + k_{T2}\nabla\ln T_2) - \frac{\rho_1\rho_2\,\lambda_b\,(\mathbf{U}_1 - \mathbf{U}_2)}{m_2}\,, \tag{3.2.3}$$

$$E = - n^2 \sigma_t (T_1 - T_2) ,$$ (3.2.4)

from which the moment equations (A26-28) become closed. As in the preceding chapter, the transport coefficients may be evaluated from variational principles,[t] noticing that the operator $\underline{K}$ is symmetric and non-positive with respect to the inner product (3.1.23) (see Ref.I, Sec.4.4). It results (Ref.III, Sec.IV)

$$\mu_{ii} = kT \frac{\Lambda_{Bi}(\Gamma_{Bi}^*)}{10} , \quad i=1,2,$$ (3.2.6a)

$$\mu = kT \frac{\Lambda_B(\Gamma_B^*)}{10} ,$$ (3.2.6b)

$$\mu_{12} = \mu_{21} = (\mu - \mu_{11} - \mu_{22})/2 ,$$ (3.2.6c)

$$\lambda_{ii} = \frac{k}{3} (\Lambda_{Ai}(\Gamma_{Ai}^*) - \{ \Gamma_D^* c^2, a_i\}^2 / \Lambda_D(\Gamma_D^*)), \quad i = 1, 2,$$ (3.2.6d)

$$\lambda_{12} = \lambda_{21} = -\frac{k}{3} (\{ \Gamma_{A2}^* c^2, a_1\}$$
$$+ \{ \Gamma_D^* c^2, a_1\}\{ \Gamma_D^* c^2, a_2\}/ \Lambda_D(\Gamma_D^*)),$$ (3.2.6e)

$$\lambda_b = \frac{3kT}{\rho_1 n_2 \Lambda_D(\Gamma_D^*)} ,$$ (3.2.6f)

$$k_{Ti} = - \{ \Gamma_D^* c^2, a_i\} / n \Lambda_D(\Gamma_D^*) , \quad i= 1, 2,$$ (3.2.6g)

$$\sigma_t = \frac{k}{n^2 \Lambda_F(\Gamma_F^*)} ,$$ (3.2.6h)

where $\Gamma_{Bi}^*, \Gamma_B^*, \Gamma_{Ai}^*, \Gamma_D^*$ and Γ_F^* are the functions that make maxima the respective functionals

$$\Lambda_{Bi}[\Gamma_B] = \{\Gamma_B c \cdot c :, \underline{K} (\Gamma_B) c \cdot c - 2b_i c \cdot c\}, \quad i = 1, 2,$$ (3.2.7a)
$$\Lambda_B[\Gamma_B] = \{\Gamma_B c \cdot c :, \underline{K} (\Gamma_B) c \cdot c - 2(b_1 + b_2) c \cdot c\},$$ (3.2.7b)
$$\Lambda_{Ai}[\Gamma_A] = \{\Gamma_A c \cdot, \underline{K} (\Gamma_A) c - 2a_i c\}, \quad i = 1, 2,$$ (3.2.7c)
$$\Lambda_D[\Gamma_D] = \{ \Gamma_D c \cdot, \underline{K} (\Gamma_D) c - 2dc\},$$ (3.2.7d)

and

$$\Lambda_F[\Gamma_E] = \{\Gamma_E, \underline{K} (\Gamma_E) - 2 e\}.$$ (3.2.7e)

In Ref.III, Sec.IV, and in the Appendix of Ref.V, we give explicit expressions for the above

[t] Bernstein (1969b). See Appendix B for the general ideas.

transport coefficients when Sonine polynomials expansions are used as the trial functions Γ_B, Γ_A, Γ_D and Γ_F, retaining only the first order of these expansions. For completeness, these expressions are repeated in Appendix D. There we show that these transport coefficients coincide with those of the near-equilibrium hydrodynamic equations of Secs. 2.4 and 2.5.2 in the limit $M \ll 1$ and $n_2/n_1 \geq O(1)$. The transport coefficients given in Appendix D are valid for arbitrary potentials of molecular interaction with spherical symmetry. When the Maxwell molecules model is used (that is, molecules repelling each other with a fifth order potential law), it is shown that these transport coefficients coincide with those calculated by Goldman and Sirovich (1967).

3.3 Comparison with the classical CE theory for binary mixtures

In Ref.III, Sec.III, we show that the quantities μ, λ, k_T and D_{12} defined by

$$\mu \equiv \mu_{11} + \mu_{22} + 2\,\mu_{12}\,, \tag{3.3.1a}$$

$$\lambda \equiv \lambda_{11} + \lambda_{22} + 2\,\lambda_{12}\,, \tag{3.3.1b}$$

$$k_T \equiv k_{T1} + k_{T2}\,, \tag{3.3.1c}$$

$$D_{12} \equiv \frac{kT}{m_1 n\,\lambda_b}\,, \tag{3.3.1d}$$

correspond to the transport coefficients of the standard CE theory for binary mixtures (Ref.I, Ch.8). Therefore, the conservation equations (A26-28) with Eqs.(3.2.1-4) reduce to the standard NSEs for binary mixtures if one makes $U_1 = U_2 = U$ in Eqs.(3.2.1) and $T_1 = T_2 = T$ in Eqs.(3.2.1-4). This equivalence between both theories is associated to the fact that the functions $-(\underline{A}_1 + \underline{A}_2)$, $-(\underline{B}_1 + \underline{B}_2)$ and $-n\underline{D}$ are equal to the functions $\underline{A}$, $\underline{B}$ and $\underline{D}$ of Ref.I, while there is no equivalent to our function $\underline{F}$ in the standard CE theory for binary mixtures (since there is only one temperature in that theory). However, except for the function $\underline{D}$, the above equivalence makes no sense when $T_1 \neq T_2$ and $U_1 \neq U_2$. In addition, the role played by our function $\underline{D}$ is substantially different from that played in the standard CE theory: in the standard CE theory, the function $\underline{D}$ is associated to the driving force d_{12} which fixes the diffusion flux in the species conservation equations; in the present theory, the function $\underline{D}$ is associated to the momentum transfer M between species that couples two different momentum equations.

In order to see under what conditions $T_1 \approx T_2$ and $U_1 \approx U_2$, so that the two-fluid equations reduce to the standard NSEs for binary mixtures, we shall estimate the order of magnitude of the quantities

$$s_i \equiv \frac{|\rho_i U_i \cdot \nabla U_i|}{|M|} ,$$

(3.3.2a)

and

$$t_i \equiv \frac{|\frac{3}{2} k n_i U_i \cdot \nabla T_i|}{|E|} .$$

(3.3.2b)

If s_1 or s_2 are much smaller than one, in first approximation we have $U_1 = U_2$ since the transfer of momentum between species is the dominant term in the respective momentum equation. Similarly, if t_1 or t_2 are much smaller than unity, in first approximation $T_1 = T_2$. From Eqs.(3.2.3-4), (2.4.31) and the expressions for the transport coefficients given in Appendix D, it results

$$s_i \sim \frac{\rho_i}{\rho_2} \omega \tau_e ,$$

$$t_i \sim \frac{n_i}{n_2} \omega \tau_e ,$$

where we have made $|U_i \cdot \nabla| \sim \omega$. For M~1 and $Kn_i << 1$, we have $U_1 \approx U_2$ and $T_1 \approx T_2$, since $\omega \tau_e \sim Kn_1$, independently of the value of n_2/n_1. Then, as expected, the two fluid theory reduces to the standard NSEs when the molecular weights of both components are comparable. When $M << 1$ and $Kn_1 \sim M$, we have $\omega \tau_e \sim Kn_1/M$ (see Sec.2.1), and the order of magnitude of s_i and t_i depend on whether $n_2 \sim n_1$ or $n_2/n_1 \sim M$. In the first case, $s_i << 1$, $s_1 \sim 1$, $t_1 \sim 1$, $t_2 \sim 1$, so that $T_1 \neq T_2$, while $U_1 \approx U_2$. In the second case, both $T_1 \neq T_2$ and $U_1 \neq U_2$. Hence, for $M << 1$, the effect of the two velocities on the two-fluid equations is important when $n_2 << n_1$. In the case $n_2 \sim n_1$ one can therefore use a mixture momentum equation plus a diffusion-like equation for $U_1 - U_2$, as in the standard NSEs. However, different energy equations must be used for each species separately. On the other hand, when $n_2 << n_1$ (and $M << 1$), both momentum and energy equations ought to be used for each species separately.

Chapter 4.
HYPERSONIC LIMIT FOR THE HEAVY GAS

4.1 Hypersonic closure of the moment equations

This chapter deals with the heavy gas hypersonic limit $Ma_2 \gg 1$. In particular, except in the last section, we shall treat the case $n_2/n_1 \ll M$ and $v \ll 1$, in which the heavy gas is governed by the FP equation (2.5.20). In addition, we shall assume that the light gas Mach number Ma_1 is of order one, so that $Ma_2 = O(M^{-1/2})$. We shall perform an expansion of the FP equation in powers of $M^{1/2}$ and obtain closed sets of hydrodynamic equations for the heavy gas. Physically, the expansion is based on the smallness of the heavy gas thermal speed compared to its own mean velocity. Thus, of the two basic DMM features stated at the beginning of this work, the hypersonic expansion is the mathematical formalization of the almost deterministic behavior of the heavy gas molecules, while the derivation of the FP collision operator (from which the hypersonic expansion is made) is a consequence of the small recoil velocity of the heavy gas upon collision with its light partner.

Before undertaking the hypersonic expansion of the FP equation at a kinetic level, it is convenient to say a few words about the more traditional hypersonic closure as applied to the hydrodynamic equations. The equations for the successive moments of the FP equation (2.5.20) (that is, the moments with respect to the functions 1, u, uu, *etc.*, see Appendix A) may be written as

$$\frac{\partial n_2}{\partial t} + \nabla \cdot (n_2 U_2) = 0 , \tag{4.1.1a}$$

$$\frac{\partial (n_2 U_2)}{\partial t} + \nabla \cdot (n_2 U_2 U_2 + \frac{P_2}{m_2}) = \frac{n_2 (W - U_2)}{\tau_e} , \tag{4.1.1b}$$

$$\frac{\partial P_2}{\partial t} + \nabla \cdot (2Q_2 + U_2 P_2) + P_2 \cdot \nabla U_2 + (P_2 \cdot \nabla U_2)^T = \frac{2 n_2 k}{\tau_e} (T_1 I - T_2) , \tag{4.1.1c}$$

and so on, where the superscript T denotes the transposed tensor. In the hypersonic limit, the mean speed of the heavy gas U_2 is larger than its thermal speed c_2 by a factor of order $M^{-1/2}$ (with the assumptions $Ma_1 = O(1)$ and $v \ll 1$ stated above). Therefore, the pressure tensor term in Eq.(4.1.1b) and the heat flux term in Eq.(4.1.1c) can be neglected relative to the terms $n_2 U_2 U_2$ and $U_2 P_2$, respectively, with errors of the order of (at most) $M^{1/2}$ for P_2, and of order M for n_2 and the component of U_2 in the direction of the flow, closing the system of moment equations (hypersonic closure of the moment equations). It is clear that the hypersonic closure can be made in many different ways and at different levels of approximation. The lowest possible order (zeroth order) is equivalent to Newton's equation of motion written in Eulerian

form, and results from dropping P_2 in Eq.(4.1.1b) and ignoring Eq.(4.1.1c). To first order, one would neglect the heat flux term in Eq.(4.1.1c) or, more generally, to order N-2, the (N+1)th moment would be dropped in the equation for the Nth moment of f_2.

In the next section we shall perform a systematic hypersonic expansion (in powers of $M^{1/2}$) of the FP equation. The set of lowest order hydrodynamic equations corresponding to this expansion will be a hypersonic closure of the moment equations. In particular, we shall consider two hypersonic expansions differing from each other in the order of the momentum equation used as the basis of the expansion: in one of them (which we shall term hypersonic expansion A), the lowest order momentum equation will be Eq.(4.1.1b) without the pressure tensor term, while in the second expansion (hypersonic expansion B), the pressure tensor term will be retained in the lowest order momentum equation. If we choose a reference frame in which one of the components of U_2 is always hypersonic, the errors in the lowest order hydrodynamic quantities of the hypersonic expansion A are $O(M)$ for n_2 and the hypersonic component of U_2, while they are $O(M^{1/2})$ for P_2 and the remaining components of U_2 (provided that these components of U_2 are of order of the thermal speed of the heavy gas c_2). In the hypersonic expansion B, these errors are $O(M^{3/2})$ for n_2 and the hypersonic component of U_2, $O(M)$ for the remaining components of U_2 and $O(M^{1/2})$ for P_2. A more rigorous estimate of the errors at the lowest order of the hypersonic expansions will be made in the next section. In Sec.4.3 we shall see that the lowest order *normal* solution of the FP equation in both hypersonic expansions is an anisotropic Gaussian distribution. As a consequence, the error for P_2 at the lowest order will be $O(M)$, instead of $O(M^{1/2})$ as we have just deduced (notice that a Gaussian distribution does not contribute to the heat flux). Hence, the accuracy of the lowest order of the hypersonic expansion is greatly enhanced in problems where the normal solution applies. More generaly, we shall see that the errors at the lowest order of P_2 are $O(M)$, provided that the heat flux vanishes initially, independently of whether the distribution function is Gaussian.

It must be noticed that the lowest order of the hypersonic expansion B is not equivalent to the first order of the hypersonic expansion A because, for instance, the lowest order errors in P_2 are of the same order in both expansions. The differences between the two expansions and the relative advantages of each one of them will be discussed in the next sections.

Hypersonic closures of the moment equations were considered by Hamel and Willis (1966) and by Edwards and Cheng (1966) in the one-dimensional spherical and cylindrical expansion of a pure gas into a vacuum. If the Knudsen number at the source is very small, the flow becomes hypersonic before rarefaction effects set in, and these authors truncated the moment equations in this region by neglecting the heat flux term. The problem was extended to binary mixtures by Cooper and Bienkowski (1967) and by Miller and Andres (1969) who neglected the heat flux

terms for *both* species. In the sense explained above in which the hypersonic closure is only applied to the heavy species in a DMM and, therefore, it can be used even for subsonic conditions of the light gas, the hypersonic truncation of the momentum equation (4.1.1b) has been used implicitly in the literature on aerosol dynamics (e.g., Friedlander, 1977). Fernández de la Mora *et al.*(1986) have used the hypersonic closure to describe the impingement of seeded free jets against surfaces. It has also been used in the shock wave problem (see Chapter 6).

4.2 Hypersonic expansion of the Fokker-Planck equation. Moment equations

Since the hypersonic expansion of the FP equation is based on the smallness of the heavy gas thermal velocity c_2 compared to the mean velocity U_2, it is convenient to write the FP equation (2.5.20) with c_2 as the independent variable (instead of the molecular velocity u). However, to define the thermal velocity, we shall not use the exact value of the heavy gas mean velocity , but a value U_{20} given by some level of the hypersonic closure of the equations (4.1.1),

$$c_{20} \equiv u\text{-}U_{20}. \tag{4.2.1}$$

Depending on how U_{20} is defined, we shall consider two different hypersonic expansions. In a first case (hypersonic expansion A or HEA), U_{20} is the Newtonian deterministic velocity satisfying the equation

$$\frac{\partial U_{20}}{\partial t} + U_{20}\cdot\nabla U_{20} = \frac{W\text{-}U_{20}}{\tau_e} , \tag{4.2.2a}$$

while in the hypersonic expansion B (HEB), U_{20} satisfies

$$\frac{\partial U_{20}}{\partial t} + U_{20}\cdot\nabla U_{20} + \frac{\nabla\cdot P_{20}}{m_2 n_{20}} = \frac{W\text{-}U_{20}}{\tau_e} , \tag{4.2.2b}$$

n_{20} and P_{20} being the number density and pressure tensor resulting from Eqs.(4.1.1a,b,c) with $Q_2=0$.

It would seem superfluous to consider the hypersonic expansion B since, strictly speaking, the lowest order momentum equation is (4.2.2a). However, it has very significant advantages over the HEA regarding its range of validity (see next section). Moreover, the lowest order of the HEB is more accurate for n_2 and U_2, avoiding the necesity of going to further orders in some problems (this is particularly important for the non-hypersonic components of U_{20}). On the other hand, in addition to being simpler, the main advantage of the

hypersonic expansion A over its counterpart B is the decoupling of the lowest order continuity and momentum equations from the pressure tensor equation. We shall use the HEA in the shock wave problem considered in chapters 6 and 7 because this decoupling will permit an algebraic solution in phase space for U_2.

Let us nondimensionalize the FP equation (2.5.20) taking into account that the heavy gas mean velocity is of the same order as the light thermal speed, whereas the heavy gas thermal velocity is much smaller. In order to avoid unnecessary complications in the notation, we shall use the same scripts for the dimensionless variables:

$$\frac{x}{\tau_0}\left(\frac{m_1}{2kT_0}\right)^{1/2} \to x, \qquad \frac{t}{\tau_0} \to t, \qquad\qquad (4.2.3a)$$

$$\frac{f_2}{n_0}\left(\frac{2kT_0}{m_2}\right)^{3/2} \to f_2, \qquad c_{20}\left(\frac{m_2}{2kT_0}\right)^{1/2} \to c_{20}, \qquad (4.2.3b)$$

$$U_{20}\left(\frac{m_1}{2kT_0}\right)^{1/2} \to U_{20}, \qquad \frac{T_1}{T_0} \to T_1, \qquad\qquad (4.2.3c)$$

$$W\left(\frac{m_1}{2kT_0}\right)^{1/2} \to W, \qquad \frac{\tau_e}{\tau_0} \to \tau_e, \qquad\qquad (4.2.3d)$$

$$\frac{P_2}{2n_0kT_0} \to P_2, \qquad \frac{n_2}{n_0} \to n_2, \qquad\qquad (4.2.3e)$$

where T_0, n_0 and τ_0 are constants. Using c_{20} as independent variable and (4.2.2), the FP equation (2.5.20) becomes

$$\frac{\partial f_2}{\partial t} + U_{20}\cdot\nabla f_2 - \left(c_{20}\cdot\nabla U_{20} + \frac{c_{20}}{\tau_e}\right)\cdot\nabla_c f_2 - \frac{3f_2}{\tau_e} - \frac{T_1}{2\tau_e}\nabla_c^2 f_2$$

$$= - M^{1/2} c_{20}\cdot\nabla f_2 , \qquad\qquad (4.2.4a)$$

for the hypersonic expansion A, and

$$\frac{\partial f_2}{\partial t} + U_{20}\cdot\nabla f_2 - \left(c_{20}\cdot\nabla U_{20} + \frac{c_{20}}{\tau_e}\right)\cdot\nabla_c f_2 - \frac{3f_2}{\tau_e} - \frac{T_1}{2\tau_e}\nabla_c^2 f_2$$

$$= - M^{1/2} [c_{20}\cdot\nabla f_2 + \frac{\nabla\cdot P_{20}}{n_{20}}\cdot\nabla_c f_2], \qquad\qquad (4.2.4b)$$

for the HEB, where ∇_c stands for the gradient in c_{20} space. From the assumptions made so far, the left-hand sides of Eqs.(4.2.4) are of order unity (or larger), while the right-hand sides are $O(M^{1/2})$, provided that the combination of spatial gradients of the distribution function appearing there are $O(1)$. Therefore, away from regions where $M^{1/2}\nabla f_2$ (and the corresponding right-

hand side in the HEB) are O(1) (or larger), we can expand f_2,

$$f_2 = f_2^{(0)} + M^{1/2} f_2^{(1)} + M f_2^{(2)} + \cdots, \tag{4.2.5}$$

in such a way that the resulting sets of moment equations at each order of the expansion become closed once the previous orders have been solved; for the unclosed nature of the system of moment equations is a consequence of the first term on the right-hand sides of Eqs.(4.2.4). Notice that the expansion (4.2.5) is not limited with respect to the temporal derivatives of the distribution function f_2.

It is convenient to use the Fourier transform of f_2,

$$F(t,x,K) \equiv \int d^3 c_{20} \, f_2(t,x,c_{20}) \, \exp\{-iK \cdot c_{20}\}. \tag{4.2.6}$$

Equations (4.2.4) then transform to

$$\frac{\partial F}{\partial t} + U_{20} \cdot \nabla F + \nabla_K F \cdot (\nabla U_{20} \cdot K + \frac{K}{\tau_e}) + F \nabla \cdot U_{20}$$
$$+ \frac{K^2 T_1}{2\tau_e} F = -iM^{1/2} \nabla \cdot \nabla_K F \tag{4.2.7a}$$

and

$$\frac{\partial F}{\partial t} + U_{20} \cdot \nabla F + \nabla_K F \cdot (\nabla U_{20} \cdot K + \frac{K}{\tau_e}) + F \nabla \cdot U_{20}$$
$$+ \frac{K^2 T_1}{2\tau_e} F = -iM^{1/2} \{\nabla \cdot \nabla_K F + \frac{\nabla \cdot P_{20}}{n_{20}} \cdot KF\}, \tag{4.2.7b}$$

which after the expansion

$$F = F^{(0)} + M^{1/2} F^{(1)} + M F^{(2)} + \cdots, \tag{4.2.8}$$

become

$$\mathcal{E}(F^{(0)}) \equiv \frac{\partial F^{(0)}}{\partial t} + U_{20} \cdot \nabla F^{(0)} + \nabla_K F^{(0)} \cdot (\nabla U_{20} \cdot K + \frac{K}{\tau_e})$$
$$+ F^{(0)} \nabla \cdot U_{20} + \frac{K^2 T_1}{2\tau_e} F^{(0)} = 0, \tag{4.2.9a}$$

at the lowest order of both expansions A and B (however, U_{20} is different in each expansion), and

$$\mathcal{E}(F^{(j)}) = -i\nabla \cdot \nabla_K F^{(j-1)}, \tag{4.2.9b}$$

$$\mathcal{E}(F^{(j)}) = -i[\nabla \cdot \nabla_K F^{(j-1)} + \frac{\nabla \cdot P_{20}}{n_{20}} \cdot KF^{(j-1)}], \tag{4.2.9c}$$

for $j \geq 1$ and the hypersonic expansions A and B, respectively. We define the moments of $f_2^{(j)}$ as

$$n_2^{(j)} \equiv \int d^3 c_{20} \, f_2^{(j)} = F^{(j)} \, (\mathbf{K}=0) \, , \tag{4.2.10a}$$

$$\mathbf{J}^{(j)} \equiv \int d^3 c_{20} \, f_2^{(j)} \, c_{20} = i\nabla_K F^{(j)} \, (\mathbf{K}=0) \, , \tag{4.2.10b}$$

$$n_2^{(0)} \, \theta^{(j)} \equiv \int d^3 c_{20} \, f_2^{(j)} \, c_{20} \, c_{20} = -2\nabla_K \nabla_K F^{(j)} \, (\mathbf{K}=0) \, , \tag{4.2.10c}$$

$$q^{(j)} \equiv \int d^3 c_{20} \, f_2^{(j)} \, c_{20} \, c_{20} c_{20} = -i\nabla_K \nabla_K \nabla_K F^{(j)} \, (\mathbf{K}=0) \, , \tag{4.2.10d}$$

and so forth. Then, the successive moment equations can easily be obtained from Eqs.(4.2.9) by just taking derivatives with respect to $\mathbf{K}$ and letting $\mathbf{K}=0$. For $j=0$, and from Eqs.(4.2.2a), (4.2.9a), at the lowest order of the HEA we obtain

$$\frac{\partial \mathbf{U}_{20}}{\partial t} + \mathbf{U}_{20} \cdot \nabla \mathbf{U}_{20} = \frac{\mathbf{W} - \mathbf{U}_{20}}{\tau_e} \, , \tag{4.2.11a}$$

$$\frac{\partial n_2^{(0)}}{\partial t} + \nabla \cdot (n_2^{(0)} \mathbf{U}_{20}) = 0 \, , \tag{4.2.11b}$$

$$\frac{\partial \theta^{(0)}}{\partial t} + \mathbf{U}_{20} \cdot \nabla \theta^{(0)} + \theta^{(0)} \cdot \nabla \mathbf{U}_{20} + (\theta^{(0)} \cdot \nabla \mathbf{U}_{20})^T = 2 \frac{T_1 I - \theta^{(0)}}{\tau_e} \, , \tag{4.2.11c}$$

$$\frac{\partial q_{lmn}^{(0)}}{\partial t} + U_{20i} \frac{\partial q_{lmn}^{(0)}}{\partial x_i} + q_{lmn}^{(0)} \frac{\partial U_{20i}}{\partial x_i} + \frac{3}{\tau_e} q_{lmn}^{(0)}$$

$$+ q_{lmi}^{(0)} \frac{\partial U_{20n}}{\partial x_i} + q_{lin}^{(0)} \frac{\partial U_{20m}}{\partial x_i} + q_{imn}^{(0)} \frac{\partial U_{20l}}{\partial x_i} = 0 \, , \tag{4.2.11d}^*$$

and so on. Notice that, by definition of $\mathbf{U}_{20}$, $\mathbf{J}^{(0)} = 0$. The lowest order moment equations in the HEB are the same as for the HEA, except for the lowest order momentum equation (4.2.11a) which now is [Eq.(4.2.2b)]

$$\frac{\partial \mathbf{U}_{20}}{\partial t} + \mathbf{U}_{20} \cdot \nabla \mathbf{U}_{20} + \frac{M}{2} [\nabla \cdot \theta^{(0)} + \theta^{(0)} \cdot \nabla \ln n_2^{(0)}] = \frac{\mathbf{W} - \mathbf{U}_{20}}{\tau_e} \, , \tag{4.2.11e}$$

where we have identified $n_{20} \equiv n_2^{(0)}$, $P_{20} = \theta^{(0)} n_2^{(0)}/2$. For the subsequent orders $j \geq 1$, from Eq.(4.2.9b) (HEA) we have

$$\frac{\partial n_2^{(j)}}{\partial t} + \nabla \cdot (n_2^{(j)} \mathbf{U}_{20} + \mathbf{J}^{(j-1)}) = 0 \, , \tag{4.2.12a}$$

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* Repeated subscripts are summed.

$$\frac{\partial \mathbf{J}^{(j)}}{\partial t} + \mathbf{J}^{(j)} \cdot (\nabla \mathbf{U}_{20} + \frac{I}{\tau_e}) + \nabla \cdot (\mathbf{J}^{(j)} \mathbf{U}_{20})$$

$$= -\frac{1}{2} \nabla \cdot (n_2^{(0)} \theta^{(j-1)}) \quad , \tag{4.2.12b}$$

$$\frac{\partial \theta^{(j)}}{\partial t} + \mathbf{U}_{20} \cdot \nabla \theta^{(j)} + \theta^{(j)} \cdot \nabla \mathbf{U}_{20} + (\theta^{(j)} \cdot \nabla \mathbf{U}_{20})^T - 2 \frac{\frac{n_2^{(j)}}{n_2^{(0)}} T_1 I - \theta^{(j)}}{\tau_e}$$

$$= -2 \nabla \cdot \mathbf{q}^{(j-1)} \quad , \tag{4.2.12c}$$

$$\frac{\partial q^{(j)}_{lmn}}{\partial t} + U_{20i} \frac{\partial q^{(j)}_{lmn}}{\partial x_i} + q^{(j)}_{lmn} \frac{\partial U_{20i}}{\partial x_i} + \frac{3}{\tau_e} q^{(j)}_{lmn} + q^{(j)}_{lmi} \frac{\partial U_{20n}}{\partial x_i} + q^{(j)}_{lin} \frac{\partial U_{20m}}{\partial x_i}$$

$$+ q^{(j)}_{imn} \frac{\partial U_{20l}}{\partial x_i} - \frac{T_1}{\tau_e} (\delta_{lm} J_n^{(j)} + \delta_{ln} J_m^{(j)} + \delta_{mn} J_l^{(j)}) = \frac{\partial \Psi^{(j-1)}_{ilnm}}{\partial x_i} \quad , \tag{4.2.12d}$$

and so forth, where δ_{ij} is the Kronecker's delta and $\Psi^{(j)} \equiv -\nabla_K \nabla_K \nabla_K \nabla_K F^{(j)}(K=0)$. In the HEB, the right-hand sides of the moment equations (4.2.12b-d) must be replaced, respectively, by

$$\frac{1}{2} \{ n_2^{(j-1)} (\nabla \cdot \theta^{(0)} + \theta^{(0)} \cdot \nabla \ln n_2^{(0)}) - \nabla \cdot (n_2^{(0)} \theta^{(j-1)}) \} \quad , \tag{4.2.12e}$$

$$2 \{ \frac{(\nabla \cdot \theta^{(0)} + \theta^{(0)} \cdot \nabla \ln n_2^{(0)}) \mathbf{J}^{(j-1)}}{n_2^{(0)}} - \nabla \cdot \mathbf{q}^{(j-1)} \} \quad , \tag{4.2.12f}$$

$$\frac{\partial \Psi^{(j-1)}_{ilnm}}{\partial x_i} + \frac{3}{4} \theta^{(j-1)}_{nm} \frac{\partial \theta_{li}^{(0)} n_2^{(0)}}{\partial x_i} \quad . \tag{4.2.12g}$$

At each order j, the system of equations (4.2.12) is closed once the previous orders have been solved.

The actual values of the moments of f_2 (see Appendix A) can be obtained from the moments defined in Eqs.(4.2.10) by realizing that $c_2 = c_{20} + (\mathbf{U}_{20} - \mathbf{U}_2)$. We obtain:

$$n_2 = n_2^{(0)} + M^{1/2} n_2^{(1)} + M n_2^{(2)} + ..., \tag{4.2.13a}$$

$$\mathbf{U}_2 = \mathbf{U}_{20} + \frac{M}{n_2} (\mathbf{J}^{(1)} + M^{1/2} \mathbf{J}^{(2)} + ...) \quad , \tag{4.2.13b}$$

$$T_2 = \frac{n_2^{(0)}}{n_2}(\theta^{(0)} + M^{1/2}\theta^{(1)} + M\theta^{(2)} + ...)$$

$$- M^{-1}(U_2\text{-}U_{20})(U_2\text{-}U_{20}) ,$$ (4.2.13c)

$$Q_{2ijk} = \frac{1}{n_2}(q_{ijk}^{(0)} + M^{1/2}q_{ijk}^{(1)} + Mq_{ijk}^{(2)} + ...)$$

$$- M^{-3/2}(U_{2i} - U_{20i})(U_{2j} - U_{20j})(U_{2k} - U_{20k})$$

$$- \frac{1}{2M^{1/2}}[T_{2ij}(U_{2k} - U_{20k}) + T_{2ik}(U_{2j} - U_{20j}) + T_{2jk}(U_{2i} - U_{20i})] ,$$ (4.2.13d)

where the heat flux tensor Q_{2ijk} has been made dimensionless with $n_2kT_0(2kT_0/m_2)^{1/2}$. At zeroth order we have $n_2=n_2^{(0)}$, $U_2=U_{20}$, $T_2=\theta^{(0)}$ and $Q_2=q^{(0)}/n_2^{(0)}$.

Equations (4.2.11) are solved with the initial conditions $n_2^{(0)}(t=0)=n_2(t=0)$, $U_{20}(t=0)=U_2(t=0)$, $\theta^{(0)}(t=0)=T_2(t=0)$, $q^{(0)}(t=0)=n_2(t=0)Q_2(t=0)$, while Eqs.(4.2.12) for $j\geq1$ must be solved with the initial conditions $n_2^{(j)}(t=0)=J^{(j)}(t=0)=\theta^{(j)}(t=0)=q^{(j)}(t=0) = 0$. According to these initial conditions, and from Eqs.(4.2.12) and (4.2.13), the order of magnitude of the errors in the lowest order hydrodynamic quantities of the HEA are

$$n_2 = n_2^{(0)} + O(M) ,$$ (4.2.14a)

$$U_2 = U_{20} + O(M) ,$$ (4.2.14b)*

$$T_2 = \theta^{(0)} + O(M^{1/2}) ,$$ (4.2.14c)

since, from Eq.(4.2.12a), $n_2^{(1)}=0$ because $J^{(0)}=0$. On the other hand, for the HEB, we have

$$n_2 = n_2^{(0)} + O(M^{3/2}) ,$$ (4.2.15a)

$$U_2 = U_{20} + O(M^{3/2}) ,$$ (4.2.15b)*

$$T_2 = \theta^{(0)} + O(M^{1/2}) ,$$ (4.2.15c)

since from Eq.(4.2.12b) with the right-hand side given by Eq.(4.2.12e), $J^{(1)}=0$, so that $n_2^{(2)}=0$. Notice that, if initially the heat flux tensor vanishes, from Eq.(4.2.11d) $q^{(0)}=0$. Whence, from Eq.(4.2.12c)$\theta^{(1)}=0$ [notice that $n_2^{(1)}=0$], so that the errors at the lowest order in T_2 are $O(M)$. In addition, $J^{(2)}=0$ from Eq.(4.2.12b) and $n_2^{(3)}=0$ from Eq.(4.2.12a). (This is valid for both the HEA and the HEB.) Thus, in the HEB, $n_2 = n_2^{(0)} + O(M^2)$ and $U_2 = U_{20} + O(M^2)$. In the HEA, the errors for n_2 and U_2 at the lowest order remain unchanged because $J^{(1)}\neq0$ and $n_2^{(2)}\neq0$.

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* Notice that, according to the nondimensionalization (4.2.3), the non-hypersonic components of U_2 are not $O(1)$, but smaller [typically, $O(M^{1/2})$].

4.3 Normal solution

In the preceding section we expanded the FP equations (4.2.4) in powers of $M^{1/2}$. However, instead of solving the resulting equations (4.2.9) for the Fourier transform of the distribution function, we were content with obtaining the moment equations for the successive orders in the expansion. In the present section, an important particular solution to Eqs.(4.2.9) (termed the normal solution) is given, whose lowest order is an anisotropic Gaussian distribution.

In fact, the function

$$F_G^{(0)} \equiv n_2^{(0)} \exp\{\frac{-KK:\theta^{(0)}}{4}\} ,$$ (4.3.1)

with $n_2^{(0)}$ (x,t) and $\theta^{(0)}$ (x,t) governed by Eqs.(4.2.11b) and (4.2.11c), is a particular solution to Eq.(4.2.9a). Since the inverse Fourier transform of (4.3.1) is

$$f_G^{(0)} \equiv \frac{n_2^{(0)}}{\pi^{3/2}(\det\theta^{(0)})^{1/2}} \exp\{- \frac{c_{20i}c_{20j}}{\theta_{ij}^{(0)}}\} ,$$ (4.3.2)

at the lowest order we have a Gaussian distribution with number density $n_2^{(0)}$, mean velocity U_{20} and temperature tensor $\theta^{(0)}$ satisfying the hydrodynamic equations corresponding to a hypersonic closure of the moment equations. Notice that the solution (4.3.2) is valid for both the HEA and the HEB; the difference resides in the lowest order equation for U_{20}.

We show in the Appendix of Ref.IV that, if at t=0 (or at x=x(0) for stationary problems) $F^{(0)}$ is of the form given by Eq.(4.3.1), the general solution to Eq.(4.2.9a) is everywhere given by Eqs.(4.3.1) and (4.2.11). If in addition one were able to show that any solution of Eq.(4.2.9a) would tend to Eq.(4.3.1) as $t \to \infty$, $F_G^{(0)}$ could properly be called the normal solution of Eq.(4.2.9a). However, we have not succeeded yet in obtaining the general solution of Eq. (4.2.9a), except for some particular cases (see Appendix of Ref.IV), most of them satisfying the condition $F^{(0)} \to F_G^{(0)}$ as $t \to \infty$. (We found in that reference that, for instance, this condition is not satisfied in one-dimensional linear flows W=ax when a<-1/4.) In any case, we shall term $F_G^{(0)}$, and the solution at the subsequent orders derived from it, the normal solution of the hypersonic expansion.

Making use of Eq.(4.3.1), the first order of the HEB [Eq. (4.2.9c) for j=1] may be written as

$$\mathcal{L}\{F^{(1)}\} = -\frac{i}{8} \, \mathbf{K} \cdot \theta^{(0)} \cdot \nabla \theta^{(0)} : \mathbf{K}\mathbf{K} \, F_G^{(0)} . \tag{4.3.3}$$

The general solution of this equation is the sum of the general solution of the homogeneous equation (4.2.9a) (which, therefore, can be included into the lowest order solution), plus a particular solution cubic in $\mathbf{K}$

$$F^{(1)} = \frac{i \, q_{lmn}^{(1)} K_l K_m K_n}{n_2^{(0)}} \, F_G^{(0)} , \tag{4.3.5}$$

where the proportionality *constant* $q^{(1)}(t,x)$ obviously coincides with $q^{(1)}$ as defined by (4.2.10d) and satisfies the equation (4.2.12d) with the right-hand side substituted by Eq.(4.2.12g).

Similarly, the particular solution $F^{(j)}$ for the subsequent orders $j>1$ is made up of terms containing the moments entering at that level of the approximation, whose moment equations are those of the preceding section. Therefore, there is not much gain in pursuing this procedure beyond $j=1$. Nevertheless, the above normal solutions for $j=0$ and $j=1$ yield additional information not contained in the moment method of the preceding section. Thus, when the normal solution applies, the procedure of solving the hierarchy of moment equations (4.2.12) is enormously simplified because all the lowest order moments are known functions of the hydrodynamic quantities $n_2^{(0)}$ and $\theta^{(0)}$ [for instance, $\Psi^{(0)}=-(3/4)n_2^{(0)}\theta^{(0)}\theta^{(0)}$]. Also, since the gradient of $n_2^{(0)}$ does not appear in the right-hand side of Eq.(4.3.3), the hypersonic expansion B with $F^{(0)}=F_G^{(0)}$ fails inside density boundary layers with $|\nabla n_2|=O(M^{-1})$, instead of $O(M^{-1/2})$ as one might have expected from considering Eq.(4.2.7) alone. (The gradient of $n_2^{(0)}$ does appear in the equation for $F^{(2)}$.) In real velocity space, the right hand side of Eq.(4.3.3) reads [from Eq.(4.2.4b)]:

$$f_G^{(0)}\{c_{20}\cdot[\frac{1}{2}\nabla \ln(\det\theta^{(0)}) + \frac{c_{20}ic_{20}j}{\theta_{ij}^{(0)2}}\nabla\theta_{ij}^{(0)}] + \frac{c_{20}j}{\theta_{ij}^{(0)}}\frac{\partial\theta_{ij}^{(0)}}{\partial x_j}\}.$$

The first consequence of the normal solution just mentioned also applies, obviously, to the HEA. However, the extension in the validity range of the hypersonic expansion with respect to the density gradients is a consequence of the inclussion of the pressure tensor term in the lowest order momentum equation and, thus, it does not apply to the HEA.

Wherever the normal solution applies, the order of magnitude of the errors in the lowest order hydrodynamic quantities are those given at the end of the preceding section with $q^{(0)}=0$. In particular, the error in the lowest order temperature tensor is smaller by a factor $M^{1/2}$ than that given by Eqs.(4.2.14) and (4.2.15).

4.4 Extension of the hypersonic theory to $n_2/n_1 \sim M$ and $v = O(1)$

In addition to the hypersonic assumption, the theory considered in the preceding sections is valid for $Kn_1 \ll 1$, $n_2/n_1 \ll M$ and $v \ll 1$. Also, it cannot be applied in regions where the right-hand sides of Eqs.(4.2.4) are $O(1)$ or larger (see, however, last section).

The two most restrictive conditions are $n_2/n_1 \ll M$ and and $v \ll 1$, which are not met in some situations of interest. To relax the first of them, $n_2/n_1 \ll M$, one has to include a self-collision integral term on the right-hand side of the kinetic FP equation (2.5.20).[*] Restricting our analysis to the lowest order hydrodynamic equations, the inclusion of this new term in the FP equation will only affect the pressure tensor equation (4.1.1c), in whose right-hand side a new self-collision transfer term, $2E_2{}'$ (see Appendix A), has to be added.

$E_2{}'$ cannot be obtained without knowledge of the distribution function f_2. However, if we assume that the lowest order distribution function is Gaussian (as in the case in which the self-collisions are neglected), the new term $2E_2{}'$ can be obtained in a closed form:

$$2E_2{}' = \frac{2k\,n_2{}^2}{\pi(\det T_2)^{1/2}}\, [A_1 e_1 e_1 + A_2 e_2 e_2 + A_3 e_3 e_3]\;, \qquad (4.4.1a)$$

where $\{e_1, e_2, e_3\}$ is the reference frame in which the temperature tensor T_2 is diagonal, and the coefficients A_i are functions of T_2 :

$$A_1 = \int_0^{2\pi} dx \int_0^1 dy\; [1-3(1-y^2)\cos^2 x]\, T_e{}^{5/2}\, \Omega_2{}^{(2,1)}(T_e)\;,$$

$$A_2 = \int_0^{2\pi} dx \int_0^1 dy\; [1-3(1-y^2)\sin^2 x]\, T_e{}^{5/2}\, \Omega_2{}^{(2,1)}(T_e)\;,$$

$$A_3 = \int_0^{2\pi} dx \int_0^1 dy\; [1-3y^2]\, T_e{}^{5/2}\, \Omega_2{}^{(2,1)}(T_e)\;,$$

$$\frac{1}{T_e} \equiv [\frac{(1-y^2)\cos^2 x}{T_{11}} + \frac{(1-y^2)\sin^2 x}{T_{22}} + \frac{y^2}{T_{33}}]\;.$$

(See Appendix C for the Ω-integrals.) In the case of an one-dimensional problem along the direction $e_3 \equiv (U_2-U_1)/\,|U_2-U_1|$, $T_{11} = T_{22} \equiv T_\perp$, so that

$$\frac{1}{T_e} = [\frac{1-y^2}{T_\perp} + \frac{y^2}{T_{||}}]\;,$$

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[*] With this addition the theory is valid for any value of n_2/n_1; however, for $n_2/n_1 \gg M$, we can use the near-equilibrium equations for the heavy gas.

where $T_{\parallel} \equiv T_{33}$. Therefore, Eq.(4.4.1a) reduces to

$$2E_2' = \frac{2k\, n_2{}^2}{(\det T_2)^{1/2}} \int_0^1 dy\ [3y^2 -1]\ T_e{}^{5/2}\ \Omega_2{}^{(2,1)}(T_e)\ [I - 3\ e_3 e_3]\ . \qquad (4.4.1b)$$

This expression was derived by Toennies and Winkelmann (1977); see also Riesco-Chueca *et al.* (1986). In the last reference, the integral in Eq.(4.4.1b) was computed using the repulsive part of a Lennard-Jones potential of molecular interaction, which approximates the full Lennard-Jones potential for $T_2 \gg \varepsilon_2/k$ (ε_2 is the depth of the Lennard-Jones well). We shall use this expression in Chapter 8.

The second limitation $v \ll 1$ can be overcome by using the FP equation (2.5.23), instead of its version linearized in v (2.5.20). Again, we will restrict our considerations to the lowest order hydrodynamic equations (4.2.11), and compute the new terms on interspecies transfer of momentum and energy (see Ref.VIII). But before taking moments of Eq.(2.5.23), we expand the integrals b and Π [Eqs.(2.5.21-22)] in powers of c_2 (which is order $M^{1/2}$ relatively to U_2):

$$b(u_2) = (1 + c_2 \cdot \nabla U_2 + c_2 c_2 : \nabla U_2 \nabla U_2 + ...)b(U_2)\ , \qquad (4.4.2a)$$

$$\Pi(u_2) = (1 + c_2 \cdot \nabla U_2 + c_2 c_2 : \nabla U_2 \nabla U_2 + ...)\Pi(U_2)\ , \qquad (4.4.2b)$$

where $b(U_2)$ and $\Pi(U_2)$ are given by Eqs.(2.5.21-22) and (2.5.25) with u and δ substituted by U_2 and v, respectively, and $e_\delta = e_3 = (U_2 - U_1)/|U_2 - U_1|$. Using the above expansions, the task of taking moments of the right side of the FP equation becomes much easier. From Appendix A, we have

$$M_2 = m_2\, [u, F(f_2)], \qquad (4.4.3a)$$

$$2E_2 = m_2\, [uu, F(f_2)] - (M_2 U_2 + U_2 M_2), \qquad (4.4.3b)$$

where $F(f_2)$ is the FP collision operator,

$$F(f_2) \equiv \nabla_u \cdot [b f_2 + \frac{1}{2}\ \nabla_u \cdot \{\Pi f_2\}]. \qquad (4.4.4)$$

Then, using Eqs.(2.5.21-22) and the expansions (4.4.2), to first order in M we get

$$M_2 = - m_2\, n_2\, b\ , \qquad (4.4.5)$$

$$2E_2 = m_2\, n_2 \{\frac{1}{2T_1}\ [\Pi_1 \cdot (T_1 I - T_2) + (\Pi_1 \cdot (T_1 I - T_2))^T]\ + \Pi_2$$

$$+ \frac{M}{T_1}[T_2 \cdot (U_2 - U_1)b + (T_2 \cdot (U_2 - U_1)b)^T]\} , \qquad (4.4.6)$$

where b, Π_1 and Π_2 are given by Eqs.(2.5.21-22) and (2.5.25) with u and δ substituted by U_2 and v, and $e_\delta = e_3 = (U_2 - U_1)/|U_2 - U_1|$. Therefore, when v is not small, the right-hand side of the moment equations (4.1.1b) and (4.1.1c) must be substituted by M_2/m_2 and $2E_2$ given by Eqs.(4.45) and (4.46), respectively [Riesco-Chueca et al.,1986, Eq.(1-2)]. At the lowest order of the hypersonic expansion B [Eqs.(4.2.11b,c,e)], we have[*]

$$\frac{\partial n_2^{(0)}}{\partial t} + \nabla \cdot (n_2^{(0)} U_{20}) = 0 , \qquad (4.4.7a)$$

$$\frac{\partial U_{20}}{\partial t} + U_{20} \cdot \nabla U_{20} + \frac{M}{2}[\nabla \cdot \theta^{(0)} + \theta^{(0)} \cdot \nabla \ln n_2^{(0)}] = \frac{v_B}{\tau_e}(W - U_{20}) , \qquad (4.4.7b)$$

$$\frac{\partial \theta^{(0)}}{\partial t} + U_{20} \cdot \nabla \theta^{(0)} + \theta^{(0)} \cdot \nabla U_{20} + (\theta^{(0)} \cdot \nabla U_{20})^T$$

$$= \Pi_1' \cdot (T_1 I - \theta^{(0)}) + [\Pi_1' \cdot (T_1 I - \theta^{(0)})]^T + \Pi_2'$$

$$+ \frac{2 v_B}{\tau_e T_1}\{\theta^{(0)} \cdot (U_{20} - U_1)(U_{20} - U_1) + [\theta^{(0)} \cdot (U_{20} - U_1)(U_{20} - U_1)]^T\} , \qquad (4.4.7c)$$

where

$$\Pi_1' \equiv [v_B(I - e_3 e_3) + v_{\Pi 1} e_3 e_3]/\tau_e , \qquad (4.4.7d)$$

$$\Pi_2' \equiv 2T_1 v^2 G \, v_{\Pi 2}(I - 3 e_3 e_3)/\tau_e . \qquad (4.4.7e)$$

Obviously, the above equations reduce to (4.2.11b,e,c) in the limit $v \to 0$. [Notice that $W = U_1$ since the FP equation (2.5.23) was obtained at the lowest order in Kn_1.] When n_2/n_1 is $O(M)$ or larger, the self-collision term given above must be included in the right-hand side of Eq.(4.4.7c).

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[*] Notice that these equations are dimensionless; see Eqs.(4.2.3).

Chapter 5

ABSORPTION AND DISPERSION OF SOUND IN DMM

5.1 Introduction

The two-fluid theory of Chapter 3 will be applied in this chapter to the problem of sound propagation. The results on absorption and dispersion of sound will be compared to the experimental values of Fuentes Losa (1972) and Bowler (1984).

The problem of sound propagation is, perhaps, the best example to test the Knudsen (or frequency) range of validity of a CE theory; for the frequency is the only parameter varied in the problem at a given concentration. We shall see that the two-fluid results on sound absorption agree reasonably well with the experimental data of Bowler for He-Xe mixtures in all the frequency range measured by this author, which, for most He-concentrations, is far larger than $Kn_1 << M \approx 0.03$, corresponding to the validity range of the standard CE theory for binary mixtures. At low frequencies, the absorption of sound predicted by the two-fluid CE theory coincides with that of the classical CE theory, and agrees remarkably well with the experiments. However, the predictions of the standard CE theory become poor as the frequency increases, confirming the estimate made in Chapter 2 on the Knudsen number range of validity of both the two-fluid and the classical CE theories for binary mixtures.

Some of the two-fluid theories cited in Sec.2.2 have been applied to the acoustic problem. For instance, Goldman (1968) used the two-fluid theory for Maxwell molecules developed by Goldman and Sirovich (1967) to predict the absorption of sound in He-Ar mixtures. These results were subsequently compared by Prangsma et al.(1970) with experimental data. The two-fluid theory of Goebel et al.(1976) (based on Grad's thirteen moments approximation) was applied by Huck and Johnson (1980,1981) to the acoustic problem, and compared by Bowler (1980) and by Bowler and Johnson (1985,1986) with experimental data on He-Xe mixtures. These authors predicted two modes of sound propagation for moderately high frequencies but such that $\omega \tau_e = O(1)$ and, thus, within the range of validity of the two-fluid theory. Similar features were predicted by Fernández de la Mora and Puri (1986) by means of a simpler Euler-level two-fluid theory, obtaining excellent agreement with experimental data on the dispersion of sound in He-Xe mixtures for Xe molar fraction less than 0.4.

5.2 Dispersion relation

In the acoustic limit, we linearize the two-fluid hydrodynamic equations (A26-30) with (3.2.1-4) around the equilibrium densities n_{10}, n_{20}, velocities $U_{10} = U_{20} = 0$, and temperature

T_0. The perturbed hydrodynamic quantities are assumed to be plane waves propagating in the positive x-direction; that is

$$\Upsilon = \Upsilon_0 + \Upsilon' \exp\{i(\omega t - Kx)\}, \qquad (5.2.1)$$

where Υ represents any of the variables n_i, U_i (x-component of the velocity U_i) and T_i (i=1,2); ω is the frequency and K is the wave number. The resulting linearized equations may be written as

$$(A + \zeta B) \cdot X = 0, \qquad (5.2.2)$$

where

$$X = \begin{pmatrix} y_1 \\ y_2 \\ z_1 \\ z_2 \end{pmatrix}, \qquad (5.2.3a)$$

with

$$y_i = \frac{U_i'}{c}, \qquad (5.2.3b)$$

$$z_i = \frac{T_i'}{T_0}, \qquad (5.2.3c)$$

and where

$$c \equiv \frac{\omega}{K} \qquad (5.2.4)$$

is the complex speed of sound. The matrices A and B are

$$A = \begin{bmatrix} M + \dfrac{x_2}{\beta} & -\dfrac{x_2}{\beta} & 0 & 0 \\[2mm] -\dfrac{x_1}{\beta} & 1 + \dfrac{x_1}{\beta} & 0 & 0 \\[2mm] -\dfrac{2}{3}\left(\dfrac{kT_1}{x_1} + 1\right) & \dfrac{2kT_1}{3x_1} & 1 + \dfrac{E}{\beta} & -\dfrac{E}{\beta} \\[2mm] -\dfrac{2kT_2}{3x_2} & \dfrac{2}{3}\left(\dfrac{kT_2}{x_2} - 1\right) & -\dfrac{Ex_1}{\beta x_2} & 1 + \dfrac{Ex_1}{\beta x_2} \end{bmatrix} \qquad (5.2.5a)$$

$$B = \begin{bmatrix} -1 - \dfrac{4M\beta\, S_{11}}{3x_1} & -\dfrac{4M\beta\, S_{12}}{3x_1} & -1 - \dfrac{kT_1}{x_1} & -\dfrac{kT_2}{x_1} \\[2mm] -\dfrac{4M\beta\, S_{12}}{3x_2} & -1 - \dfrac{4M\beta\, S_{22}}{3x_2} & \dfrac{kT_1}{x_2} & -1 + \dfrac{kT_2}{x_2} \\[2mm] 0 & 0 & -\dfrac{2\beta\, L_{11}}{3x_1} & -\dfrac{2\beta\, L_{12}}{3x_1} \\[2mm] 0 & 0 & -\dfrac{2\beta\, L_{12}}{3x_2} & -\dfrac{2\beta\, L_{22}}{3x_2} \end{bmatrix} \qquad (5.2.5b)$$

where

$$S_{ij} = \frac{\lambda_b \mu_{ij}}{kT_0} ,$$

(5.2.5c)

$$L_{ij} = \frac{\lambda_b \lambda_{ij} m_1}{k^2 T_0} ,$$

(5.2.5d)

$$E = \frac{2\sigma_t}{3x_1 M k \lambda_b} .$$

(5.2.5e)

All the transport coefficients (Appendix D) are calculated at the unperturbed temperature T_0 and molar fractions x_i. β is the dimensionless frequency

$$\beta \equiv \frac{i\omega x_1}{\lambda_b n_{10} M} = \frac{is}{a_0}$$

(5.2.6a)

where

$$s \equiv \omega \tau_e x_1 , \qquad a_0 \equiv \frac{3\lambda_b}{16\Omega_{12}^{(1,1)}(T_0)} ,$$

(5.2.6b)

and τ_e is given by Eq.(2.4.31). [$a_0 = m_2/(m_1+m_2) \approx 1$ when the first approximation of the Sonine polynomial expansion is used for λ_b, see Appendix D.] The eigenvalue ζ of Eq.(5.2.2) is

$$\zeta \equiv \frac{kT_0}{c^2 m_2} .$$

(5.2.7)

The condition for the existence of nontrivial solutions of Eq.(5.2.2),

$$det[A + \zeta B] = 0,$$

(5.2.8)

yields four complex eigenvalues ζ as functions of β and, thus, four dispersion relations $c=c(\omega)$, corresponding to four different modes. For real frequencies ω, the imaginary part of the dispersion relation is related to the absorption coefficient α as

$$\alpha \equiv Im(-K) = Im(-\frac{\omega}{c}) ,$$

(5.2.9)

while the real part is related to the speed of sound propagation c_r as

$$\frac{1}{c_r} \equiv Re(c^{-1}) .$$

(5.2.10)

5.3 Low frequency limit : absorption and dispersion coefficients

In this section we consider the limit $s \ll 1$. If the first approximation in the Sonine polynomials expansion is used for μ_1 [Ref.I, Eq.(9.7,1)], s can be written in terms of the Knudsen number of the light gas Kn_1 as

$$s = \frac{Kn_1 x_1}{M \, b_0} \; , \qquad\qquad (5.3.1)$$

where

$$b_0 = \frac{10 \, \Omega^{(2,2)}_{1}(T_0)}{3\Omega^{(1,1)}_{12}(T_0)} \; . \qquad\qquad (5.3.2)$$

Therefore, $s \ll 1$ corresponds to the limit $Kn_1 \ll M$, where the classical CE theory for binary mixtures applies.

First we look for the propagating mode at low frequencies, also called acoustic mode; that is, we look for the solution to Eq.(5.2.2) that at low frequencies behaves as

$$X = X_0 + \beta \, X_1 + \beta^2 \, X_2 + ... \qquad\qquad (5.3.3a)$$

$$\zeta = \zeta_0 + \beta \, \zeta_1 + \beta^2 \, \zeta_2 + ... \; . \qquad\qquad (5.3.3b)$$

Writing the matrices A and B as

$$A \equiv \frac{A_0}{\beta} + A_1 \; , \qquad\qquad (5.3.4a)$$

$$B \equiv B_0 + \beta \, B_1 \; , \qquad\qquad (5.3.4b)$$

at the lowest order we have

$$A_0 \cdot X_0 = 0 \; , \qquad\qquad (5.3.5a)$$

whose solution is

$$X_0 = \begin{pmatrix} Y_0 \\ Y_0 \\ Z_0 \\ Z_0 \end{pmatrix} \qquad\qquad (5.3.5b)$$

with Y_0 and Z_0 arbitrary constants. To first order, we have the equation

$$A_0 \cdot X_1 = - (A_1 + \zeta_0 B_0) \cdot X_0 \; , \qquad\qquad (5.3.6)$$

whose compatibility condition $x_0{}^T \cdot (A_1 + \zeta_0 B_0) \cdot x_0 = 0$, (where $x_0{}^T$ is the solution of $x_0{}^T \cdot A_0 = 0$ and the superscript T denotes the transposed tensor), yields

$$\zeta_0 = \frac{3(Mx_1 + x_2)}{5} \qquad\qquad (5.3.7)$$

and

$$Z_0 = \frac{2}{3} Y_0 \; . \qquad\qquad (5.3.8)$$

Equation (5.3.7) corresponds, obviously, to the equilibrium sound speed of the mixture (Laplace's expression for low frequencies):

$$c_e^2 = \frac{5\,k\,T_0\,M}{3m_1(Mx_1 + x_2)} = \frac{5\,p_0}{3\,\rho_0} \,, \tag{5.3.9}$$

where p_0 and ρ_0 are the equilibrium pressure and density of the mixture. Selecting $Y_0=1$ and the remaining $Y_{i1}=0$, $i \geq 1$, so that the first component of the eigenvector X is unity, from Eq.(5.3.6) we have

$$X_1 = \begin{pmatrix} 0 \\ \Delta Y_1 \\ Z_1 \\ Z_1 \end{pmatrix} \tag{5.3.10a}$$

where

$$\Delta Y_1 = M - 1 - \frac{2\zeta_0 \alpha_T}{3} \,, \tag{5.3.10b}$$

and α_T is the thermal diffusion ratio, $\alpha_T \equiv \dfrac{k_{T1}+k_{T2}}{x_1 x_2}$.

At the second order we have

$$-A_0 \cdot X_2 = (A_1 + \zeta_0 B_0) \cdot X_1 + (\zeta_0 B_1 + \zeta_1 B_0) \cdot X_0 \,, \tag{5.3.11}$$

and the compatibility condition yields

$$-\frac{\zeta_1}{\zeta_0} = \frac{4MS}{5} + \frac{4(Mx_1 + x_2)L}{25} + \frac{x_1 x_2 \left(M-1-\frac{2\alpha_T \zeta_0}{3}\right)^2}{Mx_1 + x_2} \,, \tag{5.3.12}$$

$$Z_1 = \frac{4(Mx_1 + x_2)L}{15} + \frac{2}{3}\Delta Y_1 x_2 (1 - x_1 \alpha_T) \,, \tag{5.3.13}$$

where $S \equiv S_{11}+2S_{12}+S_{22}$, $L \equiv L_{11}+2L_{12}+L_{22}$. Then, from Eq.(5.3.11),

$$X_2 = \begin{pmatrix} 0 \\ \Delta Y_2 \\ 0 \\ \Delta Z_2 \end{pmatrix} \,, \tag{5.3.14a}$$

with

$$-\Delta Y_2 x_2 = \frac{5Z_1}{3} + \frac{4}{3x_1} M \zeta_0 (S_{11} + S_{12}) + (1 + x_2 \alpha_T)\zeta_0 Z_1 + \frac{2}{3}\zeta_1 x_2 \alpha_T \,, \tag{5.3.14b}$$

$$\Delta Z_2 E = Z_1 - \frac{4}{9x_1} \zeta_0 (L_{11} + L_{12}) + \frac{2\Delta Y_1 k_{T1}}{3x_1} \,. \tag{5.3.14c}$$

Finally, ζ_2 is obtained from the compatibility relation of the third order equation,

$$-A_0 \cdot X_3 = (A_1 + \zeta_0 B_0) \cdot X_2 + (\zeta_0 B_1 + \zeta_1 B_0) \cdot X_1 + (\zeta_2 B_0 + \zeta_1 B_1) \cdot X_0 \,, \tag{5.3.15}$$

yielding

$$- \frac{5\zeta_2}{3\zeta_0} = \frac{\zeta_1}{\zeta_0} \Delta Y_1 \, x_2 + \frac{4M}{3} [(S_{22} + S_{12}) \Delta Y_1 + S \frac{\zeta_1}{\zeta_0}]$$

$$+ \frac{x_1 x_2 \Delta Y_1 \Delta Y_2}{\zeta_0} + \frac{\zeta_1}{\zeta_0} Z_1 + \frac{2L}{3} [\zeta_0 Z_1 + \frac{2\zeta_1}{3\zeta_0}] \ . \qquad (5.3.16)$$

The real and imaginary parts of the expansions (5.3.3b) can be related to the speed of sound c_r and the absorption coefficient α through

$$\frac{c_e}{c_r} \equiv Re(\frac{\zeta}{\zeta_0})^{1/2} = 1 - d_2 s^2 + \ldots , \qquad (5.3.17)$$

$$\frac{\alpha c_e}{\omega} \equiv - Im(\frac{\zeta}{\zeta_0})^{1/2} = d_1 s + \ldots , \qquad (5.3.18)$$

where

$$d_1 \equiv - \frac{\zeta_1}{2 a_0 \zeta_0} , \qquad (5.3.19)$$

$$d_2 \equiv \frac{1}{2 a_0} [\frac{\zeta_2}{\zeta_0} - (\frac{\zeta_1}{2\zeta_0})^2] . \qquad (5.3.20)$$

Equation (5.3.18) with (5.3.19) and (5.3.12) is Kohler's (1941) expression for the absorption of sound at low frequencies, which he derived from the standard NSEs for binary mixtures, corroborating the equivalence between the two-fluid CE theory and the classical CE theory for binary mixtures when $Kn_1 \ll M$.

The other three eigenvalues of Eq.(5.2.2) correspond to non-propagating modes at low frequencies (they tend to infinity as the frequency goes to zero). Two of them behave at low frequencies as

$$X = \frac{X_0'}{\beta} + X_1' + \beta X_2' + \ldots , \qquad (5.3.21a)$$

$$\zeta = \frac{\zeta_0'}{\beta} + \zeta_1' + \beta \zeta_2' + \ldots . \qquad (5.3.21b)$$

At the lowest and first orders one obtains

$$(A_0 + \zeta_0' B_0) \cdot X_0' = 0 , \qquad (5.3.22a)$$

$$(A_0 + \zeta_0' B_0) \cdot X_1' + (A_1 + \zeta_1' B_0 + \zeta_0' B_1) X_0' = 0 . \qquad (5.3.22b)$$

From these equations, proceeding as before, ζ_0' is given by the roots of the equation

$$\zeta_0'(\zeta_0' - 1)L - x_1 \, x_2 \alpha_T^2 \zeta_0' - \frac{5}{2} (\zeta_0' - 1) = 0. \qquad (5.3.23)$$

These two modes are identifiable with the so-called thermal and diffusion modes. In fact, neglecting the thermal diffusion in Eq.(5.3.23), one obtains $\zeta_0'=1$ and $\zeta_0' = \frac{5}{2L}$ which, in physical variables, yield the low frequency dispersion relations

$$K^2 = -i\,\omega\,\frac{5k}{2\lambda}\,(n_{10} + n_{20})\ ,\qquad\qquad (5.3.24a)$$

and

$$K^2 = -\frac{i\,\omega}{D_{12}}\ ,\qquad\qquad (5.3.24b)$$

where $\lambda = \lambda_{11} + \lambda_{22} + 2\lambda_{12}$ is the mixture thermal conductivity and D_{12} is the diffusion coefficient [see Eqs.(3.3.1b) and (3.3.1d)].

Finally, the behavior of the fourth mode at low frequencies is

$$X = \frac{X_0''}{\beta^2} + \frac{X_1''}{\beta} + \ldots\ ,\qquad\qquad (5.3.25a)$$

$$\zeta = \frac{\zeta_0''}{\beta^2} + \frac{\zeta_1''}{\beta} + \ldots\ ,\qquad\qquad (5.3.25b)$$

where ζ_0'' turns out to be

$$\zeta_0'' = \frac{3ELx_1}{2(L_{11}L_{22} - L_{12}^2)}\ .\qquad\qquad (5.3.26)$$

Therefore, this mode is associated to the transfer of energy between species (parameter E), and it does not appear in the classical CE theory for binary mixtures (which yields only three modes).

5.4 Results and comparison with experiments

We compare in this section the solution of Eq.(5.2.2) with experimental values of the absorption coefficient $\alpha(\omega)$ and the dispersion of sound $c_r(\omega)$ in He-Xe mixtures. The numerical solution of Eq.(5.2.2) has been obtained using the subroutine EIGZC of the IMSL library. All the results are computed with M=4/131.2, T_0=300K. The transport coefficients used are the first approximation in the Sonine polynomials expansion given in Appendix D with a Lennard-Jones intermolecular potential [see Hirshfelder et al.(1954), Sec.8.3; we have taken from this reference the values of the parameters σ_i and ε_i while the values of σ_{12} and ε_{12} are from Hogervorst (1971)].

A characteristic feature of the solution of Eq.(5.2.2) is the presence of a mode degeneracy at a critical frequency and gas composition, first observed by Huck and Johnson (1980). For the present case, we found that the critical value of the frequency is $\omega_c \approx 2.2/\tau_e x_{1c}$, where the critical light gas molar fraction x_{1c} is between 0.450 and 0.455. At these critical values of ω and x_1, the acoustic mode [the mode that at low frequencies is given by Eq.(5.3.3)], and one of the other modes which are non-propagating at low frequencies, become degenerate, interchanging their roles for $\omega > \omega_c$ (see Fig.2). In particular, we found that the interfering mode is the one that at low frequencies becomes the diffusion mode [Eq.(5.3.24b)]. Bowler and Johnson (1985), using Grad's thirteen moments approximation for Maxwell molecules, obtained the thermal mode as the interfering one. However, using a more realistic intermolecular potential (Bowler and Johnson, 1986), but still Grad's method, they also obtained the diffusion mode. The diffusion mode is also the interfering one at the Euler-level of the two-fluid theory, which only contains the acoustic and the diffusion modes, becoming degenerate at a critical frequency (see Fernández de la Mora and Puri, 1986).

Figures 1a-g contain the comparison of our results for the absorption coefficient with the experimental data of Bowler (1984) at several light gas (He) molar fractions. In the same figures we have also included the absorption coefficient obtained from the standard CE theory for binary mixtures. These last results are obtained from the linearized form of the standard NSEs,

$$(A' + \zeta B')\cdot X' = 0, \tag{5.4.1a}$$

where the eigenvalue ζ is defined by Eq.(5.2.7), while

$$A' = \begin{bmatrix} Mx_1 + x_2 & 0 & 0 \\ -\dfrac{2}{3} & -\dfrac{2}{3}\left[\dfrac{(1-M)x_2 x_1}{Mx_1 + x_2} + k_T\right] & 1 \\ 0 & -\dfrac{x_2}{\beta} & 0 \end{bmatrix}, \tag{5.4.1b}$$

$$B' = \begin{bmatrix} -1 - \dfrac{4}{3} M\beta S & -\dfrac{(1-M)x_2 x_1}{Mx_1 + x_2} & -1 \\ 0 & 0 & -\dfrac{2}{3}\beta L \\ 1 - \dfrac{M}{Mx_1 + x_2} & \dfrac{x_2}{Mx_1 + x_2}\left[1 - \dfrac{M(1-M)x_1}{Mx_1 + x_2}\right] & 1 - \dfrac{M}{Mx_1 + x_2} + \dfrac{k_T}{x_1} \end{bmatrix}, \tag{5.4.1c}$$

$$X' = \begin{pmatrix} u \\ \delta \\ z \end{pmatrix} \,, \qquad\qquad\qquad (5.4.1d)$$

$u \equiv U'/c$, $\delta \equiv (U_1' - U_2')/c$, $z = T'/T_0$; U' and T' being the perturbed mean velocity and temperature of the mixture. (Notice that the equation $\det(A' + \zeta B')=0$ only yields three dispersions relations or modes.) Using the same procedure as in Section 5.3, it is easy to obtain from Eq.(5.4.1) Kohler's expression for the absorption of sound at low frequencies which, as said in Sec.5.3, coincides with the expression (5.3.12) obtained from the two-fluid theory when $Kn_1 \ll M$. In this low frequency limit, one observes in Figs. 1a-g an excellent agreement between the experimental values of Bowler on absorption and both the two-fluid and the classical CE theories. However, as the frequency increases, the absorption coefficient predicted by the classical CE theory becomes poor, while that predicted by the two-fluid theory remains in reasonable agreement with the experiments. It must be noticed that the condition $Kn_1 - M$ corresponds, roughly, to $f/p - 160\, x_1$ (MH_z/Atm). Hence, in terms of the frequency f/p used in Figs.1a-g, the validity range of the standard CE increases with the light gas molar fraction, as one can see in the figures. On the other hand, all the experimental data of Figs.1a-g are, roughly, within the limit $Kn_1 \ll 1$ where the two-fluid CE theory is valid.

Figure 2 shows a comparison of our results for the dispersion of sound [Eq.(5.2.10)] with experimental values of Fuentes Losa (1972) and Bowler (1984). The speed of sound c_r is made dimensionless relative to the light gas sound velocity,

$$c_1 = \sqrt{\frac{5kT_0}{3m_1}} \,,$$

instead of with respect to the equilibrium speed of sound of the mixture used in Eq.(5.3.17). The results from the standard CE theory (NSEs) have not been included in this figure because there is a substantial disagreement with the experiments, even for small frequencies. The reason for this disagreement is twofold. First because, for DMM, the principal source of sound dispersion is the relaxation between species, which is not properly taken into account in the classical NSEs. Secondly because the dispersion of sound is a second order effect in the frequency or Knudsen number [see Eq.(5.3.17)], and cannot be predicted correctly by a theory which is a first order approximation in the Knudsen number, as the NSEs. The present two-fluid CE theory is also a first order theory in the Knudsen number (Navier-Stokes level). However, since the relaxation among species is the main source of sound dispersion in He-Xe mixtures, the results of this theory agree reasonably well with the experimental data given in

Fig.2. In fact, it has been shown (Fernández de la Mora and Puri, 1986) that the dispersion of sound resulting from the Euler-level of the two-fluid theory (which is a zeroth order theory in the frequency and, therefore, its only contribution to the dispersion comes from the relaxation terms) agrees also very well with the experimental data on He-Xe mixtures for $x_1 > 0.6$, as one can see in the same Fig.2, where the Euler-level results have also been included. For $x_1 < 0.6$, the corrections to the Euler-level made by the Navier-Stokes level of the two-fluid theory considered in this chapter are sufficient to fit the experimental data. A rigorous prediction of the dispersion of sound would need the next level (Burnett) of the two-fluid CE theory. However, Fig.2 shows that the corrections introduced by this new level of the CE theory would be very small. As a corroboration, Riesco-Chueca and Fernández de la Mora (1987) have shown that the dispersion coefficient d_2 [Eq.(5.3.20), which corresponds to the slope of the dispersion curves of Fig.2 at $s=0$] coincides, in the limit $M \to 0$, with the exact coefficient d_2 calculated from a variational formulation of the BEs, so that the dispersion of sound predicted by the two-fluid theory is quite accurate for He-Xe mixtures ($M=0.0304$). As M increasses, the relaxation between species is no longer the main source of sound dispersion, and the coefficient d_2 predicted by the two-fluid theory becomes poor, until, for $M \approx 1$, it coincides with that predicted by the standard CE theory for binary mixtures (as expected).

Figures 1a-1g. Experimental data of Bowler (1984) on sound absorption in He-Xe mixtures compared with the results (accoustic mode) from the standard CE theory [Eq.(5.4.1a); sCE curves] and those of the present two-fluid CE theory [Eq.(5.2.2); tfCE curves]. The curve tf-diff on Fig 1d corresponds to the diffusion mode of the two-fluid theory. The vertical axis represents the dimensionless absorption parameter $\alpha c_e/\omega$ [Eq.(5.3.18)].

Fig. 1c
40% He

Fig. 1d
50% He

Fig. 1e
60% He

tfCE
sCE

f/p (MHz/Atm)

tfCE
sCE

Fig. 1f
70% He

f/p (MHz/Atm)

Fig. 1g
80% He
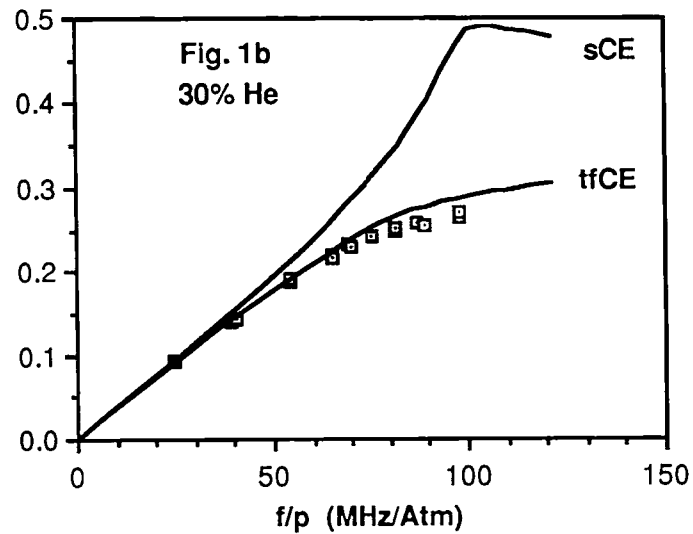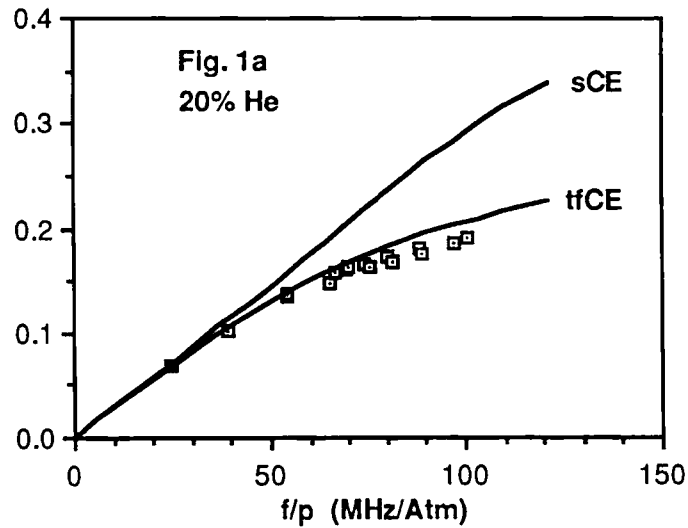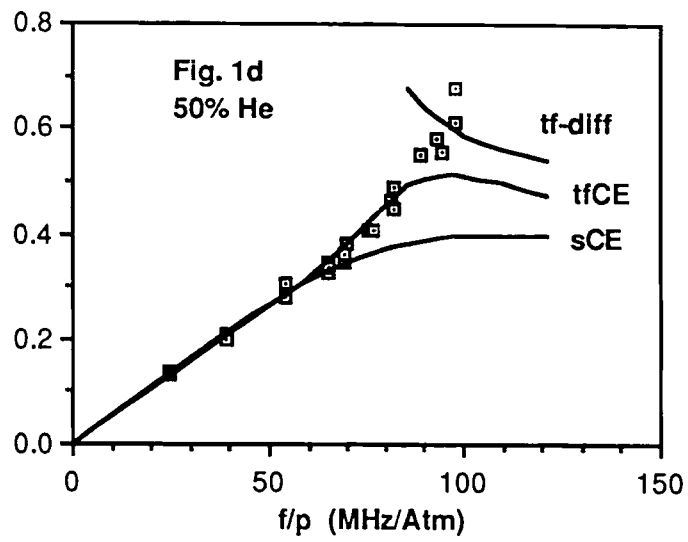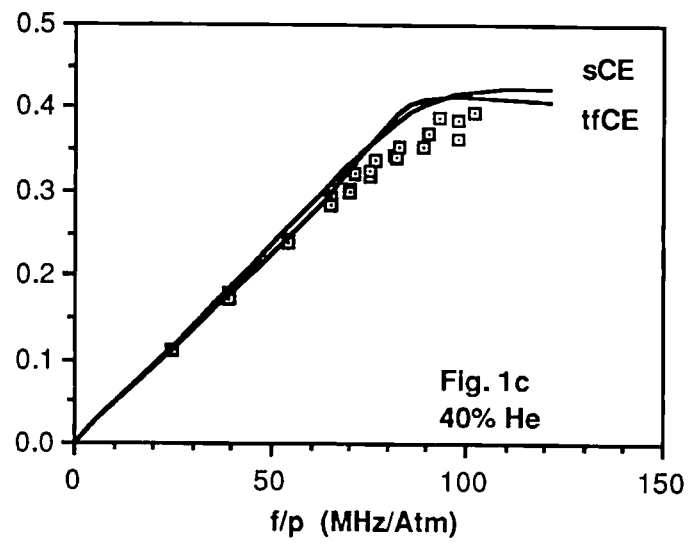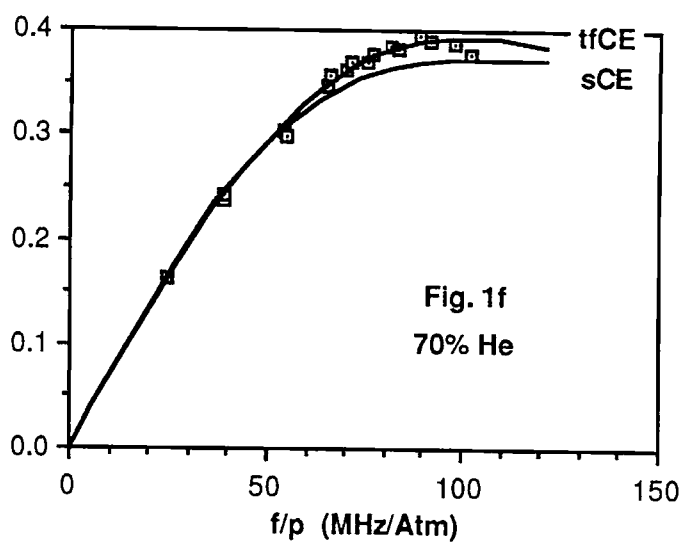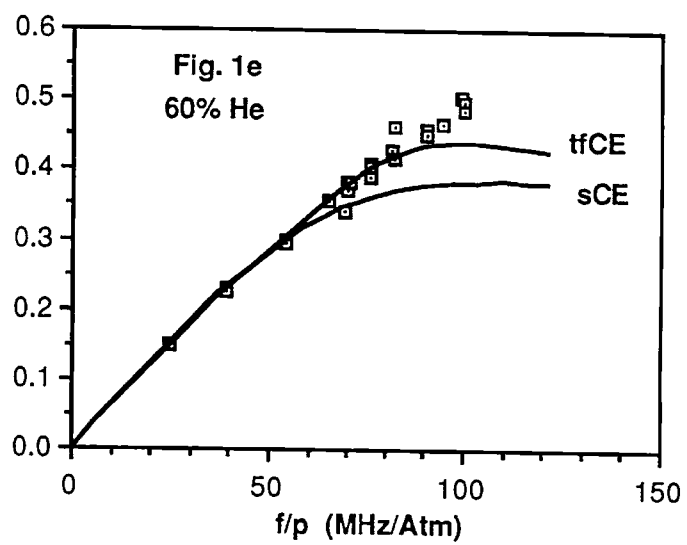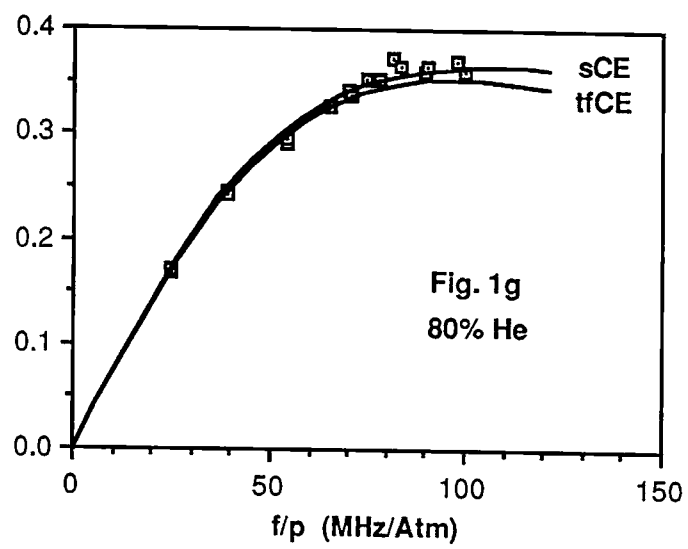
Figure 2. Dimensionless sound speed c_1/c_r versus dimensionless frequency s in He-Xe mixtures for some values of He molar fraction. _____ : accoustic mode; - - - - : accoustic mode at the Euler-level; 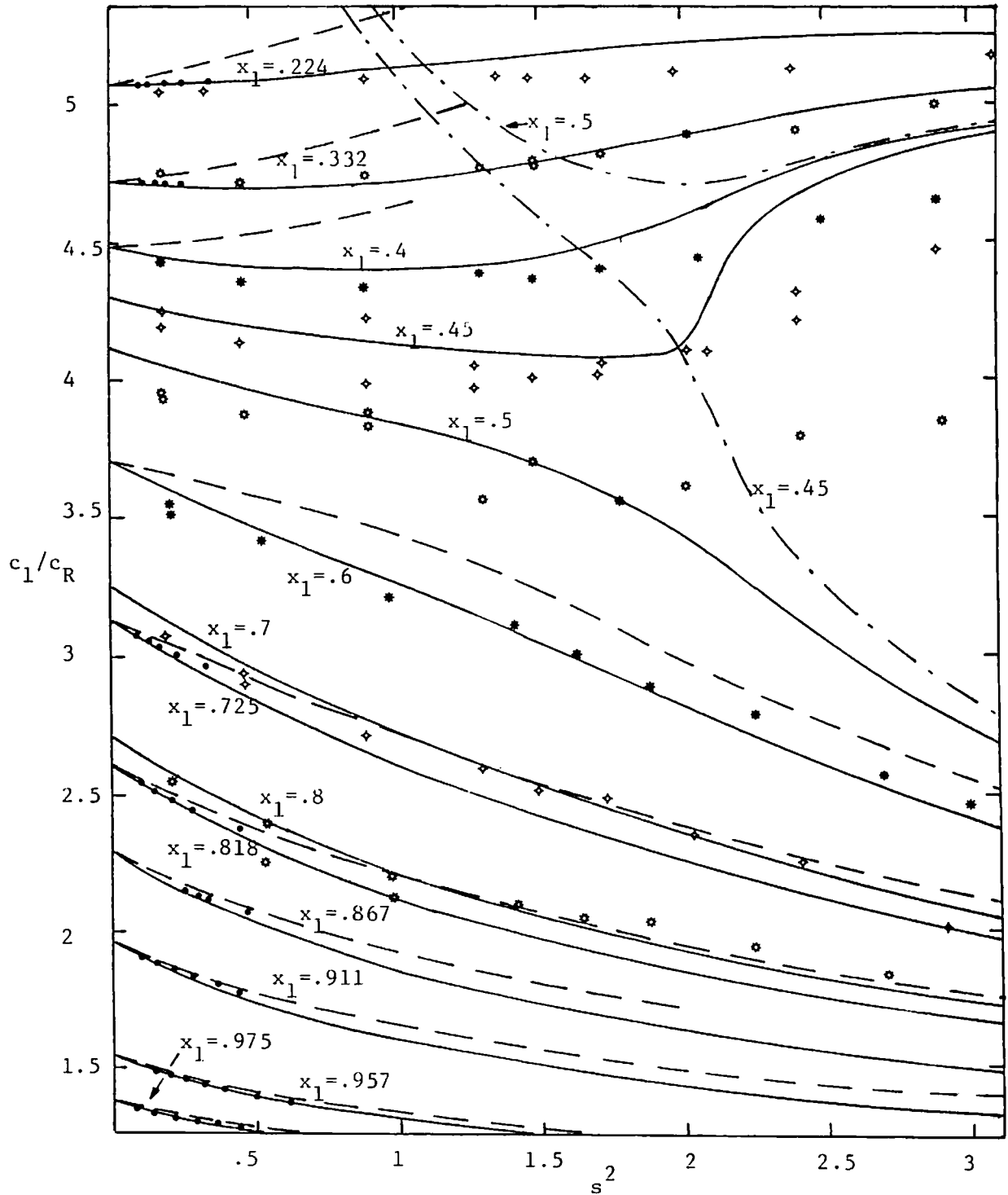- · · · · : diffusion mode. • :experimental data of Fuentes Losa (1972); * ◊ ✸:experimental data of Bowler (1984; from top to botom, x_1 = 0.2, 0.3, 0.4, 0.45, 0.5, 0.6, 0.7 and 0.8).

Chapter 6
SHOCK WAVE STRUCTURE IN DISPARATE-MASS MIXTURES WHEN $n_2/n_1 \leq O(M)$

6.1 Introduction

We consider in this chapter an example in which $\rho_2/\rho_1 \leq O(1)$, so that the near-equilibrium equations for the heavy gas of Chapter 3 cannot be used, even when the light gas is in near-equilibrium conditions ($Kn_1 \ll 1$). Nevertheless, the shock wave problem is the perfect example for the application of the heavy gas hypersonic approximation of Chapter 4, since the light gas Mach number is $O(1)$. Moreover, far upstream of the shock wave both species are in equilibrium, so that the normal solution for the heavy gas distribution function of Section 4.3 applies throughout the shock, with the consequent reduction in the magnitude of the errors at the lowest order hypersonic approximation. In order to decouple the lowest order momentum equation from the pressure tensor equation, we shall use the hypersonic expansion A. This decoupling is interesting because it will permit an algebraic solution in phase space for U_2.

For the light gas we shall use the near-equilibrium closure of the moment equations considered in Chapter 2 (Sec.2.4), valid for $Kn_1 \ll 1$ and $v \ll 1$. Although the condition $Kn_1 \ll 1$ fails for large Mach numbers, the region where this condition is not valid is very narrow compared to the overall thickness of the shock. We shall see that, when the light gas Mach number is larger than unity, the shock comprises two regions: a very thin inner layer where the light gas behaves, in first approximation, as in a shock wave of a pure gas and the heavy gas is frozen, and a much broader relaxation region whose thickness is on the order of M^{-1} times larger than the thickness of the inner layer. The condition $Kn_1 \ll 1$ fails, for large light gas Mach numbers, inside the inner region, as it fails in a shock wave of a pure gas. However, that condition is normally satisfied in the much broader outer relaxation region.

Using the classical CE theory for binary mixtures, the shock wave structure was studied by Dyakov (1954) and by Sherman (1960). In the particular case of a He-Ar mixture ($M \approx 0.1$) and $n_2/n_1 \approx 0.02$ (which is within the parameter range considered in this chapter), Sherman predicted an overshoot of the heavy species velocity (see Fig.7). Using the same NSEs, Sherman did not find this overshoot when the molar fractions of the heavy and light species were comparable. Moreover, the overshoot was not observed in He-Ar experiments made by Center (1967) at the same conditions where the anomaly was predicted. Therefore, it became clear that, even for weak shocks, the standard CE theory for binary mixtures fails for DMM when the heavy gas is dilute. According to the discussion made in Chapter 2, this failure comes from two sources: first because the classical CE theory is limited to $Kn_1 \ll M$, a condition not very likely to be met in a shock problem; secondly because, even if we use a two-fluid theory

valid for $Kn_1 \ll 1$, the near-equilibrium closure of the heavy gas hydrodynamic equations is not valid when n_2/n_1 is very small [$n_2/n_1 \leq O(Kn_1)$].

Goldman and Sirovich (1969b) applied their two-fluid theory for Maxwell molecules (1967,1969a) to the shock wave problem, not finding Sherman's anomaly for the case of weak shocks. Harris and Bienkowski (1971) used the moment equations of the BEs for Maxwell molecules, giving a complete description of the shock wave structure in binary gas mixtures for a broad range of the parameters M and n_2/n_1 [not restricted to $M \ll 1$ and $n_2/n_1 \leq O(M)$]. To close the system of moment equations in the limit considered in this chapter, they used an abbreviated Grad (1949) thirteen-moment approximation for the heat flux. Harris and Bienkowski also made an expansion of the governing equations in powers of M, obtaining, at the lowest order, a phase space solution very similar to our *outer* solution (see Ref. VI, fig.6). However, these authors did not consider the limit in which the inner shock is very weak ($Ma_1 - 1 \ll 1$), for which the outer solution is not valid (see sec.3.3).

The similar problem of a shock wave in a *dusty* gas has been treated by a number of authors. A review of these works can be found in Ref.VI, Sec.1.

6.2 Governing equations

The one-dimensional conservation equations for the species mass, momentum and energy of the mixture, can be integrated to give

$$\rho_1 U_1 = \rho_1^- U^-,$$ (6.2.1)

$$\rho_2 U_2 = \epsilon \rho_1^- U^-,$$ (6.2.2)

$$\rho_1 U_1^2 + \rho_2 U_2^2 + P_{1xx} + P_{2xx} = \rho_1^-(1+\epsilon)(U^-)^2,$$ (6.2.3)

$$\rho_1 U_1(\tfrac{1}{2} U_1^2 + e_1) + \rho_2 U_2(\tfrac{1}{2} U_2^2 + e_2) + U_1 P_{1xx} + U_2 P_{2xx} + Q_{1x} + Q_{2x}$$

$$= \rho_1^- U^-[\tfrac{1}{2}(1+\epsilon)(U^-)^2 + e_1^- + \epsilon e_2^-)],$$ (6.2.4)

where

$$\epsilon \equiv \frac{\rho_2^-}{\rho_1^-},$$ (6.2.5)

$$e_i \equiv \frac{k\,T_i}{(\gamma_i - 1)\,m_i},$$ (6.2.6)

and the superscript *minus* stands for the conditions upstream of the shock. γ_i is the specific heat ratio of species i (equal to 5/3 for monoatomic gases).

We are going to consider a first order theory in the mass ratio M. Since $n_2/n_1 \leq O(M)$, the

terms in P_{2xx}, e_2 and Q_{2x} in Eqs.(6.2.3.3-4) can be neglected with errors $O(M)$, provided that T_1/T_2 remains $O(1)$ inside the shock. Notice that this approximation has nothing to do with the hypersonic approximation. On the other hand, the near equilibrium approximation for the light gas yields [to first order in Kn_1, see Eqs.(2.4.16-17)]

$$P_{1xx} = \frac{\rho_1}{m_1} k\, T_1 - \frac{4}{3}\mu_1 \frac{dU_1}{dx} \quad , \qquad (6.2.7a)$$

$$Q_{1x} = -\lambda_1 \frac{dT_1}{dx} \quad , \qquad (6.2.7b)$$

where the thermal diffusion effect has been neglected in (6.2.7b), and the transport coefficients μ_1 and λ_1 are given by Eqs.(C1) and (C2) of Appendix C (first order of a Sonine polynomials expansion). Since $n_2/n_1 \leq O(M)$, within an error $O(M)$, these transport coefficients are those of a pure light gas.

For the heavy gas we shall use the hypersonic expansion A. In a first order theory in the parameter M (see Eqs.4.2.14), we shall only retain the lowest order equations (4.2.11a,c), with $W=U_1$ in Eq.(4.2.11a) (we neglect the thermal diffusion effect):

$$U_{20} \frac{dU_{20}}{dx} = \frac{U_1 - U_{20}}{\tau_e} \quad , \qquad (6.2.8a)$$

$$U_{20} \frac{d\theta_{\parallel}^{(0)}}{dx} + 2\theta_{\parallel}^{(0)} \frac{dU_{20}}{dx} = 2\, \frac{T_1 - \theta_{\parallel}^{(0)}}{\tau_e} \quad , \qquad (6.2.8b)$$

$$U_{20} \frac{d\theta_{\perp}^{(0)}}{dx} = 2\, \frac{T_1 - \theta_{\perp}^{(0)}}{\tau_e} \quad , \qquad (6.2.8c)$$

where $\theta_{\parallel}^{(0)} \equiv \theta_{xx}^{(0)}$, $\theta_{\perp}^{(0)} \equiv \theta_{yy}^{(0)} = \theta_{zz}^{(0)}$. At the upper limit of the number density ratio considered in this chapter, i.e. $n_2/n_1 = O(M)$, a self-collision term must be added to the right-hand side of Eqs.(6.2.8b-c) (see Sec.4.4). Also, the nonlinear effects in the slip velocity, which were considered in the same Sec.4.4, may be of some importance in this problem. These two effects have been included in the problem by Riesco-Chueca *et al.*(1986) finding that, although the results for $\theta_{\parallel}$ and $\theta_{\perp}$ are modified appreciably, U_2 remains practically unchanged. In fact, the self-collisions do not affect the momentum equation (6.2.8a), which is decoupled from

Eqs.(6.2.8b-c), in first approximation in M.

In what follows of this chapter, we shall only consider Eqs.(6.2.1-4) and (6.2.8a), forgetting for the moment the heavy gas temperature tensor (it will be considered in the next chapter in a simplified version of the shock wave problem). Using the dimensionless variables

$$\eta = \frac{U_1}{U^-}$$ (6.2.9a)

$$\xi = \frac{U_{20}}{U^-}$$ (6.2.9b)

$$\theta = \frac{T_1}{T^-}$$ (6.2.9c)

$$ds = \frac{3\rho_1^- U^-}{4\mu_1} dx \ ,$$ (6.2.9d)

Eq. (6.2.1-4) and (6.2.8a) can be written as [Ref.VI, Eqs.(11)]

$$\frac{d\eta}{ds} = \eta - 1 + \varepsilon\,(\xi - 1) + \frac{1}{\gamma\,Ma_1^2}\left(\frac{\theta}{\eta} - 1\right) \ ,$$ (6.2.10a)

$$\frac{3}{2Pr_1(\gamma-1)Ma_1^2}\frac{d\theta}{ds} = -(\eta - 1)^2 + \varepsilon\,(\xi - 2\eta + 1)(\xi - 1)$$

$$+ \frac{2}{\gamma(\gamma - 1)Ma_1^2}\,[\theta + (\gamma - 1)\eta - \gamma] \ ,$$ (6.2.10b)

$$Fe\frac{\eta\xi}{\theta}\frac{d\xi}{ds} = \eta - \xi \ ,$$ (6.2.10c)

where the light gas Mach and Prandtl numbers are

$$Ma_1 = \frac{U^-}{\left(\frac{\gamma kT^-}{m_1}\right)^{1/2}}$$ (6.2.11)

$$Pr_1 = \frac{\mu_1 k\gamma}{\lambda_1 m_1(\gamma-1)} \ .$$ (6.2.12)

The mixture or equilibrium Mach number Ma is related to Ma_1 through

$$Ma^2 = Ma_1^2\,\frac{1 + \varepsilon}{1 + M\varepsilon} \approx Ma_1^2\,(1 + \varepsilon).$$ (6.2.13)

The dimensionless parameter Fe is the large quantity

$$F_e = \frac{3\gamma Ma_1^2}{4Sc_1 M} \, ,$$

(6.3.14)

where $Sc_1 \equiv \mu_1/\rho_1 D_{12}$ is a Schmidt number. Since Pr_1 and Sc_1 vary very weakly with temperature [Srivastava and Rosner, (1979)], both are considered as constants given by their upstream values. An important feature of the above equations (6.2.10) is their independence of the particular details of the intermolecular interaction. The solution in s-space depends on the microscopic features of the system only through the group Sc_1, absorbed into the mass ratio parameter F_e ($Pr_1=2/3$ for a monmoatomic gas). The real x-space shock structure does depend on the interaction potential of the pure light gas, but only through its viscosity coefficient μ_1 [Eq.(6.2.9d)].

6.3 Results and comparison with experiments

The solution to Eqs.(6.2.10) is given with some detail in Ref.VI, Sec.3. In this section we only outline its principal features and compare it with recent experiments made by Herczynski, Tarczynski and Walenta (1986).

In phase space (ξ,η,θ) , Eqs.(6.2.10) may be written as

$$\frac{(\eta-\xi)\theta}{\eta\xi} F_e^{-1} \frac{d\eta}{d\xi} = \eta - 1 + \varepsilon (\xi - 1) + \frac{1}{\gamma Ma_1^2} \left(\frac{\theta}{\eta} - 1\right) \, ,$$

(6.3.1a)

$$\frac{(\eta-\xi)\theta}{\eta\xi} F_e^{-1} \frac{3}{2Pr_1(\gamma-1) Ma_1^2} \frac{d\theta}{d\xi}$$

$$= -(\eta - 1)^2 + \varepsilon (\xi - 2\eta + 1)(\xi - 1) + \frac{2}{\gamma(\gamma - 1)Ma_1^2} [\theta + (\gamma - 1)\eta - \gamma] \, .$$

(6.3.1b)

We are interested in the particular solution of these equations which starts at the singular point

$$\xi_1 = \eta_1 = \theta_1 = 1 \, ,$$

(6.3.2)

and finishes at the second singular point given by

$$\xi_2 = \eta_2 = \frac{(1+\varepsilon)Ma_1^2(\gamma-1) + 2}{(1+\varepsilon)(\gamma+1)Ma_1^2}$$

(6.3.3a)

$$\theta_2 = 1 + \frac{2(\gamma-1)[Ma_1^2(1+\epsilon)-1][\gamma Ma_1^2(1+\epsilon)+1]}{(\gamma+1)^2(1+\epsilon)Ma_1^2} \tag{6.3.3b}$$

The separation between these two fixed points gives the jump across the shock (Rankine-Hugoniot relations). Because this particular solution starts and finishes with neither the largest nor the smallest eigenvalues corresponding to the local behavior around the respective singular points (see Ref.VI,Sec.3.2), the numerical integration of Eqs.(6.3.1) is unstable. However, we exploit the large parameter F_θ to find a solution to these equations with errors O(M): at the lowest order we neglect the left-hand side of Eqs.(6.3.1), obtaining an algebraic solution (hyperbolae) in phase space:

$$\eta = 1 + \frac{1}{(\gamma+1)} \left\{ \frac{1-Ma_1^2}{Ma_1^2} - \gamma\epsilon\,(\xi\text{-}1) \pm \left[\left(\frac{1-Ma_1^2}{Ma_1^2} - \gamma\epsilon\,(\xi\text{-}1) \right)^2 \right. \right.$$

$$\left. \left. + (\gamma+1)\left(\epsilon\,(\gamma\text{-}1)(\xi\text{-}1)^2 - 2\,\epsilon\,(\xi\text{-}1)\right) \right]^{1/2} \right\} \tag{6.3.4a}$$

$$\theta = \eta - \gamma Ma_1^2\,\eta\,[\eta - 1 + \epsilon\,(\xi\text{-}1)]. \tag{6.3.4b}$$

Figure 3.Phase space outer solution [Eqs.(6.3.4)] for a He-Xe mixture with ϵ=0.5 and different values of the upstream light gas Mach number Ma_1.

Mach = 2

2.0
θ

1.5

1.3

1.1

Fig. 3b

1

.95 .85

1.0

0.3 0.4 0.5 0.6 ξ 0.7 0.8 0.9 1.0
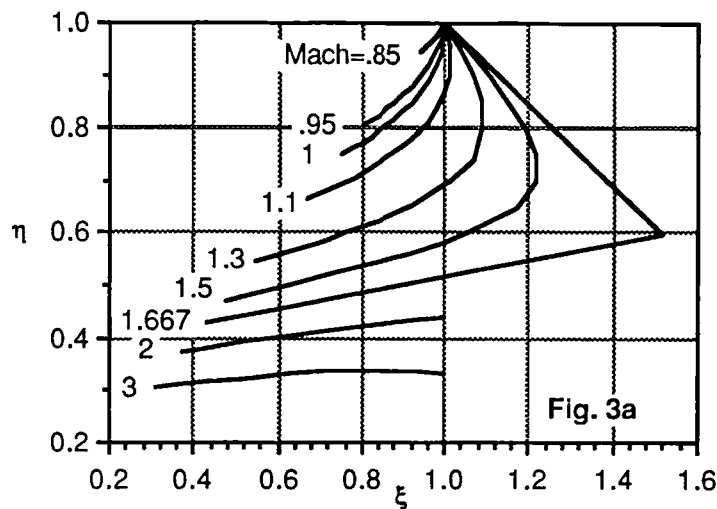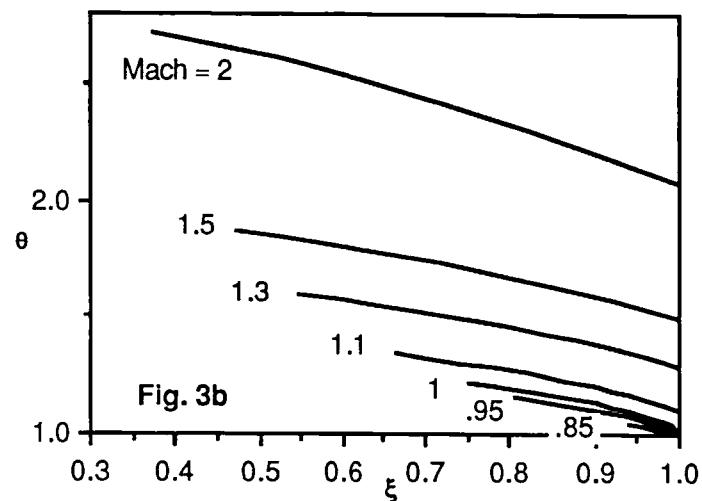
Since the derivatives have been neglected in the differential equations, the above may be called the *outer* solution, and it may have to be complemented with a boundary layer in the upstream region (located in the vicinity of $\xi=1$, as we shall see presently). The solution (6.3.4) is represented in Fig.3 for a He-Xe mixture with $\varepsilon=0.5$ and different values of Ma_1. We observe that, for $1>Ma_1>(1+\varepsilon)^{-1/2}$ (or $(1+\varepsilon)^{1/2}>Ma>1$), this solution is uniformly valid throughout the shock, corresponding to a fully dispersed wave. For $Ma_1>1$, the algebraic outer solution (6.4.4) is only valid for $\xi<1$ [we show in Ref.VI that, for $\xi>1$, Eq.(6.3.4) is closely related to Sherman's overshooting solution], and a discontinuity appears at $\xi=1$. This discontinuity corresponds, in first approximation, to the light-gas shock wave as a pure gas. Therefore, to first order in M and for $Ma_1>1$, the solution in phase space is given by a very thin region (boundary layer) of thickness O(M) where the light gas behaves as in a shock wave of a pure gas with the heavy gas frozen, and an outer or relaxation region governed by the algebraic equations (6.3.4).

As the light gas Mach number Ma_1 approaches unity, $|Ma_1^2-1|\ll1$, the thickness of the boundary layer increases and the above approximation is no longer valid. Therefore, we are faced with the task of integrating the numerically unstable system of differential equations (6.3.1). Nevertheless, we take advantage of the weak variation of the light gas entropy at the head of the shock to find a first integral of Eqs.(6.3.1) valid throughout the shock with errors of order M (Ref,VI,Sec.3.3):

Figure 4. Numerical results for the phase space structure of the shock wave compared to the outer solution for $Ma_1=0.95$ and $Ma_1=1.15$ (He-Xe, $\varepsilon=0.5$). The numerical results have been obtained with Eqs. (6.3.5) and (6.3.1a).

Fig. 4a

Fig. 4b
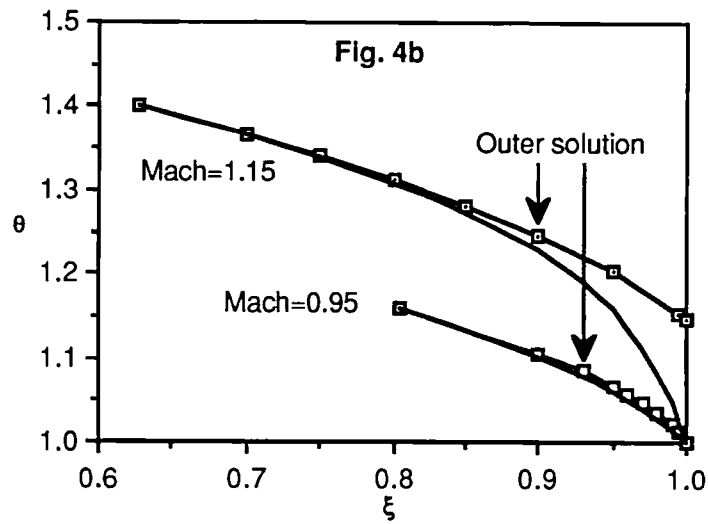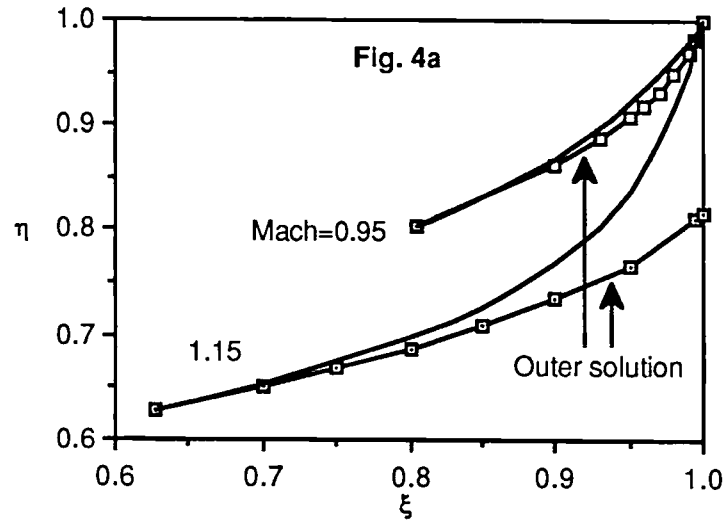
$$A\left[(\eta\text{-}1) + \varepsilon\,(\xi\text{-}1) + \frac{1}{\gamma\,Ma_1^2}\left(\frac{\theta}{\eta}\text{-}1\right)\right] \qquad (6.3.5a)$$

$$+ \frac{2}{3}Pr_1(\gamma\text{-}1)\,Ma_1^2\left\{-(\eta\text{-}1)^2 + \varepsilon\,(\xi\text{-}1)(\xi\text{-}2\eta+1) + \frac{2}{(\gamma\text{-}1)\gamma\,Ma_1^2}\left[\theta + (\gamma\text{-}1)\eta\text{-}\gamma\right]\right\} = 0 \quad,$$

where

$$A = \gamma Ma_1^2 (1-\lambda_2) - 1 + \frac{\epsilon\gamma Ma_1^2}{1+\lambda_2 Fe} \approx \gamma-1,$$ (6.3.5b)

λ_2 being the starting eigenvalue [see Ref.VI, Eq.(17)]. This algebraic equation, in addition to either Eq.(6.3.1a) or (6.3.1b), gives the solution in phase space for $|Ma_1^2-1|<<1$, whose integration is now numerically stable (See Fig.4).

Figure 5 compares our phase-space solution with He-Xe shock-tube experiments made at the Polish Academy of Sciences by Herczynski *et al.*(1986). We select two experiments corresponding to the smallest heavy-gas molar fraction (3% Xe or $\epsilon=1.015$): one for a weak shock ($Ma_1=1.09$) in which the solution given by Eqs.(6.3.5) and (6.3.1a) may be applied, and another one for a strong shock ($Ma_1=3.09$), for which the phase space solution is given by the outer solution (6.3.4). It must be noticed that these phase space solutions are independent of the details of the molecular interaction. Also, the algebraic phase space solution of Fig.5b is not affected by the assumption $v <<1$ used for the momentum transfer between species.

Figure 5. Phase space comparison with shock-tube experiments on He-Xe mixtures of Herczynski *et al.*(1986). In Fig.5a, $Ma_1=1.09$, $\epsilon=1.015$ ($Ma=1.54$, 3% molar fraction of Xe), and the theoretical curve is calculated using Eqs. (6.3.5) and (6.3.1a). Figure 5b corresponds to $Ma_1=3.09$, $\epsilon=1.015$ ($Ma=4.38$, 3% molar fraction of Xe), and compares the experiments with the outer solution (6.3.4). The experimental data are taken from a preprint of the paper by Herczynski *et al.*(1986), where the figures are larger than in the published paper.

Fig. 5b
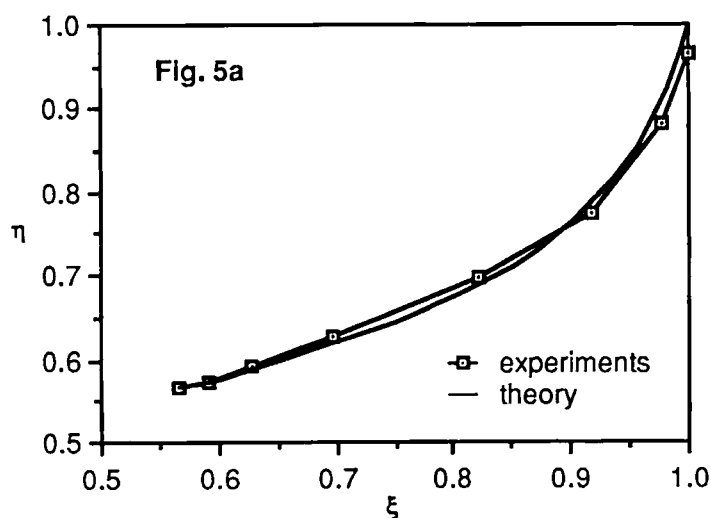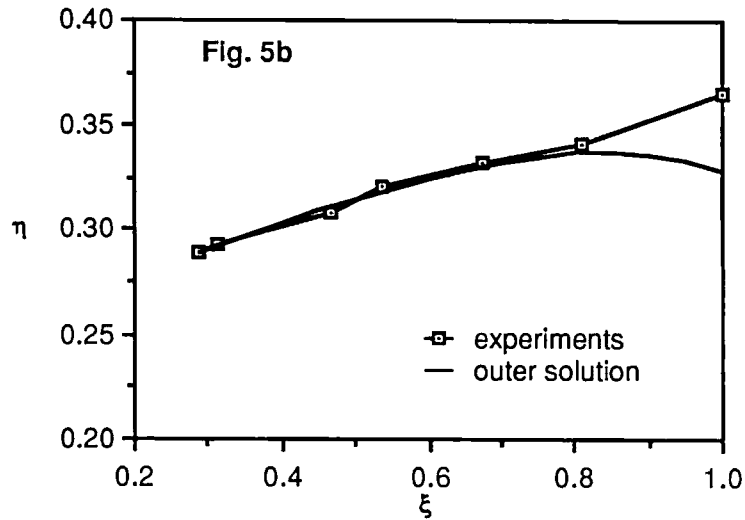
To obtain the real x-space solutions we may use either of the equations (6.2.10a-c) and Eq.(6.2.9d). In Fig.6 we have compared our x-space results with the experiments of Herzynski et al. (1986) for the same cases of Fig.5. As it was said before, the microscopic features enter into the solution only through the light gas viscosity μ_1, for which we have used the expression C1 of Appendix C [Riesco-Chueca et al.(1986) used experimental values for μ_1]. The variables plotted in Fig.6 are the dimensionless densities

$$\rho_1^* \equiv \frac{\rho_1 - \rho_1^-}{\rho_1^+ - \rho_1^-} = \frac{(1-\eta)\eta_2}{(1-\eta_2)\eta}$$

$$\rho_2^* \equiv \frac{\rho_2 - \rho_2^-}{\rho_2^+ - \rho_2^-} = \frac{(1-\xi)\xi_2}{(1-\xi_2)\xi} \ .$$

An important feature of these real space solutions is the double humped structure of the light gas density profile (see Fig.6b), occuring for high values of Ma_1: one hump corresponds to the light gas internal shock, while the other one is in the relaxation layer. This double humped structure is associated with the existence of an intermediate inflexion point in the light gas density profile. In Ref.VI, Sec.3.1, we give an approximate criterion for the existence of this particular extructure, finding that it may exist for $Ma_1^2 \geq 2\gamma/(\gamma-1)$.

Figure 6. Real space comparison with shock-tube experiments on He-Xe mixtures of Herczynski *et al.*(1986). Figures 6a and 6b correspond to the same cases of figures 5a and 5b, respectively. $z=x/\lambda$, where λ is the experimental value of the mean free path of the mixture in front of the shock ($\lambda=1.24$mm in Fig.6a and $\lambda=.47$ mm in Fig.6b). The theoretical curves in both figures have been obtained from Eqs. (6.2.9d), (6.2.10a), (6.2.10c) and (6.3.5). For μ_1 we have used the first approximation of the Sonine polynomials expansion [Eq.(C1) in the limit $n_2/n_1 \ll 1$]. The horizontal line in Fig.6b corresponds to the density *jump* in a shock wave of pure He, which coincides with the end of the first *hump* in the light gas density profile.
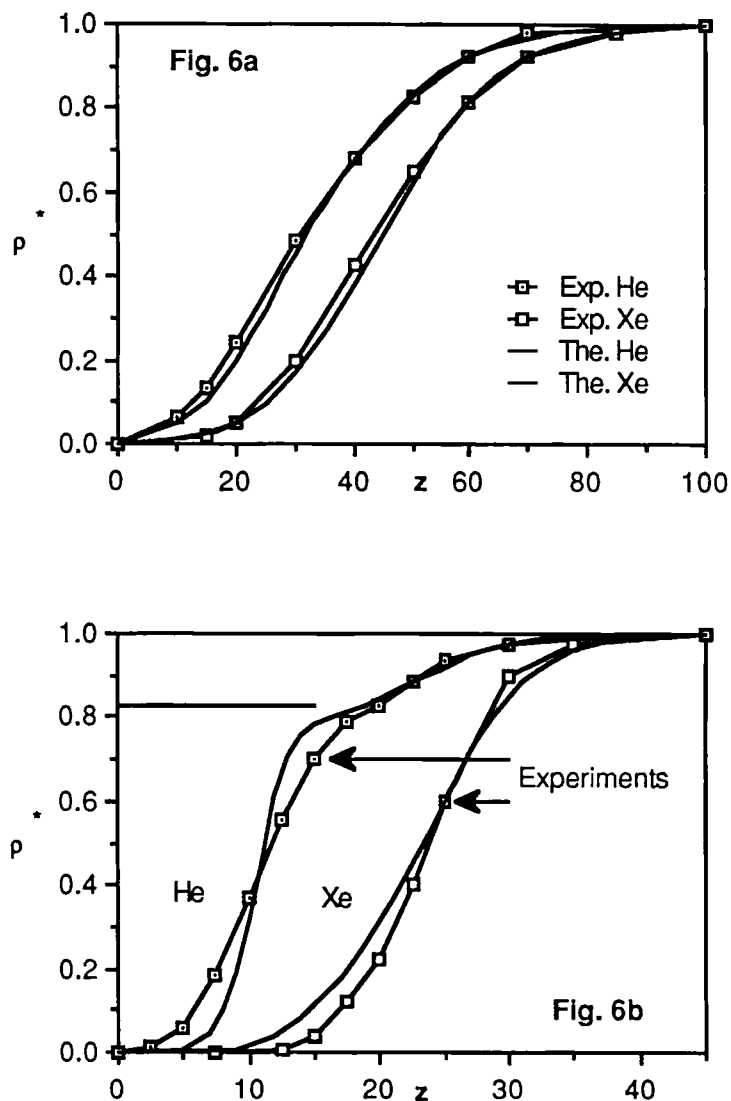
The agreement between theory and experiments is excellent for the case $Ma_1=1.09$ in both phase and real space (Figs.5a and 6a), where use has been made of Eq.(6.3.5). For

$Ma_1=3.09$ (Figs.5b and 6b) the agreement is not good in the inner boundary layer because we have used either the outer solution (Fig.5b), which is not correct in the vicinity of $\xi=1$ for $Ma_1>1$, or Eq.(6.3.5) (Fig.6b), which is not valid in the inner layer when $|Ma_1^2-1|$ is not small. A more precise procedure of integrating the real space equations (6.2.10a-c) for large values of Ma_1 is given in Riesco-Chueca *et al.*(1986).

Finally, in Fig.7 we have plotted the x-space solution for η and ξ in the case in which Sherman (1960, using the classical CE theory for binary mixtures) found an overshoot in the heavy gas velocity profile : a He-Ar mixture with $Ma_1=1.8676$ and $\epsilon = 0.204$.
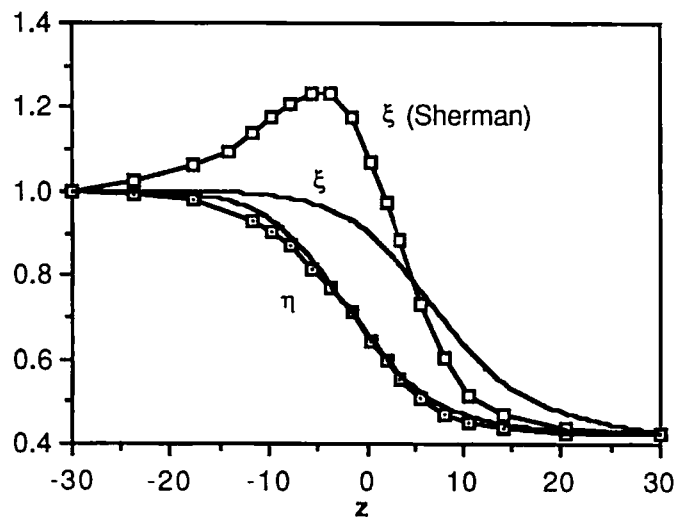
Figure 7. Real space solution for a He-Ar mixture with $Ma_1=1.8676$ and $\epsilon=0.204$. Sherman's solution for this case is also plotted. $z=\rho_1^- U^-(1+\epsilon)x/\mu^-$, where μ^- is the viscosity of the mixture in front of the shock ($T^-=300K$). Use has been made of Eqs. (6.2.9d), (6.2.10c), (6.3.1a) and (6.3.5), with μ_1 given by Eq.(C1) in the limit $n_2/n_1<<1$.

Chapter 7
FOKKER-PLANCK DESCRIPTION OF THE SHOCK WAVE PROBLEM

7.1 Solution of the FP equation for the shock wave problem

In the limit $n_2/n_1 \ll M$, the shock wave problem may be treated without the heavy gas hypersonic approximation of the preceding chapter by using the kinetic FP equation. In such a formulation, the light gas is still governed by near-equilibrium hydrodynamic equations [Eqs.(6.3.10a-b)], while the heavy gas distribution function is governed by the FP equation (2.5.20) [or Eq.(2.5.23) if v is not very small; in this chapter we shall assume $v \ll 1$].

To make Eq.(2.5.20) solvable, we shall restrict our analysis to the case in which the thickness of the light gas internal shock is negligible, so that the light gas shock wave may be considered as a discontinuity occuring at x=0. Moreover, we shall assume that n_2/n_1 is so small that the light gas properties remain constant behind its discontinuity. Thus, Eq.(2.5.20) may be written as

$$\tau_e^- u_x \frac{\partial f_2^-}{\partial x} = \nabla_u \cdot [(u - U^- e_x) f_2^- + \frac{kT^-}{m_2} \nabla_u f_2^-], \qquad x<0, \qquad (7.1.1a)$$

$$\tau_e^+ u_x \frac{\partial f_2^+}{\partial x} = \nabla_u \cdot [(u - U^+ e_x) f_2^+ + \frac{kT^+}{m_2} \nabla_u f_2^+], \qquad x>0, \qquad (7.1.1b)$$

where e_x is the unit vector in the x-direction. The light gas mean velocities and temperatures U^-, U^+, T^- and T^+ (which are constants) are related to each other through the Rankine-Hugoniot conditions for the light gas:

$$\frac{U^+}{U^-} = \frac{Ma_1^2(\gamma - 1) + 2}{(\gamma + 1)Ma_1^2}, \qquad (7.1.2a)$$

$$\frac{T^+}{T^-} = 1 + \frac{2 (\gamma - 1) (Ma_1^2 - 1)(\gamma Ma_1^2 + 1)}{(\gamma + 1)^2 Ma_1^2}, \qquad (7.1.2b)$$

where Ma_1 is, as in the preceding chapter, the light gas Mach number computed at upstream conditions [Eq.(6.2.11)]. The constants τ_e^- and τ_e^+ are given by Eq.(2.4.31) evaluated at n_1^-, T^- and n_1^+, T^+, respectively.

Equations (7.1.1) have to be solved with the boundary conditions

$$f_2^- = n_2^- \left(\frac{m_2}{2\pi kT^-}\right)^{3/2} \exp\{- \frac{m_2|u - U^- e_x|^2}{2kT^-} \}, \quad \text{as } x \to -\infty, \tag{7.1.3a}$$

$$f_2^+ = n_2^+ \left(\frac{m_2}{2\pi kT^+}\right)^{3/2} \exp\{- \frac{m_2|u - U^+ e_x|^2}{2kT^+} \}, \quad \text{as } x \to +\infty, \tag{7.1.3b}$$

$$f_2^-(x=0) = f_2^+(x=0), \tag{7.1.4}$$

that is, as $x \to -\infty$ and $x \to +\infty$, f_2^- and f_2^+ are Maxwellian distributions with number densities, mean velocities, and temperatures n_2^-, U^-, T^- and n_2^+, U^+, T^+, respectively. The number densities are related to the mean velocities through the continuity equation $n_2^- U^- = n_2^+ U^+$.

We shall give in the present section an *almost exact* solution of Eqs.(7.1.1) and (7.1.3-4), with errors of order $\exp\{-1/M\}$, or smaller.[*] This solution will be compared with the results from the hypersonic expansion A in the next section. There we shall see that the errors of the lowest order hypersonic approximation are $O(M)$ for both U_2 and T_2, as we predicted in Sec.4.3. Notice that the normal solution of Sec.4.3 applies at the lowest order in this problem; in fact, we shall see that the distribution function obtained from the FP equation differs by a quantity $O(M)$ from the Gaussian distribution given by the lowest order of the hypersonic expansion A. The next order in the HEA will also be considered in Sec.7.2

The solution of Eqs.(7.1.1) and (7.1.3-4) is obtained in Ref.VII, Sec.2, where we show that Eqs.(7.1.1) can be separated, so that both f_2^- and f_2^+ may be written in terms of an eigenexpansion. As discussed in that reference, there are two important features that distinguish this eigenfunction solution from similar one-dimensional FP solutions [for instance, the one-dimensional problem with an absorbing boundary, studied by Burschka and Titulaer, (1981)]. First, the eigenexpansion is complete; that is to say, the so-called diffusion or normal solution[†] is contained in the eigenexpansion. Secondly, due to the nature of the boundary condition at $x=0$, the coefficients in the eigenexpansion can be obtained via orthogonality properties.

With errors $O(\exp\{-1/M\})$, the solution to Eqs.(7.1.1), (7.1.3-4) can be written as (Ref.VII, Sec.2):

$$f_2^- = n_2^- \left(\frac{m_2}{2\pi kT^-}\right)^{3/2} \exp\{- \theta(\xi - V_0)^2 - \theta\eta^2 \}, \tag{7.1.5.a}$$

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[*] For a He-Xe mixture ($M \approx 0.03$) the errors are $O(10^{-14})$.

[†] See, e.g., Stein and Bernstein (1976) and Fish and Kruskal (1980).

$$f_2^+ = \sum_{n=0}^{\infty} \sum_{m=0}^{\infty} a_{nm} \, G_{nm}(\xi) \, L_m(\eta^2) \, \exp\{- \eta^2 -\gamma_{nm}y\} , \tag{7.1.5b}$$

where

$$\xi = u_x \left(\frac{m_2}{2kT^+}\right)^{1/2} \tag{7.1.6a}$$

$$\eta = (u_y{}^2 + u_z{}^2)^{1/2} \left(\frac{m_2}{2kT^+}\right)^{1/2} \tag{7.1.6b}$$

$$y = \frac{x}{\tau_e{}^+} \left(\frac{m_2}{2kT^+}\right)^{1/2} \tag{7.1.6c}$$

$$G_{nm}(\xi) = \exp\left\{-\left(\xi-V - \frac{\gamma_{nm}}{2}\right)^2\right\} H_n(\xi-V -\gamma_{nm}) \tag{7.1.7}$$

$$a_{nm} \, 2^n \, n! \, (V+\gamma_{nm}) = n_2^- \left(\frac{m_2}{2\pi kT^+}\right)^{3/2} \exp\left\{ (V_0-V)\gamma_{nm} + \gamma_{nm}^2 \frac{\frac{1}{\theta} - 3}{4}\right\} \left(\frac{\theta-1}{\theta}\right)^{n/2+m}$$

$$\times \left\{- \frac{1}{2}[\theta(\theta-1)]^{-1/2} H_{n+1}(s_{nm}) + \left[\left(\frac{\theta}{\theta-1}\right)^{1/2} s_{nm} + V + \gamma_{nm}\right] H_n(s_{nm})\right\}, \tag{7.1.8a}$$

$$s_{nm} = \frac{(V_0-V)2\theta + \gamma_{nm} (1-2\theta)}{2 \left(\theta(\theta-1)\right)^{1/2}}, \tag{7.1.8b}$$

$$\gamma_{nm} = -V + \sqrt{V^2 + 4m + 2n}, \tag{7.1.9}$$

$$V = U^+\left(\frac{m_2}{2kT^+}\right)^{1/2} , \tag{7.1.10}$$

$$V_0 = U^-\left(\frac{m_2}{2kT^+}\right)^{1/2}, \tag{7.1.11}$$

$$\theta = \frac{T^+}{T^-} , \tag{7.1.12}$$

$$n,m = 0,1,2,... ,$$

while H_n and L_m are the Hermite and Laguerre polynomials of orders n and m, respectively.[*]

Using Eq.(7.1.5b) and the moments defined in Appendix A, we obtain the following expressions for the dimensionless moments of f^+ (x>0):

$$n_2 = \frac{n_2}{n_2^-} = \sum_{n=0}^{\infty} d_{no}(-\gamma_{no})^n \exp(-\gamma_{no}y) , \tag{7.1.13}$$

$$U_2 = U_2\left(\frac{m_1}{2kT^+}\right)^{1/2} = \frac{V_0 M^{1/2}}{n_2} , \tag{7.1.14}$$

$$T_{2\parallel} = \frac{T_{2xx}}{T^+} = \frac{2}{n_2} \{d_{00}(V^2 + \frac{1}{2})$$

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[*] See, e.g., Abramowitz and Stegun (1965), Ch.22.

$$+ \sum_{n=1}^{\infty}[d_{no}\,(-\gamma_{no})^n \exp(-\gamma_{no}y)\,(\tfrac{1}{2} - \tfrac{n}{\gamma_{no}^2})\,]\ -\ \frac{V_0^2}{n_2}\}, \qquad (7.1.15)$$

$$T_{2\perp} = \frac{T_{2yy}}{T^+} = \frac{T_{2zz}}{T^+} = \frac{1}{n_2}\{d_{00} - d_{01}\exp(-\gamma_{01}y)$$

$$+ \sum_{n=1}^{\infty}[d_{no}\,(-\gamma_{no})^n \exp(-\gamma_{no}y) - d_{n1}\,(-\gamma_{n1})^n \exp(-\gamma_{n1}y)\,]\}\ , \qquad (7.1.16)$$

$$Q_{2\parallel} = \frac{Q_{2xxx}}{U_2 P_{2xx}} = \frac{\theta}{V_0 T_{2\parallel}}\{d_{00}(V^2 + \tfrac{3}{2})V\ -\ \sum_{n=1}^{\infty}[d_{no}\,(-\gamma_{no})^n\,\frac{2n}{\gamma_{no}^3}\exp(-\gamma_{no}y)\,]\,\}$$

$$-\ \frac{3}{2}\ -\ \frac{\theta V_0^2}{T_{2\parallel} n_2^2}\ , \qquad (7.1.17)$$

$$Q_{2\perp} = \frac{Q_{2xyy}}{U_2 P_{2yy}} = \frac{Q_{2xzz}}{U_2 P_{2zz}} = \frac{\theta}{2V_0 T_{2\perp}}\{d_{00}V$$

$$-\ \sum_{n=1}^{\infty}[\frac{2d_{n1}}{\gamma_{n1}}(-\gamma_{n1})^n \exp(-\gamma_{n1}y)\,]\,\}\ -\ \frac{1}{2}\ , \qquad (7.1.18)$$

where

$$d_{nm} = \frac{a_{nm}}{n_2^-}\,(\frac{m_2}{2\pi k T^+})^{-3/2}\ , \qquad (7.1.19)$$

and use has been made of the same scripts for both dimensional and dimensionless number density and mean velocity (notice that all the variables are dimensional right after the identity symbol, while on the right-hand side of the above equations all the quantities are dimensionless).

7.2 Comparison with the hypersonic theory

For the present shock wave problem, the hydrodynamic equations at the lowest and first orders of the hypersonic expansion A can be written as (see Secs.4.2 and 6.2)[†]

$$n_2^{(0)}\,U_{20} = V_0\,M^{1/2}\ , \qquad (7.2.1a)$$

$$\frac{dU_{20}}{dx} = \frac{M^{1/2}V}{U_{20}} - 1\ , \qquad (7.2.1b)$$

[†] The equations are, obviously, for $x>0$. For $j\geq 1$ we use the moments defined in Eqs.(4.2.10), which are dimensionless according to Eqs.(4.2.3). Notice that we have used T^+, n_2^- and τ_e^+ as the constants T_0, n_0 and τ_0, respectively, in Eqs.(4.2.3); also, $W=M^{1/2}V$ and $x=M^{1/2}y$.

$$\frac{d\theta_\parallel^{(0)}}{dx} = 2 \frac{1 - \theta_\parallel^{(0)} \frac{M^{1/2}V}{U_{20}}}{U_{20}}, \tag{7.2.1c}$$

$$\frac{d\theta_T^{(0)}}{dx} = 2 \frac{1 - \theta_T^{(0)}}{U_{20}}, \tag{7.2.1d}$$

$$q_\parallel^{(0)} = q_T^{(0)} = 0, \tag{7.2.1e}$$

$$n_2^{(1)} = \theta_\parallel^{(1)} = \theta_T^{(1)} = 0, \tag{7.2.2a}$$

$$\frac{dJ^{(1)}}{dx} = -\frac{J^{(1)}}{U_{20}}\left(\frac{2M^{1/2}V}{U_{20}} - 1\right) - \frac{n_2^{(0)}}{2U_{20}}\left[\theta_\parallel^{(0)}\frac{d\theta_\parallel^{(0)}}{dx} - \theta_\parallel^{(0)}\frac{dU_{20}}{dx}\right], \tag{7.2.2b}$$

$$\frac{dq_\parallel^{(1)}}{dx} = -\frac{q_\parallel^{(1)}}{U_{20}}\left(\frac{4M^{1/2}V}{U_{20}} - 1\right) + \frac{3J^{(1)}}{U_{20}} - \frac{3}{p}\frac{4U_{20}}{d}\frac{d}{dx}\left(n_2^{(0)}\theta_\parallel^{(0)}\theta_\parallel^{(0)}\right), \tag{7.2.2c}$$

$$\frac{dq_T^{(1)}}{dx} = -\frac{q_T^{(1)}}{U_{20}}\left(\frac{2M^{1/2}V}{U_{20}} + 1\right) - \frac{1}{p}\frac{4U_{20}}{d}\frac{d}{dx}\left(n_2^{(0)}\theta^{(0)}\theta_T^{(0)}\right), \tag{7.2.2d}$$

where $q_\parallel \equiv q_{xxx}$, $q_T \equiv q_{xyy} = q_{xzz}$. To complete the first order correction to the lowest order approximation, we also need the equations for $n_2^{(2)}$ and $\theta^{(2)}$:

$$n_2^{(2)} = -\frac{J^{(1)}}{U_{20}}, \tag{7.2.3a}$$

$$\frac{d\theta_\parallel^{(2)}}{dx} = -2 \frac{\theta_\parallel^{(2)}M^{1/2}V}{2U_{20}} + \frac{n_2^{(0)}U_{20}}{2n_2^{(2)}} - \frac{U_{20}}{2}\frac{dq_\parallel^{(1)}}{dx}, \tag{7.2.3b}$$

$$\frac{d\theta_T^{(2)}}{dx} = -2 \frac{\theta_T^{(2)}}{U_{20}} + \frac{n_2^{(0)}U_{20}}{2n_2^{(2)}} - \frac{U_{20}}{2}\frac{dq_T^{(1)}}{dx}. \tag{7.2.3c}$$

Equations (7.2.1-3) must be solved with the boundary conditions

$$x = 0, \qquad U_{20} = V_0 M^{1/2}, \quad \theta_\parallel^{(0)} = \theta_T^{(0)} = \theta - 1, \tag{7.2.4a}$$

Using the dimensionless moments of f_2^+ defined in Eqs.(7.1.13-18) and Eqs.(4.2.13), at the lowest order we have

$$J^{(1)} = q_\parallel^{(1)} = q_\perp^{(1)} = 0, \qquad (7.2.4b)$$

$$n_2^{(2)} = \theta_\parallel^{(2)} = \theta_\perp^{(2)} = 0. \qquad (7.2.4c)$$

$$n_2 = n_2^{(0)}, \qquad (7.2.5a)$$

$$U_2 = U_{20}, \qquad (7.2.5b)$$

$$T_{2\parallel} = \theta_\parallel^{(0)}, \qquad (7.2.5c)$$

$$T_{2\perp} = \theta_\perp^{(0)}, \qquad (7.2.5d)$$

$$q_{2\parallel} = q_{2\perp} = 0, \qquad (7.2.5e)$$

whereas, up to first order in M, one obtains

$$n_2 = n_2^{(0)} + M\, n_2^{(2)}, \qquad (7.2.6a)$$

$$U_2 = U_{20} + \frac{M}{n_2^{(0)}} J^{(1)}, \qquad (7.2.6b)$$

$$T_{2\parallel} = \frac{n_2^{(0)}}{n_2^{(0)} + M\, n_2^{(2)}}\, \theta_\parallel^{(0)} + M\left[\theta_\parallel^{(2)} - \left(\frac{J^{(1)}}{n_2^{(0)}}\right)^2\right], \qquad (7.2.6c)$$

$$T_{2\perp} = \frac{n_2^{(0)}}{n_2^{(0)} + M\, n_2^{(2)}}\, \theta_\perp^{(0)} + M\, \theta_\perp^{(2)}, \qquad (7.2.6d)$$

$$q_{2\parallel} = \frac{M}{n_2^{(0)} U_{20}}\left[\frac{q_\parallel^{(1)}}{\theta_\parallel^{(0)}} - \frac{3 J^{(1)}}{2}\right], \qquad (7.2.6e)$$

$$q_{2\perp} = \frac{M}{n_2^{(0)} U_{20}}\left[\frac{q_\perp^{(1)}}{\theta_\perp^{(0)}} - \frac{J^{(1)}}{2}\right], \qquad (7.2.6f)$$

We have plotted in figures 8-11 the quantities (7.2.5) and (7.2.6) for a He-Xe mixture (M=0.03) and a He-Ar mixture (M=0.1) with Ma_1=1.5. We have also included the almost exact FP results given by Eqs.(7.1.13-18). As predicted, the difference between the results from
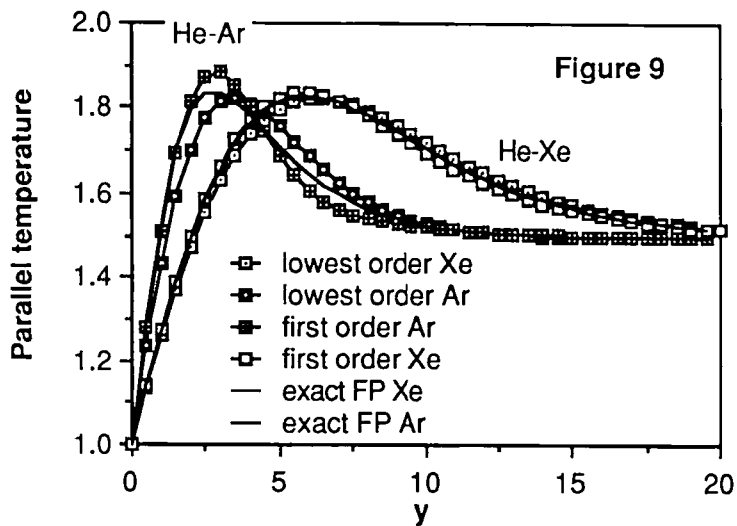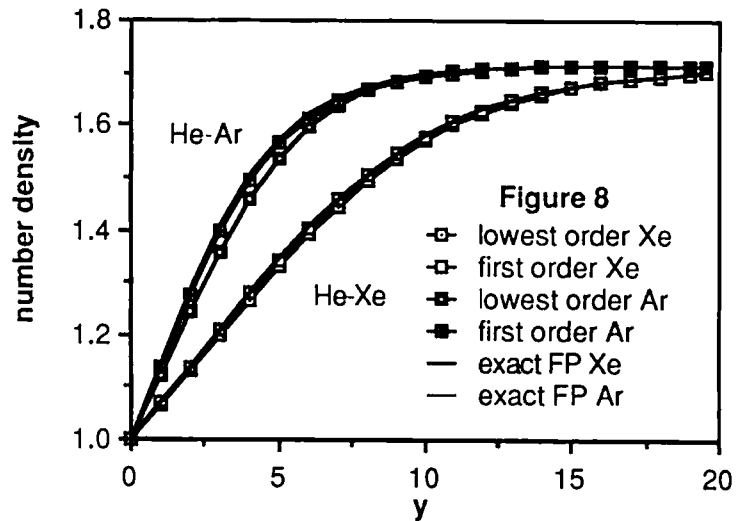
the lowest order of the hypersonic expansion A [Eqs.(7.2.5)] and the FP equation [Eqs.(7.1.13-18)] for n_2, U_2 and T_2 remain $O(M)$ or less. The next order results (7.2.6) for n_2, U_2 and T_2 practically coincide with the FP results, except for $T_{2\parallel}$, just after its maximum, in the He-Ar mixture (Fig.9). The reason of the excellent agreement between the hypersonic approximation and the exact FP results even downstream of the shock where the Mach number of the heavy gas is not very large (for a He-Ar mixture with $Ma_1=1.5$, the downstream value of the heavy gas Mach number is 3.38, while for a He-Xe mixture is 6.13), is the approach to equilibrium of the mixture as $y \to \infty$, so that the Gaussian distribution corresponding to the lowest order hypersonic approximation becomes exact as $y \to \infty$. Hence, the lowest order of the hypersonic expansion works very well throughout the shock. The subsequent corrections are more accurate in the head than in the tail of the shock (as it is observed in Figs.8-10).

In Fig.12, we have compared the FP distribution function (7.1.5b) [after making it dimensionless with $n_2^-(m_2/2\pi kT^+)^{3/2}$] with the Gaussian distribution

$$f_{20} \equiv \frac{n_2^{(0)}}{\theta_\perp^{(0)} \sqrt{\theta_\parallel^{(0)}}} \exp\left\{- \frac{(\xi-V_0 M^{-1/2})^2}{\theta_\parallel^{(0)}} - \frac{\eta^2}{\theta_\perp^{(0)}}\right\}, \qquad (7.2.7)$$

corresponding to the lowest order of the hypersonic expansion A. The comparison is made at the most unfavorable conditions where, roughly, the parallel temperature $T_{2\parallel}$ reaches a maximum (see Fig.9). The magnitude of this maximum, $T_{2\parallel max}$, computed from Eq.(7.1.15), and for different DMM, is plotted in Fig.13 as a function of Ma_1. It is observed that the curves for $T_{2\parallel max}$ approach the one predicted by the lowest order hypersonic approximation (which, obviously, does not depend on M) as $M \to 0$.

Figures 8-11. Comparison of the FP results for n_2, $T_{2\parallel}$, $T_{2\perp}$, $Q_{2\parallel}$ and $Q_{2\perp}$ [Eqs.(7.1.13-17)] with the corresponding results at the lowest order [Eqs.(7.2.5)] and first order in M [Eqs.(7.2.6)] of the hypersonic expansion A. The comparison is made for He-Ar (M=0.1) and He-Xe (M=0.0304) mixtures with Ma_1=1.5. In figure 9, we have plotted $T_{2\parallel}\theta$ and $T_{2\perp}\theta$ instead of $T_{2\parallel}$ and $T_{2\perp}$, so that these quantities are equal to one at y=0, and they go to θ as y$\to\infty$. Notice that $y=M^{-1/2}x$.

Figure 8

- -□- lowest order Xe
- -□- first order Xe
- -■- lowest order Ar
- -■- first order Ar
- — exact FP Xe
- — exact FP Ar

Figure 9

- -□- lowest order Xe
- -■- lowest order Ar
- -■- first order Ar
- -□- first order Xe
- — exact FP Xe
- — exact FP Ar

Figure 10

lowest order Ar
lowest order Xe
first order Ar
first order Xe
exact FP Ar
exact FP Xe

He-Ar

He-Xe

Figure 11a

First order Ar
First order Xe
Exact FP Ar
Exact FP Xe

He-Xe

He-Ar

Perp. heat flux

0.001

0.000

-0.001

-0.002

-0.003

-0.004

He-Xe

He-Ar

Figure 11b

-□- First order Xe
— Exact FP Ar
-□- First order Ar
— Exact FP Xe

0   5   10   15   20

y

Figure 12. Comparison of the $\eta=0$ section of the distribution function f_2 obtained from the FP equation [Eq.(7.1.5b)] with the $\eta=0$ section of the Gaussian distribution (7.2.7) corresponding to the lowest order of the hypersonic expansion A. The comparison is made for He-Ar (M=0.1) and He-Xe (M=0.0304) mixtures at y=3 and y=6, respectively, with $Ma_1=1.5$.

2

1

0

□ Eq.(7.2.7) Xe
■ Eq.(7.2.7) Ar
■ FP Xe
□ FP Ar

Figure 12

He-Ar   He-Xe

-1   0   1   2   3   4   5   6   7   8

ξ
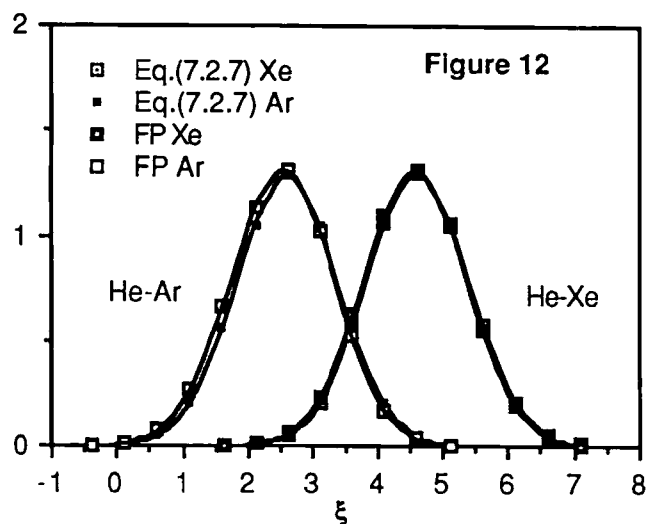
Figure 13. Maximum value of the parallel temperature ($T_{2\|max}$) as a function of the light gas Mach number for different DMM. $T_{2\|max}$ is computed from Eq. (7.1.15). The lowest order hypersonic results from Eq.(7.2.1c) (HEA), which does not depend on M, are also included.

Figure 13
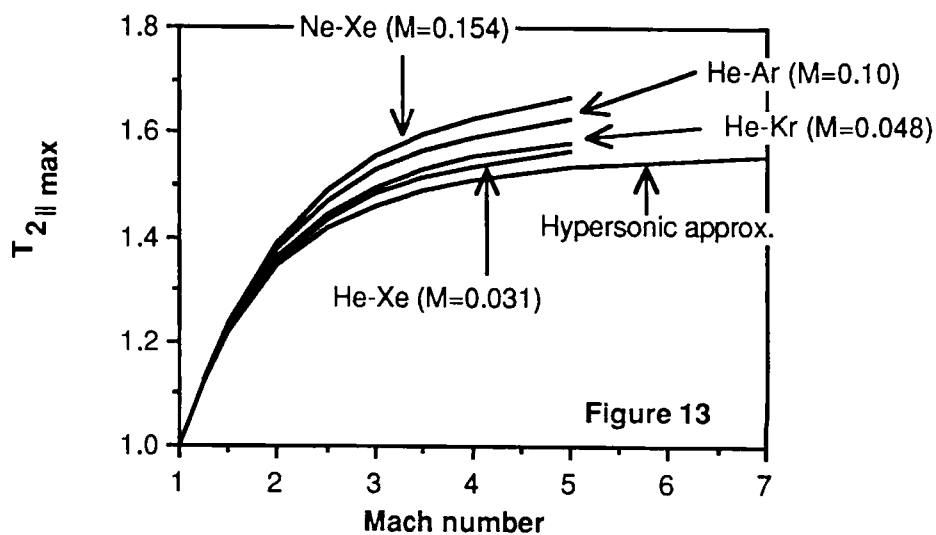
Chapter 8
ONE-DIMENSIONAL FLOW THROUGH A CONVERGING NOZZLE

8.1 Introductory remarks

As the last example of this dissertation we consider the one-dimensional (or rather quasi-one-dimensional) flow through a converging nozzle. Although this problem will be treated in an idealized form (one-dimensional flow and without viscous effects), in contrast with the previous examples, it models a more complex situation which has intrinsic technological interest. In fact, as we saw in Sec.1.2, it is a relatively important problem in the field of DMM, since many of its applications are based on the acceleration of heavy molecules through a nozzle. Thus, the equations given below may be used to predict the terminal mean velocity and energy of the heavy molecules after being accelerated through a converging nozzle of arbitrary shape. However, since the main purpose of this chapter is (like that of the preceding ones) to test the theories given in chapters 2-4, we shall use these equations to calculate a parameter which is easily measured experimentally: the discharge coefficient.

For the light gas we shall use the Euler-level of the CE theory; that is to say, we shall use the conservation equations (A26-28) with $P_1 = n_1 k T_1 I$ and $Q_1 = 0$ (ideal flow). The theory is thus restricted to large light gas Reynolds numbers, where the non-ideal effects are confined to a very narrow (compared to the section of the nozzle) boundary layer adjacent to the wall. On the other hand, the theory will be valid for a wide range of concentrations of the heavy gas. To this end, we shall not assume near-equilibrium conditions for the heavy gas, using a hypersonic approximation (lowest order of the hypersonic expansion B; see next section for more details on this point). The hypersonic equations are made valid for non-negligible heavy species concentrations by including the self-collision terms considered in Sec.4.4. We shall also use the expressions given in Sec. 4.4 for the transfer of momentum and energy between species, so that the equations will not be limited to $v \ll 1$.

To test the theory, we have measured discharge coefficients (C_d) in CCl_4-He mixtures exhausting through a conical-shaped converging nozzle. For a binary gas mixture, the discharge coefficient is defined as the ratio between the actual mass flow, and the maximum mass flow predicted by the one-dimensional Euler-level of the classical CE theory for binary mixtures (that is, assuming that both species are in equilibrium). In mixtures whose constituents have similar molecular weights (for which the classical CE theory applies), the discharge coefficient measures the relative importance of the non-ideal effects in the problem, tending to unity as the Reynolds number goes to infinity (provided that the pressure ratio is above a certain value, see Sec.8.3). However, for DMM, we shall use the discharge coefficient

as a measure of the non-equilibrium among species. To this end, the experimental values of C_d are corrected taking into account the viscosity effects, in such a way that $C_d > 1$ implies the existence of distinct species temperatures and mean velocities at the throat of the nozzle. We shall see that the corrected experimental values of C_d for CCl_4-He mixtures agree reasonably well with the theory.

The enhancement of the discharge coefficient for DMM was experimentally observed by Bley et al.(1979) in UF_6-H_2 mixtures. Nanbu (1979) studied the velocity slip and temperature difference in DMM nozzle flows using the isentropic equations for the mixture plus additional equations for U_1-U_2 and T_1-T_2 taken from the two-fluid thirteen moment theory of Goebel et al.(1976). Mitra et al.(1984) used the complete two-fluid equations of Goebel et al. for quasi-one-dimensional inviscid flows to describe the problem. These authors considered the unsteady equations and integrated them in time until the steady state was reached. In undertaking such a considerable numerical task, no advantage was taken of the three first integrals of the steady state problem [see Eqs.(8.2.1), (8.2.2) and (8.2.4) below].

8.2 Governing equations

Neglecting the stress tensor and heat flux of the light gas, the quasi-one-dimensional conservation equations for the species mass, momentum and energy of the mixture may be written as

$$\rho_1 U_1 A = \text{constant} \equiv m_1' \,, \tag{8.2.1}$$

$$\rho_2 U_2 A = \varepsilon \, m_1' \,, \tag{8.2.2}$$

$$\frac{d}{dx} \left[(U_1 + \varepsilon \, U_2) \, m_1' + (n_1 k T_1 + n_2 k T_{2\parallel}) A \right] - a \, (n_1 k T_1 + n_2 k T_{2\parallel}) = 0 \,, \tag{8.2.3}$$

$$h_1 + \frac{U_1^2}{2} + \varepsilon \, (h_2 + \frac{U_2^2}{2}) = \text{constant} \equiv h_{10} + \varepsilon \, h_{20} \,, \tag{8.2.4}$$

where $A = A(x)$ is the nozzle cross-sectional area, $a \equiv dA/dx$, $T_{2\parallel}$ is the component of the heavy gas temperature tensor parallel to the flow, and the enthalpy of species i is given by

$$h_i = \frac{\gamma_i}{\gamma_i - 1} \frac{k}{m_i} T_i \; ; \tag{8.2.5}^*$$

the subscript 0 corresponds to the stagnation conditions (zero velocity) and

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* $T_2 = \frac{1}{3} (T_{2\parallel} + 2 T_{2\perp})$.

$$\varepsilon = \frac{\rho_{20}}{\rho_{10}} \ . \tag{8.2.6}$$

The main differences between the above Eqs.(8.2.1-4) and the similar conservation equations (6.2.1-4) used in the shock wave problem are the following: (i) due to the varying cross-section of the flow (therefore its *quasi*-one-dimensionality), the mixture momentum conservation equation cannot be integrated as Eq.(6.2.3); (ii) the partial pressure and the enthalpy of the heavy component are not neglected in Eqs.(8.2.3) and (8.2.4) because we are not assuming n_2/n_1 small.

The remaining equations for U_2 and T_2 may be written as (lowest order of the hypersonic expansion B for arbitrary v and including self-collisions, see Sec.4.4)

$$m_1' \varepsilon \frac{dU_2}{dx} + A \frac{d(n_2 k T_{2\parallel})}{dx} = A \frac{\rho_2 v_B}{\tau_e} (U_1 - U_2), \tag{8.2.7}$$

$$U_2 \frac{dT_{2\parallel}}{dx} + 2T_{2\parallel} \frac{dU_2}{dx} = \frac{2v_{\Pi1}}{\tau_e} (T_1 - T_{2\parallel}) - \frac{2Gm_1 v_{\Pi2}}{k\tau_e} (U_1 - U_2)^2$$

$$+ \frac{2m_1 T_{2\parallel} v_B}{k\tau_e T_1} (U_1 - U_2)^2 + \frac{2m_2}{\rho_2 k} E'_{2\parallel} \ , \tag{8.2.8}$$

$$U_2 \frac{dT_{2\perp}}{dx} = \frac{2v_B}{\tau_e} (T_1 - T_{2\perp}) + \frac{Gm_1 v_{\Pi2}}{k\tau_e} (U_1 - U_2)^2 + \frac{2m_2}{\rho_2 k} E'_{2\perp} \ , \tag{8.2.9}$$

where $E'_{2\parallel} \equiv E'_{2xx}$ and $E'_{2\perp} \equiv E'_{2yy} = E'_{2zz}$. This hypersonic closure is not correct throughout the nozzle because the initial velocity is zero (stagnation conditions). However, as a consequence of the mass disparity between species, the sonic condition for the heavy gas is reached far upstream of the nozzle throat, where both species may still be considered in equilibrium. Therefore, the (numerical) integration of the above equations can be started after the heavy gas sonic point assuming that the mixture is in equilibrium and isentropic. After that point, the hypersonic closure of the heavy gas moment equations is approximately valid (it is exact if equilibrium still prevails), and its accuracy increases as we approach the nozzle throat.

Using the dimensionless variables

$$\eta_i \equiv U_i \left(\frac{m_1}{kT_0}\right)^{1/2}, \ \theta_1 \equiv \frac{T_1}{T_0} \ , \ \theta_\parallel \equiv \frac{T_{2\parallel}}{T_0} \ , \ \theta_\perp \equiv \frac{T_{2\perp}}{T_0} \ , \tag{8.2.10a}$$

$$z \equiv \frac{x}{d} \ , \ \alpha \equiv \frac{ad}{A} \ , \tag{8.2.10b}$$

equations (8.2.1-4) and (8.2.7-9) can be written as

$$\Delta \frac{d\eta_1}{dz} = \Delta'G_1 - \frac{\varepsilon M G_3}{\eta_1} \left[\frac{\gamma_1 - 1}{\eta_1 \gamma_1} - \frac{\gamma_0}{3}\left(1 - \frac{1}{3 M_\parallel^2}\right)\right]$$

$$+ \varepsilon G_2 \left[-\Delta' - \frac{2\theta_\parallel \gamma_0 M}{3\eta_1} + \frac{\gamma_1 - 1}{\gamma_1} \frac{\eta_2^2}{\eta_1} \right], \qquad (8.2.11a)$$

$$\Delta' \frac{d\eta_2}{dz} = G_2 \eta_2 - \frac{M G_3}{\eta_2}, \qquad (8.2.11b)$$

$$\Delta' \frac{d\theta_\parallel}{dz} = -2 G_2 \theta_\parallel + G_3 \left(1 - \frac{1}{3 M_\parallel^2}\right), \qquad (8.2.11c)$$

$$\eta_2 \frac{d\theta_\perp}{dz} = G_4, \qquad (8.2.11d)$$

$$\theta_1 = 1 - \frac{\gamma_1 - 1}{2\gamma_1}(\eta_1^2 + \varepsilon \eta_2^2) + \varepsilon M \gamma_0(1 - \theta_2). \qquad (8.2.11e)$$

In the above equations, the following functions and constants have been defined:

$$Ma_1^2 = \frac{\eta_1^2}{\theta_1 \gamma_1}, \qquad (8.2.12a)$$

$$M_\parallel^2 = \frac{\eta_2^2}{3 M \theta_\parallel}, \qquad (8.2.12b)$$

$$\Delta = \frac{\Delta'}{\gamma_1}\left(1 - \frac{1}{Ma_1^2}\right), \qquad (8.2.13a)$$

$$\Delta' = \eta_2 \left(1 - \frac{1}{M_\parallel^2}\right), \qquad (8.2.13b)$$

$$G_1 = \alpha \left(\frac{\theta_1}{\eta_1} + \frac{\varepsilon M \theta_\parallel}{\eta_2}\right) + \frac{2\gamma_0 M \varepsilon}{3\eta_1 \eta_2} G_4, \qquad (8.2.14a)$$

$$G_2 = \frac{\alpha \theta_\parallel M}{\eta_2} + F_1 \frac{\eta_1 - \eta_2}{\eta_1 \eta_2}, \qquad (8.2.14b)$$

$$G_3 = \frac{2F_1}{\eta_1}\left[\nu_{\Pi 1}(\theta_1 - \theta_\parallel) + \left(\frac{\theta_\parallel}{\theta_1} - G\right)(\eta_1 - \eta_2)^2\right] - F_2 \frac{\eta_1 \theta_2^{11/6} \theta_1^{-1/3}(\theta_2 - \theta_\perp)}{\eta_2 \theta_\parallel^{1/2} \theta_\perp}, \qquad (8.2.14c)$$

$$G_4 = \frac{2F_1}{\eta_1}\left[\theta_1-\theta_\perp + \frac{G}{2}(\eta_1-\eta_2)^2\right] + \frac{F_2}{2}\frac{\eta_1\theta_2^{11/6}\theta_1^{-1/3}(\theta_2-\theta_\perp)}{\eta_2\theta_\parallel^{1/2}\theta_\perp} \,, \qquad (8.2.14d)$$

$$F_1 = M\frac{A_0}{A}\frac{16\Omega_{12}^{(1,1)}(T_1)}{3\Omega_{12}^{(1,1)}(T_0)}\,F_0 \,, \qquad (8.2.15a)$$

$$F_2 = \varepsilon\frac{A_0}{A}\frac{9\Omega_1^{(2,2)}(T_0)\Omega_2^{(2,2)}(T_0)}{25[\Omega_{12}^{(1,1)}(T_0)]^2}\,F_0 \,, \qquad (8.2.15b)$$

$$F_0 = \frac{m'_1\,d}{A_0}\frac{\Omega_{12}^{(1,1)}(T_0)}{kT_0} \,, \qquad (8.2.16)$$

A_0 = throat cross-sectional area,

$$\alpha = \frac{ad}{A} \,,$$

$$\gamma_0 = \frac{\gamma_2(\gamma_1-1)}{\gamma_1(\gamma_2-1)} \,. \qquad (8.2.17)$$

The self-collision term [which for one-dimensional problems is given by Eq.(4.4.1b)] has been simplified by using the repulsive part of a Lennard-Jones potential of molecular interaction [Riesco-Chueca et al.(1986)]. Also, we have taken $v_B=v_{\Pi2}=1$ since, as shown by Riesco-Chueca et al.(1986), these parameters are approximately equal to one even for $v=O(1)$. For the coefficient $v_{\Pi1}$ we shall use the expression*

$$v_{\Pi1} = [1 + 0.718\,|\eta_1-\eta_2|^{1.8}]^{1.4815} \qquad (8.2.18)$$

valid for $T_1^*>>1$.

8.3. Numerical solution and comparison with experiments

Equations (8.2.11) have two singular points given by $\Delta=0$: the light gas sonic point $Ma_1=1$, and $M_\parallel=1$, which is the sonic point of the heavy gas based on the parallel temperature.

As pointed out before, we shall start the numerical integration of Eqs.(8.2.11) after the singular point $M_\parallel=1$ (which, for $M<<1$ and sufficiently high pressure ratio, see below, is reached far before the nozzle throat), assuming equilibrium between species. That is, we shall start the numerical integration at a point z_1, located just after the condition $M_\parallel=1$ is satisfied, with $\eta_1=\eta_2=\eta$, $\theta_1=\theta_\parallel=\theta_\perp=\theta_2=\theta$, and isentropic conditions for the mixture. From the original

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* Riesco-Chueca et al. (1986), Eq.(6).

Eqs.(8.2.1-4) with $U_1=U_2$, $T_1=T_{2\parallel}=T_2$, and making use of the isentropic relation for the mixture, one gets (e.g. Liepmann and Roshko, 1956, Ch.5)

$$\frac{A}{A_0} = \frac{C_d}{1+M\varepsilon} \frac{1}{Ma} \left[\frac{2}{\gamma+1}\left(1 + \frac{\gamma-1}{2}Ma^2\right)\right]^{(\gamma+1)/2(\gamma-1)} ,$$ (8.3.1)

$$\theta = \left(1 + \frac{\gamma-1}{2}Ma^2\right)^{-1} ,$$ (8.3.2)

$$\eta = \frac{1+M\varepsilon}{1+\varepsilon} \frac{\gamma Ma^2}{1 + \frac{\gamma-1}{2}Ma^2} ,$$ (8.3.3)

where Ma and γ are the Mach number and specific heat ratio of the mixture. C_d is de discharge coefficient, defined as

$$C_d = \frac{m'_1(1+\varepsilon)}{m'_{is}} ,$$ (8.3.4)

m'_{is} being the maximum isentropic mass flow, attained when the mixture is sonic at the throat:

$$m'_{is} \equiv A_0 U^* \rho^* = A_0 \frac{p_0}{\sqrt{kT_0}} \left(m_2\gamma\frac{M(1+\varepsilon)}{1+M\varepsilon}\right)^{1/2} \left(\frac{2}{\gamma+1}\right)^{(\gamma+1)/2(\gamma-1)} ,$$ (8.3.5)

where p_0 and T_0 are the stagnation pressure and temperature of the mixture. In terms of the light gas Knudsen number

$$Kn'_1 \equiv \frac{(kT_0)^{3/2}}{p_0 d} \frac{[(1+\varepsilon)(1+M\varepsilon)]^{1/2}}{\sqrt{\gamma m_1}\Omega_{12}^{(1,1)}(T_0)} \left(\frac{2}{\gamma+1}\right)^{-(\gamma+1)/2(\gamma-1)} ,$$ (8.3.6)

we have

$$C_d = F_0 Kn'_1 .$$

For a given gas mixture and nozzle geometry, there are three parameters in the problem: the density ratio ε (fixed by the gas composition at the stagnation chamber), the Knudsen number Kn'_1 (fixed by the stagnation conditions and ε), and the mass flow parameter F_0, which can be related to the light gas Reynolds number through

$$Re_1 \equiv \frac{U_1 \rho_1 d}{[\mu(T_0)]_1} = \frac{8\Omega_1^{(2,2)}(T_0)}{5\Omega_{12}^{(1,1)}(T_0)} F_0.$$ (8.3.7)

If we fix the gas composition and the stagnation pressure (ϵ and Kn'_1), the mass flow through the nozzle (F_0) becomes fixed in such a way that the pressure p_e at the exit of the nozzle is met. Thus, as it is well known from the theory of nozzle flows for a pure gas (or a mixture with M~1), if we increase the pressure ratio Π_p,

$$\Pi_p \equiv \frac{p_0}{p_e},$$ (8.3.8)

from 1 up to a critical value Π_p^* (which for an ideal mixture is $(\frac{2}{\gamma+1})^{1/(\gamma-1)}$, corresponding to the sonic conditions of the mixture at the throat), the mass flow increases from zero to its maximum value m'^*. For an ideal binary gas mixture, the maximum value of the mass flow m'^* is given by Eq.(8.3.5), so that C_d is, at most, unity (when $\Pi_p \geq \Pi_p^*$). However, for DMM, as a consequence of the velocity slip and temperature difference among species, C_d may be larger than one.

In the case of a DMM, the maximum value of the mass flow is reached when the light gas sonic condition $Ma_1=1$ is satisfied at some point of the nozzle. From the numerical results, we conclude that this sonic point is not attained at the throat of the nozzle, but slightly afterwards. Thus, when M<<1, we have a singular point far before the nozzle throat, and another one just after it. As M increases these two singular points approach each other until they meet at the throat when M≈1, corresponding to sonic conditions of the mixture.
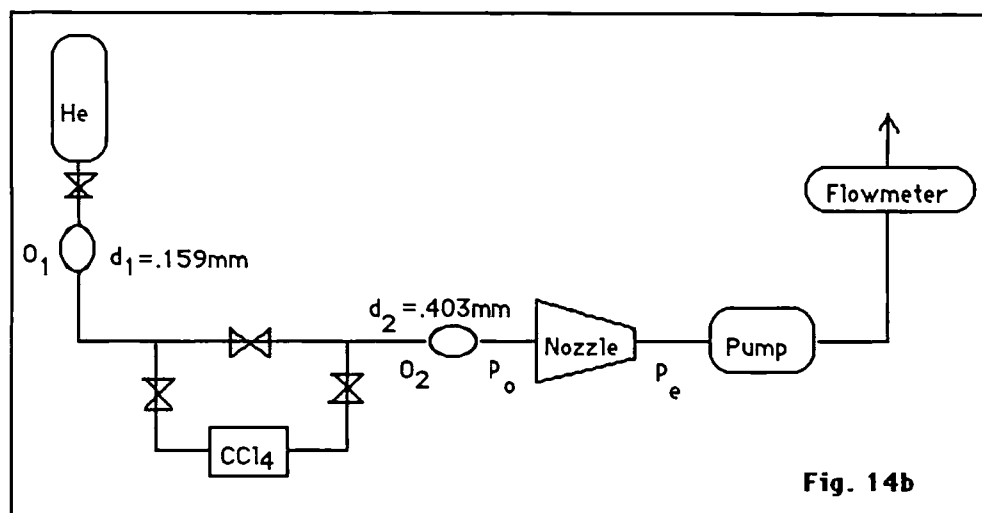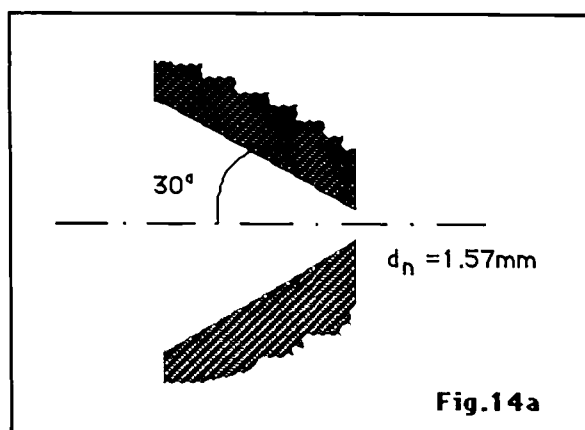
An upper limit for C_d in DMM is reached in the so-called *frozen* limit, in which the heavy gas is completely decoupled from its light partner. In this limit, the maximum mass flow is attained when the light gas is sonic at the throat, so that $C_d = \sqrt{\frac{1+\epsilon}{1+M\epsilon}}$.

For the experiments we have used a conical-shaped nozzle, whose dimensions are depicted in Fig.14a (the nozzle length is much larger than the nozzle throat diameter), and a CCl_4-He mixture (M=0.026). A sketch of the experimental system is given in Fig.14b. The nozzle is located inside a vacuum chamber at a pressure p_e. Helium from a tank flows through the nozzle at a constant flow rate (constant Re_1) fixed by a critical orifice O_1 located before the nozzle. The flow rate V' (cm^3/s) is measured by a soap bubble flowmeter at the exit of the vacuum pump. After the orifice O_1, the light gas (He) passes through a cell containing CCl_4. To determine the concentration of CCl_4, we place a second critical orifice O_2 after the cell, and measure the pressure just before this orifice, both when only the light gas (He) is passing through the system (p_m), and when the heavy vapor flows together with the light gas

$(p_m + \Delta p_m)$. Since the mass flow of the light gas remains constant (because of the orifice O_1), ε is related to $\Pi_m \equiv \Delta p_m / p_m$ through

$$\varepsilon = \frac{(1 + \Pi_m)^2 - 1}{1 - M(1 + \Pi_m)^2} \approx \Pi_m(\Pi_m + 2) \ .$$

(8.3.8)

Figure 14. Nozzle dimensions and sketch of the experimental system.

30^a

$d_n = 1.57mm$

Fig.14a

He

Flowmeter

O_1 $d_1 = .159mm$

$d_2 = .403mm$

O_2 P_o Nozzle P_e Pump

CCl_4

Fig. 14b

The value of ε is maintained approximately constant by immersing the cell into an isothermal bath.[*] After the orifice O_2, the mixture passes through the nozzle, and then exhausts through the vacuum pump. During the experiment we change the value of the pressure ratio Π_p

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[*] Since the flow rate of He is constant, ε only depends on the cell temperature.

[Eq.(8.3.8)] regulating the exhausting valve of the pump. Typical results of C_d versus Π_p are shown in Fig.15 for $Re_1 \approx 33$ ($F_0 \approx 24$) and ε between 4.667 and 4.387 (x_2 between 0.108 and 0.102). Even for such a low value of Re_1 (for which the viscous effects are important, as one can see in the figure), we have measured discharge coefficients larger than one.

Figure 15 also contains the corresponding results from the numerical integration of Eqs.(8.2.11) (we have use the subroutine DGEAR of the IMSL library). They are obtained with $T_0 = 292K$ and using a Lennard-Jones potential with parameters ε_1 and σ_1 taken from Hirshfelder *et al.* (1954), ε_2 and σ_2 from Svehla (1962), and $\sigma_{12}=\frac{1}{2}(\sigma_1+\sigma_2)$, $\varepsilon_{12}=\sqrt{\varepsilon_1\varepsilon_2}$. The specific heat ratios used are: $\gamma_1 = 5/3$, $\gamma_2 = 15/13$ and $\gamma = 1.49$. † To model the nozzle shape we have used the function

$$\frac{A}{A_0} = C' \frac{z^2}{\{arctan[n(z_0+1)]\}^2} \, , \qquad (8.3.9)$$

where

$$C' = \frac{n^2}{\{1+[n(z_0+1)]^2\}^2} = \frac{\{arctan[n(z_0+1)]\}^2}{z_0^2} \, , \qquad (8.3.10)$$

and n is a very large number (we have taken $n=10000$; the results are independent of n for $n>1000$, approximately). The space variable z varies from $-\infty$ to $z=z_0 \approx -1$, where A/A_0 has a minimum equal to one [the value of z_0 is computed numerically from Eq.(8.3.10)]. The constant d [Eq.(8.2.10b)] used is $d=d_n/2tan\phi$, where d_n and ϕ are, respectively, the diameter and angle of the nozzle ($d_n=1.57mm$, $\phi=30°$).

Finally, Fig.15 also shows the discharge coefficients of pure He measured at the same Reynolds number. Using these pure gas values, we have computed the frictionless discharge coefficient of the mixture, dividing the experimental values of C_d by the ratio among the corresponding pure gas discharge coefficient and that predicted from the ideal theory of pure gases (see, e.g., Liepmann and Roshko, 1956). Although this procedure of accounting for the viscosity effects is not very rigorous, the corrected values of C_d agree reasonably well with the results from the theory (the differences are within the experimental errors, which are about 7%). For a more rigorous treatment one has to include the viscous effects near the wall into the theory, especially for low Reynolds numbers where the enhancement of the discharge coefficient due to the nonequilibrium between species is of the same order or smaller than the decrement due to the viscous effects.

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† That is to say, we have assumed that all the internal degrees of freedom of the heavy molecules are in equilibrium. Using the opposite limit (i.e. $\gamma_2=\gamma= 5/3$), we found that the results only differ in about 2%.
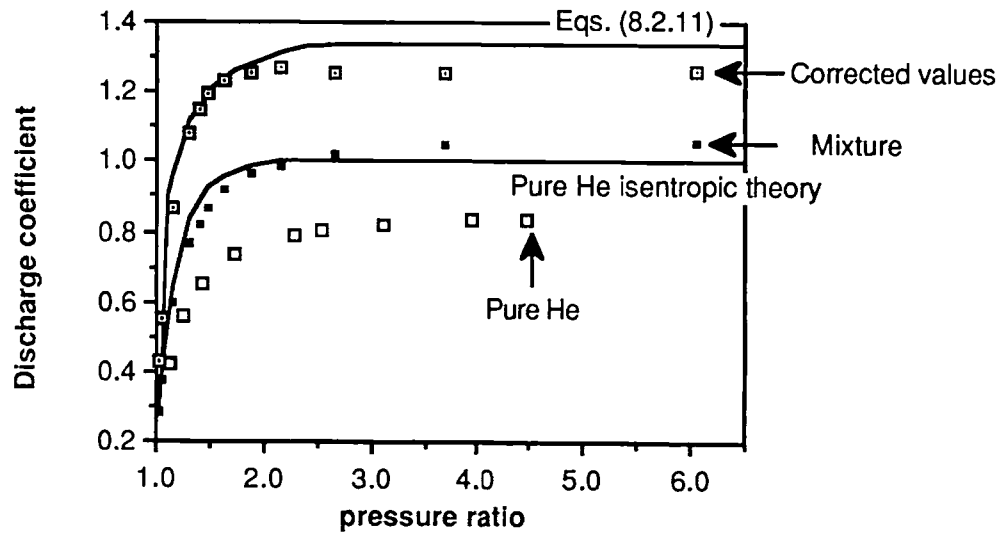
Figure 15. Experimental C_d vs. Π_p for a CCl_4-He mixture with $Re_1 \approx 33$ and ε between 4.667 and 4.387. Experimental values of C_d for pure He at the same Reynolds number are also shown. The theoretical curve [Eqs.(8.2.11)] is computed at $\varepsilon=4.58$. The corrected values of C_d are obtained by dividing them by the ratio between the experimental C_d of pure He at the same pressure ratio and the C_d predicted by the isentropic theory for pure gases (also shown in the figure).

Chapter 9
CONCLUSIONS

Starting from the kinetic BEs we have developed a number of general *theoretical tools* for binary mixtures of gases with very different molecular weights, covering a broader parameter range than that of the previous existing theories (except for the BEs themselves). These previous theories are, basically, the standard CE theory for binary mixtures (Ref.I, Ch.8), and a number of two-fluid theories most of which are reviewed in Section 2.2. As discussed in Chapter 2, the first of them, the standard CE theory, is very restricted in its Knudsen number range of applicability: $Kn_1 << M$, which excludes its use for many of the physically and industrially relevant problems involving DMM. A two-fluid theory extends this range to $Kn_1 << 1$, with the limitation that the heavy gas equations are only valid for $n_2/n_1 >> Kn_1$ [if $M \geq O(Kn_1)$]. However, among the previous two-fluid theories, only one is, to our knowledge, rigorously derived from the BEs (Goldman and Sirovich, 1967), and it is made for Maxwell molecules.

From a systematic mass ratio expansion of the cross-collision integrals in the Boltzmann equations, and after a further expansion of the light gas BE we have developed, first, near-equilibrium hydrodynamic equations for the light gas valid for $Kn_1 << 1$, independently of whether the heavy gas is also in near-equilibrium conditions. The resulting distribution function for the light gas was used to obtain an explicit expression for the FP collision operator in terms of the hydrodynamic quantities and their gradients. For $n_2/n_1 >> Kn_1$, near-equilibrium hydrodynamic equations for the heavy gas were also possible, completing a two-fluid hydrodynamic picture of the mixture. This two-fluid description was also generalized to arbitrary mass ratios.

When $n_2/n_1 << M \sim Kn_1$, the kinetic equation of the heavy gas was substantially reduced to an equation of the FP type. In contrast to previous derivations of the FP equation from the BE of the heavy gas, no assumption was made on the light gas distribution function, except for $Kn_1 << 1$, retaining terms up to the first order in Kn_1. This FP equation was also the basis of a hydrodynamic description of the heavy gas in its hypersonic limit.

Cosidered together, the hydrodynamic and simplified kinetic equations of Chapters 2, 3 and 4 cover almost completely the range $Kn_1 << 1$ for any heavy gas concentration, except for the particular limit $n_2/n_1 \sim M$ (however, this limit is also covered when the heavy gas is hypersonic, which occurs very frequently in practice). Therefore, the theories given in those chapters constitute a general framework for a large class of industrially and physically relevant problems.

To validate these theories, we have applied them to some particular examples. Thus, the two-fluid theory, whose transport coefficients have been calculated at the first order of a Sonine polynomials expansion, has successfully passed a test against experimental data on absorption and dispersion of sound in He-Xe (M=0.0304) mixtures (using a Lennard-Jones potential of molecular interaction). This acoustic example has also corroborated our predictions on the Knudsen number range of validity of both the two-fluid and the standard CE theories. As another test, the combination of a hypersonic approximation for the heavy gas and a near-equilibrium hydrodynamic closure for the light gas has been applied to the shock wave problem and to the flow through a converging nozzle. The results have been compared with experimental data in both cases, showing a good agreement. A simplified version of the shock wave problem has also been solved using the kinetic FP equation, corroborating the predictions on the errors of the lowest order of the hypersonic approximation by direct comparison of the velocity distribution function.

More complicated problems such as those arising in actual applications of DMM can obviously be treated with the equations given in Chapters 2-4. As is patent from Chapter 8, the difficulties encountered in dealing with these *real* problems are more considerable than in the simple problems studied in Chapters 5-7, which were used as tests of the theory. Nevertheless, success has been reached in some technologically relevant problems like, for instance, the determination of the impact energies of heavy molecules seeded in supersonic jets impinging on surfaces at large background pressures, studied by Fernández de la Mora *et al.* (1986). These authors considered the far field flow near the axis in the isentropic region where the heavy molecules are accelerated by the light gas, and the centerline deceleration of the heavy molecules between the detached shock and the solid surface, predicting impact energies which compared very favorably with experimental measurements made with $W(CO)_6$ molecules seeded in H_2 jets.

In conclusion, this thesis provides a fairly comprehensive and rigorous set of theoretical tools capable of describing the evolution of gas mixtures with disparate masses. Their succes in all the cases where they have been tested against experiments indicate that they are a highly reliable way to predict real flow fields involving mixtures with widely different molecular weights.

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Appendix A
MOMENT EQUATIONS

Let us define the moments of the the velocity distribution function f_i as

$$\rho_i \equiv m_i n_i \equiv m_i[1, f_i], \tag{A1}$$

$$\rho_i \mathbf{U}_i \equiv m_i[\mathbf{u}, f_i], \tag{A2}$$

$$\boldsymbol{P}_i \equiv m_i[\mathbf{c}_i \mathbf{c}_i, f_i], \tag{A3}$$

$$\boldsymbol{Q}_i \equiv \frac{m_i}{2} [\mathbf{c}_i \mathbf{c}_i \mathbf{c}_i, f_i], \tag{A4}$$

and so on, where the inner product [,] is defined as

$$[f, g] \equiv \int d^3 u \, f(u) \, g(u) \ , \tag{A5}$$

and

$$\mathbf{c}_i \equiv \mathbf{u} - \mathbf{U}_i \ . \tag{A6}$$

Multiplying the Boltzmann equation for the component i,

$$Df_i \equiv \frac{\partial f_i}{\partial t} + \mathbf{u} \cdot \nabla f_i = J_{ii}(f_i, f_i) + J_{ij}(f_i, f_j) \ , \quad i \ne j \ , \tag{A7}$$

by the functions 1, $\mathbf{u}$, $\mathbf{u}\mathbf{u}$, ... , and integrating over the velocity space, we get the following equations for the moments

$$\frac{\partial \rho_i}{\partial t} + \nabla \cdot (\rho_i \mathbf{U}_i) = 0, \tag{A8}$$

$$\frac{\partial (\rho_i \mathbf{U}_i)}{\partial t} + \nabla \cdot (\rho_i \mathbf{U}_i \mathbf{U}_i + \boldsymbol{P}_1) = \mathbf{M}_i, \tag{A9}$$

$$\frac{\partial (\rho_i \mathbf{U}_i \mathbf{U}_i + \boldsymbol{P}_i)}{\partial t} + \nabla \cdot (\rho_i \mathbf{U}_i \mathbf{U}_i \mathbf{U}_i + 2\boldsymbol{Q}_i + \mathbf{U}_i \boldsymbol{P}_i) + (\boldsymbol{P}_i \cdot \nabla) \mathbf{U}_i + \{(\boldsymbol{P}_i \cdot \nabla) \mathbf{U}_i\}^T$$
$$+ \mathbf{U}_i \nabla \cdot \boldsymbol{P}_i + \{\mathbf{U}_i \nabla \cdot \boldsymbol{P}_i\}^T = 2(E_i + E_i') \ , \tag{A10}$$

and so forth, where

$$\mathbf{M}_i \equiv m_i[\mathbf{u}, J_{ij}(f_i, f_j)] = m_i[\mathbf{c}_i, J_{ij}(f_i, f_j)], \quad i \ne j \ , \tag{A11}$$

$$E_i \equiv \frac{m_i}{2} [\mathbf{u}\mathbf{u}, J_{ij}(f_i, f_j)], \quad i \ne j \ , \tag{A12}$$

$$E_i' \equiv \frac{m_i}{2} [\mathbf{u}\mathbf{u}, J_{ii}(f_i, f_i)] = \frac{m_i}{2} [\mathbf{c}_i \mathbf{c}_i, J_{ii}(f_i, f_i)] \ , \tag{A13}$$

and the superscript T denotes the transposed tensor. Notice that, because the conservation of species and momentum,

$$[1, J_{ii}(f_i, f_i)] = [1, J_{ij}(f_i, f_j)] = 0, \quad i \ne j, \tag{A14}$$

$$[\mathbf{U}_i, J_{ii}(f_i, f_i)] = 0, \tag{A15}$$

$$M_1 = - M_2 \equiv M. \tag{A16}$$

Also,

$$E_j = E_j + \frac{M_jU_j + U_jM_j}{2}, \tag{A17}$$

where

$$E_j \equiv \frac{m_j}{2} [c_j\, c_j,\ J_{ij}(f_j\,,f_j\,)\,],\quad i \neq j. \tag{A18}$$

Using Eqs.(A8),(A9) and (A17), Eq.(A10) can be rearranged as

$$\frac{\partial P_j}{\partial t} + \nabla\cdot(\,2Q_j + U_jP_j\,) + (P_j\cdot\nabla)\,U_j + \{(P_j\cdot\nabla)\,U_j\}^T = 2(E_j + E_j'). \tag{A19}$$

The trace of the above equation yields the usual energy equation,

$$\frac{3}{2}\,k\,n_j\frac{\partial T_j}{\partial t} + \frac{3}{2}\,k\,n_j\,U_j\cdot\nabla\,T_j + \nabla\cdot Q_j + P_j : \nabla\,U_j = E_j, \tag{A20}$$

where

$$T_j \equiv \frac{P_j}{n_jk}, \tag{A21}$$

is the temperature tensor,

$$T_j \equiv \frac{T_j :I}{3}, \tag{A22}$$

$$Q_j \equiv Q_j:I, \tag{A23}$$

$$E_j \equiv E_j:I, \tag{A24}$$

and, by energy conservation,

$$E_j':I = 0. \tag{A25}$$

For easy reference, we rewrite together the conservation equations for species i:

$$\frac{\partial n_j}{\partial t} + \nabla\cdot(n_jU_j) = 0, \tag{A26}$$

$$m_j\,n_j\frac{\partial U_j}{\partial t} + m_j\,n_j\,U_j\cdot\nabla\,U_j + \nabla\cdot P_j = M_j, \tag{A27}$$

$$\frac{3}{2}\,k\,n_j\frac{\partial T_j}{\partial t} + \frac{3}{2}\,k\,n_j\,U_j\cdot\nabla\,T_j + \nabla\cdot Q_j + P_j : \nabla\,U_j = E_j, \tag{A28}$$

$$M_1 = - M_2 \equiv M, \tag{A29}$$

$$E_1 = - E_2 - M\cdot(U_1 - U_2). \tag{A30}$$

Appendix B

VARIATIONAL PRINCIPLE FOR THE DETERMINATION OF THE TRANSPORT COEFFICIENTS

We give in this appendix the general ideas of the variational principle used for the determination of the transport coefficients of the light gas in the limit M<<1 (Sec.2.4 and Appendix C), and those of the two-fluid theory of Chapter 3 (Appendix D). The variational principle is due to Bernstein (1969b).

The first order CE correction to the distribution function (ϕ_1 in Sec.2.4 and the vector function $\underline{\phi}$ in Sec.3.2) may be written as the sum of a number of functions ϕ_i that satisfy linear integral equations of the form

$$\Gamma(\phi_i) = \psi_i \qquad\qquad (B1)$$

[i.e. Eqs.(2.4.8-11) and (3.1.11); notice that Γ is a *2x2 matrix operator* in Sec.3.1]. Based in the fact that Γ is a symmetric and non-positive operator, the solution of the above integral equation maximalizes the functional

$$\Lambda\{\chi\} \equiv [\chi,\Gamma(\chi) - 2\psi_i] \ .$$

The maximum (positive) value of this functional is

$$\Lambda_{max} = - [\phi_i,\psi_i] = - [\phi_i,\Gamma(\psi_i)],$$

and it is related to, at least, one of the transport coefficients appearing in the near-equilibrium hydrodynamic equations. For instance, the contribution of ϕ_1 to the pressure tensor of the light gas in Sec.2.4 can be written as

$$P_1 - n_1 kT_1 I \equiv [m_1 c_1 c_1 , f_{10}\phi_1] = kT_1[B_1\xi_1\xi_1:,\psi_B]\nabla^{\circ}U_1 \equiv - 2\mu_1\nabla^{\circ}U_1,$$

so that

$$\frac{2\mu_1}{kT_1} = - [B_1\xi_1\xi_1:,\psi_B] \equiv - [\phi_B:,\psi_B].$$

The right-hand side of the above expression is the maximum of the functional

$$\Lambda_B\{\chi_B\} \equiv [\chi_B:, \Gamma(\chi_B) - 2\psi_B] \ ,$$

where $\Gamma(\chi_B) \equiv K_1(\chi_B) + N(f_{10}\chi_B)$.

One of the most remarkable properties of this variational principle is the folllowing: if the difference between the trial function χ and the exact solution ϕ_i of Eq.(B1) is of order $\varepsilon<<1$, the resulting value of the functional $\Lambda\{\chi\}$ differs from the exact maximum value a quantity of order ε^2; for if $\chi=\phi_i+\varepsilon\phi$,

$$\Lambda\{\chi\} = \Lambda_{max} + \varepsilon^2[\phi,\Gamma(\phi)].$$

Therefore, the transport coefficient evaluated with the trial function χ differs from its exact value a quantity of order ε^2.

Appendix C
TRANSPORT COEFFICIENTS FOR THE LIGHT GAS IN THE LIMIT M<<1

The transport coefficients for the light gas entering into Eqs. (2.4.16-18) are given in this appendix. They are evaluated from Eqs.(2.4.25-28) by means of the variational principle sketched in Appendix B, and using expansions in Sonine polynomials as trial functions (Ref.II, Appendix D).

The expressions of these transport coefficients at the first and second orders in these expansions are the following:

$$[\mu_1]_1 = \frac{5n_1kT_1}{16n_2\Omega_{12}^{(2,2)}[\frac{n_1}{n_2}\bar{a}_1+1]} \tag{C1}$$

$$[\lambda_1]_1 = \frac{75n_1k^2T_1}{64m_1n_2\Omega_{12}^{(1,1)}[\frac{n_1}{n_2}a_1+b]} \tag{C2}$$

$$[k_{T1}]_1 = \frac{5an_1T_1}{2nT[\frac{n_1}{n_2}a_1+b]} \tag{C3}$$

$$[\lambda_b]_1 = \frac{16}{3}\Omega_{12}^{(1,1)} = \frac{1}{n_1M_{T_e}} \tag{C4}$$

$$[\mu_1]_2 = \frac{5n_1kT_1}{16n_2\Omega_{12}^{(2,2)}}\frac{\bar{b}+\frac{n_1}{n_2}\bar{c}_1}{[(\frac{n_1}{n_2}\bar{a}_1+1)(\bar{b}+\frac{n_1}{n_2}\bar{c}_1)-(\bar{a}+\frac{n_1}{n_2}\bar{b}_1)^2]} \tag{C5}$$

$$[\lambda_1]_2 = \frac{75n_1k^2T_1}{64m_1n_2\Omega_{12}^{(1,1)}\Delta}\{\frac{n_1}{n_2}c_1+e-c^2-\frac{[c(\frac{n_1}{n_2}b_1+d)-a(\frac{n_1}{n_2}c_1+e)]^2}{(\frac{n_1}{n_2}a_1+b)(\frac{n_1}{n_2}c_1+e)-(\frac{n_1}{n_2}b_1+d)^2}\} \tag{C6}$$

$$[k_{T1}]_2 = \frac{5n_1T_1}{2nT\Delta}\{a(\frac{n_1}{n_2}c_1+e)-c(\frac{n_1}{n_2}b_1+d)$$

$$+[a^2(\frac{n_1}{n_2}c_1+e)+c^2(\frac{n_1}{n_2}a_1+b)-2ac(\frac{n_1}{n_2}b_1+d)]\frac{[c(\frac{n_1}{n_2}a_1+b)-a(\frac{n_1}{n_2}b_1+d)]^2}{(\frac{n_1}{n_2}a_1+b)(\frac{n_1}{n_2}c_1+e)-(\frac{n_1}{n_2}b_1+d)^2}\} \tag{C7}$$

$$[\lambda_b]_2 = \frac{16}{3}\Omega_{12}^{(1,1)}[1-\frac{a^2}{\frac{n_1}{n_2}a_1+b}] \;, \tag{C8}$$

where

$$\Delta = \left(\frac{n_1}{n_2}a_1+b\right)\left(\frac{n_1}{n_2}c_1+e\right) - \left(\frac{n_1}{n_2}b_1+d\right)^2 + 2ac\left(\frac{n_1}{n_2}b_1+d\right)$$
$$- c^2\left(\frac{n_1}{n_2}a_1+b\right) - a^2\left(\frac{n_1}{n_2}c_1+e\right),$$

$$a = \frac{5}{2}, \qquad b = \frac{25}{4} - 5\frac{\Omega_{12}^{(1,2)}}{\Omega_{12}^{(1,1)}} + \frac{\Omega_{12}^{(1,3)}}{\Omega_{12}^{(1,1)}},$$

$$c = \frac{35}{8} - \frac{7}{2}\frac{\Omega_{12}^{(1,2)}}{\Omega_{12}^{(1,1)}} + \frac{1}{2}\frac{\Omega_{12}^{(1,3)}}{\Omega_{12}^{(1,1)}},$$

$$d = \frac{175}{16} - \frac{105}{8}\frac{\Omega_{12}^{(1,2)}}{\Omega_{12}^{(1,1)}} + \frac{19}{4}\frac{\Omega_{12}^{(1,3)}}{\Omega_{12}^{(1,1)}} - \frac{1}{2}\frac{\Omega_{12}^{(1,4)}}{\Omega_{12}^{(1,1)}},$$

$$e = \frac{1225}{64} - \frac{245}{8}\frac{\Omega_{12}^{(1,2)}}{\Omega_{12}^{(1,1)}} + \frac{133}{8}\frac{\Omega_{12}^{(1,3)}}{\Omega_{12}^{(1,1)}} - \frac{7}{2}\frac{\Omega_{12}^{(1,4)}}{\Omega_{12}^{(1,1)}} + \frac{1}{4}\frac{\Omega_{12}^{(1,5)}}{\Omega_{12}^{(1,1)}},$$

$$a_1 = \frac{1}{2}\frac{\Omega_{11}^{(2,2)}}{\Omega_{12}^{(1,1)}}, \qquad b_1 = \frac{7}{2}\frac{\Omega_{11}^{(2,2)}}{\Omega_{12}^{(1,1)}} - \frac{\Omega_{11}^{(2,3)}}{\Omega_{12}^{(1,1)}},$$

$$c_1 = \frac{77}{8}\frac{\Omega_{11}^{(2,2)}}{\Omega_{12}^{(1,1)}} - \frac{7}{2}\frac{\Omega_{11}^{(2,3)}}{\Omega_{12}^{(1,1)}} + \frac{1}{2}\frac{\Omega_{11}^{(2,4)}}{\Omega_{12}^{(1,1)}},$$

$$\bar{a} = \frac{7}{2} - \frac{\Omega_{12}^{(2,3)}}{\Omega_{12}^{(2,2)}}, \qquad \bar{b} = \frac{49}{4} - 7\frac{\Omega_{12}^{(2,3)}}{\Omega_{12}^{(2,2)}} + \frac{\Omega_{12}^{(2,4)}}{\Omega_{12}^{(2,2)}},$$

$$\bar{a}_1 = \frac{1}{2}\frac{\Omega_{11}^{(2,2)}}{\Omega_{12}^{(2,2)}}, \qquad \bar{b}_1 = \frac{7}{8}\frac{\Omega_{11}^{(2,2)}}{\Omega_{12}^{(2,2)}} - \frac{1}{4}\frac{\Omega_{11}^{(2,3)}}{\Omega_{12}^{(2,2)}},$$

$$\bar{c}_1 = \frac{301}{96}\frac{\Omega_{11}^{(2,2)}}{\Omega_{12}^{(2,2)}} - \frac{7}{8}\frac{\Omega_{11}^{(2,3)}}{\Omega_{12}^{(2,2)}} + \frac{1}{8}\frac{\Omega_{11}^{(2,4)}}{\Omega_{12}^{(2,2)}}.$$

(Notice that the expressions fo c_1 and $\bar{a}_1$ must be corrected in the Appendix D of Ref.II.) The Ω-integrals are defined as [see, i.e., Hirshfelder et al.(1954), Eq.(8.2-3)]

$$\Omega_{nm}^{(i,j)}(T) \equiv \sqrt{\frac{kT}{2\pi M_{nm}}} \int_0^\infty dx \ exp\{-x^2\}x^{2j+3} \ Q_{nm}^{i}(y) \ , \tag{C9}$$

$$Q_{nm}^{i}(y) \equiv 2\pi \int_0^\pi d\theta \ (1-cos^i\theta) \ \sigma_{nm}(y,\theta) \ sin\theta, \tag{C10}$$

$$y^2 = \frac{2x^2 kT}{M_{nm}} \ ,$$

where nm is either 11, 12 or 22, and $M_{11} = m_1/2$, $M_{22} = m_2/2$, $M_{12} = \frac{m_1 m_2}{m_1 + m_2} \approx m_1$.

The above expressions for the transport coefficients are valid for arbitrary interaction potentials with spherical symmetry. All the Ω-integrals are computed at the light gas temperature T_1. Tabulated values of the Ω-integrals for different interaction potentials can be found in, for instance, Hirshfelder et al. (1954), Mason (1957), and Ferziger and Kaper (1977).

Appendix D
TRANSPORT COEFFICIENTS FOR THE TWO-FLUID THEORY OF CHAPTER 3

When the first approximation of Sonine polynomials expansions are used as the trial functions in Eqs. (3.2.7), the resulting transport coefficients (3.2.6) may be written as (Ref.III, Sec.IV):

$$[\mu_{11}]_1 = Q_1^{-1} \left[x_1^2 \left(\frac{2}{3} + \frac{M_1}{M_2} A_1 \right) + \frac{x_1 x_2 B_1}{2\mu_2} \right] \ ,$$

$$[\mu_{22}]_1 = Q_1^{-1} \left[x_2^2 \left(\frac{2}{3} + \frac{M_2}{M_1} A_1 \right) + \frac{x_1 x_2 B_1}{2\mu_1} \right] \ ,$$

$$[\mu_{12}]_1 = [\mu_{21}]_1 = Q_1^{-1} \, x_1 x_2 \left(\frac{2}{3} - A_1 \right) \ ,$$

$$[\lambda_{11}]_1 = \frac{75 x_1 k^2 T}{64 m_1 Q_2} \left(P_2 - \frac{P_1 P_6}{P_5} \right) \ ,$$

$$[\lambda_{22}]_1 = \frac{75 x_2 k^2 T}{64 m_2 Q_2} \left(P_4 - \frac{P_1 P_7}{P_5} \right) \ ,$$

$$[\lambda_{12}]_1 = [\lambda_{21}]_1 = - \frac{75 x_2 k^2 T}{64 m_2 Q_2} \left(P_3 + \frac{P_1 P_7}{P_5} \right) \ ,$$

$$[k_{T1}]_1 = - \frac{5 M_2 x_1 x_2 P_6}{2 x_0 P_5} \ ,$$

$$[k_{T2}]_1 = - \frac{5 M_1 x_2^2 P_7}{2 x_0 P_5} \ ,$$

$$[\lambda_b]_1 = \frac{16 M_2 A}{3} \ ,$$

$$[\sigma_t]_1 = 16 \, k \, x_1 x_2 M_1 M_2 A \ ,$$

where

$$Q_1 = \frac{x_1^2}{\mu_1} \left(\frac{2}{3} + \frac{M_1}{M_2} A_1 \right) + \frac{x_2^2}{\mu_2} \left(\frac{2}{3} + \frac{M_2}{M_1} A_1 \right) + x_1 x_2 \left(\frac{B_1}{2\mu_1\mu_2} + \frac{4 A_1}{3 B_1 M_1 M_2} \right) \ ,$$

$$\mu_1 = \frac{5 k T}{8 \Omega_{11}^{(2,2)}} \ , \qquad \mu_2 = \frac{5 k T}{8 \Omega_{22}^{(2,2)}} \ ,$$

$$A_1 = \frac{\Omega_{12}^{(2,2)}}{5 \Omega_{12}^{(1,1)}} \ , \qquad B_1 = \frac{k T}{8 M_1 M_2 \Omega_{12}^{(1,1)}} \ ,$$

$$Q_2 = B M_2 x_0 P_1 + (x_1 E + M_2 x_2 C) P_2 + M_1^2 M_2 x_2 G P_3 \ ,$$

$$P_1 = M_1^{3/2} M_2^{3/2} B\left(\frac{x_2 F}{x_1 M_1} + D - M_1^2 G\right) \ ,$$

$$P_2 = M^{1/2} x_0 \left[\frac{M_1}{x_2}(M_1^2 B^2 - AD) - \frac{AF}{x_1}\right] \ ,$$

$$P_3 = (M_1 M_2)^{3/2} \frac{x_0}{x_2} (AG - B^2) \ ,$$

$$P_4 = M^{1/2} x_0 \left[\frac{M_2}{x_1}(M_2^2 B^2 - AC) - \frac{AE}{x_2}\right] \ ,$$

$$P_5 = M^{1/2} \left[\left(\frac{x_1 E}{x_2} + M_2 C\right)\left(\frac{x_2 F}{x_1} + M_1 D\right) - (M_1 M_2)^3 G^2\right] \ ,$$

$$P_6 = - M^{1/2} \frac{x_0}{x_2} B\left[\frac{F x_2 M_2}{x_1} + M_1 M_2(D - M_1^2 G)\right] \ ,$$

$$P_7 = M^{1/2} \frac{x_0}{x_2} B\left[\frac{E x_1 M_1}{x_2} + M_1 M_2(C - M_2^2 G)\right] \ ,$$

$$A = \Omega_{12}^{(1,1)} \ , \qquad B = \frac{5A}{2} - \Omega_{12}^{(1,2)} \ ,$$

$$C = \frac{5}{4} A (6M_1^2 + 5M_2^2) - 5M_2^2 \Omega_{12}^{(1,2)} + M_2^2 \Omega_{12}^{(1,3)} + 2M_1 M_2 \Omega_{12}^{(2,2)} \ ,$$

$$D = \frac{5}{4} A (6M_2^2 + 5M_1^2) - 5M_1^2 \Omega_{12}^{(1,2)} + M_1^2 \Omega_{12}^{(1,3)} + 2M_1 M_2 \Omega_{12}^{(2,2)} \ ,$$

$$E = \frac{1}{2} \Omega_{11}^{(2,2)} \ , \qquad F = \frac{1}{2} \Omega_{22}^{(2,2)} \ ,$$

$$G = \frac{55}{4} A - 5\Omega_{12}^{(1,2)} + \Omega_{12}^{(1,3)} - 2 \Omega_{12}^{(2,2)} \ ,$$

$$x_0 = x_1 M_1 + x_2 M_2 \ ,$$

and M_i, $i = 1,2$, is defined in Eq.(2.3.13). The Ω-integrals are defined in Appendix C, Eq.(C10), and are evaluated at the mixture temperature T. [In fact, they can be computed at any of the temperatures T_1, T_2 or T, since the difference in the hydrodynamic quantities would be $O(Kn_1 \sigma_i)$, and therefore negligible in a first order theory in both Kn_1 and σ_i.]

The above transport coefficients are valid for arbitrary interaction potentials with spherical symmetry. In the case of Maxwell molecules (molecules repelling each other with a fifth-power potential law), these transport coefficients coincide with those calculated by Goldman and Sirovich (1967) (notice that for such molecular model, $k_{T1} = k_{T2} = 0$). Tabulated values of the Ω-integrals for different molecular models can be found in the references cited in Appendix C.

In the limits M<<1 ($M_1 \rightarrow M$, $M_2 \rightarrow 1$) and $n_2/n_1 >> M$, the transport coefficients of the light gas and λ_b given above coincide with the values given in Appendix C at the first order of the Sonine polynomials expansion. The transport coefficients for the heavy gas coincide with those of a pure gas in that limit. On the other hand, $[\mu_{11}]_1 + [\mu_{22}]_1 + 2[\mu_{12}]_1$, $[\lambda_{11}]_1 + [\lambda_{22}]_1 + [\lambda_{12}]_1$, $[k_{T1}]_1 + [k_{T2}]_1$, $\dfrac{m_1 n}{kT}[\lambda_b]_1$ and $\dfrac{n(m_1+m_2)}{3k^2 T x_1 x_2}[\sigma_t]_1$, are equal to $[\mu]_1$, $[\lambda]_1$, $[k_T]_1$, $[D_{12}]_1$, and $[D_{12}]_1$ of Ref.I, Ch.9, respectively.