HARMONIC MODES IN BINARY MONATOMIC

GAS MIXTURES

A Thesis submitted to the Faculty of Mathematical
and Physical Sciences of the University of Surrey
for the Degree of Doctor of Philosophy

by

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SUMMARY

The dispersion and absorption coefficient of sound is calculated using the linearized thirteen-moment equations for binary monatomic gas mixtures. By extending the formal results of Huck and Johnson [Phys. Rev. Letts. 44 (3) 142 (1980)] to include general interatomic force laws it is confirmed that the dispersion law for acoustic modes is influenced by the presence of other harmonic modes in the gas.

Specific predictions are made for He-Xe since interference between modes occurs at lower frequencies in disparate mass mixtures. It is shown that either the diffusion mode or the thermal mode has a major influence on the behaviour of the acoustic mode, depending on the interatomic force law. The interference is strongest in a critical region where the mole fraction of helium is roughly 0.45 and the effective frequency is approximately 75 MHz Atm\(^{-1}\).

We have reformulated the application of perturbation theory for the calculation of harmonic solutions of the coupled Boltzmann equations for a mixture at low frequencies. For higher frequencies, including the critical region, a different perturbation expansion is shown to be necessary for disparate mass mixtures. Such an expansion is given and formal results are obtained which validate the thirteen moment theory for the critical region and define the accuracy of its predictions.

Experimental apparatus has been designed and built to measure sound absorption and dispersion in He-Xe mixtures. Data were obtained for effective frequencies of up to 100 MHz Atm\(^{-1}\). The results corroborate the thirteen moment theory and suggest that the acoustic mode and at least one other mode were excited.
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CHAPTER 1. THE CALCULATION OF SOUND PROPAGATION CHARACTERISTICS IN MONATOMIC GAS MIXTURES.

1.1. Introduction

Using the equations of hydrodynamics, sound propagation at low frequencies can be described as a disturbance travelling through a fluid continuum. The empirical laws most commonly used to define the material properties of the fluid assume linear relationships between non-equilibrium fluxes and first order gradients of hydrodynamic state variables. Predictions of acoustic absorption coefficients based on these laws are known to agree with experiment in the low frequency limit for both liquids and gases\(^1\). The frequency dependence of the phase speed can also be calculated from first order hydrodynamic equations but the results do not agree with experiment\(^2\). In fact even predictions of the initial low frequency dispersion are wrong\(^3,4\). What this implies is that first order constitutive relationships are not adequate for the determination of velocity dispersion.

For disturbances whose frequency approaches the mean particle collision rate the phenomenological theories of continuum mechanics are of limited value. It is more profitable in this regime, to determine the bulk properties of the gas using kinetic theory. The correct hydrodynamic results should then be recovered at low frequencies. It is usually assumed that the distribution of particle velocities at low pressure is governed by the Boltzmann equation. Because of the complexity of this equation only approximate solutions have been obtained for the case of harmonic disturbances but these represent a considerable advance over the hydrodynamic results. In particular, initial dispersion has been calculated for pure monatomic gases\(^3\), as well as for binary monatomic gas mixtures\(^5\) and the results are confirmed by experiment\(^3,6\).

In general it is difficult to go beyond the calculation of initial...
dispersion and obtain accurate predictions from the Boltzmann equation at higher frequencies. It is especially complicated in mixtures since the usual procedures can generate a large number of terms. Even when more terms are included there is no guarantee that the predictions are improved. However in binary disparate mass mixtures where the particle mass of one species is much less than that of the other species, the particle mass ratio may be defined as a small parameter and exploited to simplify the calculations.

In order to calculate the acoustic properties of a gas mixture it is usual to consider disturbances that have the space-time dependence of a harmonic wave, but it is well known that not all longitudinal harmonic disturbances in a fluid are necessarily sound waves. For example, modes whose dominant physical processes are diffusion or heat conduction emerge as harmonic solutions of the linearized hydrodynamic equations. In Chapter 1 all the hydrodynamic modes for binary monatomic gas mixtures are discussed in order to relate the results of first order hydrodynamics to those derived from the Boltzmann equation. Also in Chapter 1 the low frequency sound absorption coefficient is derived for binary mixtures of gases which are not necessarily monatomic. This derivation is based on the relationship between acoustic absorption and the rate at which entropy is generated.

In Chapter 2 the sound propagation characteristics of binary monatomic gas mixtures are calculated using the thirteen moment approximation of the particle velocity distribution function for each species. Formal results are obtained for general interatomic force laws and numerical predictions are given for He-Xe mixtures. Although these may be regarded as disparate mass mixtures, disparate mass approximations are not applied at this stage. Some striking predictions are obtained which show that the acoustic properties of the gas mixture are substantially influenced by the non-acoustic modes.

In Chapter 3 we make use of perturbation techniques both to assess
the validity of the thirteen-moment predictions and to determine harmonic solutions of the linearized Boltzmann equations for mixtures in the form of power series expansions. A suitable expansion parameter, κ, is defined which represents the wavenumber of the disturbance in dimensionless form. Its magnitude is of the order of the particle mean free path divided by the wavelength of the disturbance. The first few terms in the wavenumber expansion for the acoustic modes in binary monatomic gases are derived following a modification of the procedure due to Foch, Uhlenbeck and Losa. Expressions for the first order transport coefficients of the mixture are deduced as a by-product of the method. The series is successful in predicting initial deviations from the correct hydrodynamic results but its validity is limited to low frequencies.

For disparate mass mixtures two small parameters may be defined; the dimensionless wavenumber and the square root of the particle mass ratio. An alternative series expansion is given which is applicable when the two small parameters are of the same order of magnitude. From the formal results obtained with the second series the accuracy of the thirteen moment predictions for disparate mass mixtures is inferred.

Experimental apparatus designed to test the thirteen moment theory is described in Chapter 4. In Chapter 5 experimental values of absorption coefficient and phase velocity in He-Xe are given and compared with the theoretical predictions.
1.2. Sound absorption and dispersion

Suppose that a plane harmonic wave in a fluid causes a local hydrodynamic variable such as pressure, temperature or stream velocity to deviate from its equilibrium value by an amount $\Delta A$. If departures from equilibrium are sufficiently small, non-linear effects can be neglected and the harmonic disturbance will propagate independently of other harmonic components. In a homogeneous medium $\Delta A$ varies in space and time as

$$\Delta A = \hat{A} \exp i (kz-\Omega t) \quad (1.1)$$

where the $z$ axis is perpendicular to the plane of the disturbance and $\hat{A}$ is a constant. When a perturbation has the form (1.1) it is usual to specify that either $k$ is real or $\Omega$ is real. The former stipulation applies to initial value problems in which the disturbance varies sinusoidally in space. In these circumstances $\Omega$ is complex and the rate at which the fluid relaxes towards equilibrium is determined by the imaginary part of $\Omega$. However we shall suppose that the disturbance is generated by the steady vibrations of a boundary and that $\Omega$ is some specified real angular frequency. $k$ is then, in general, complex.

With $\Omega$ real, the sound absorption coefficient may be defined in terms of the complex wave number $k$ as

$$\alpha(\Omega) = \frac{\text{Im} k(\Omega)}{k_0} \quad (1.2)$$

where $k_0 = \Omega/U_0$ and $U_0$ is the speed of sound in the low frequency limit, sometimes called the Laplacian speed. For an ideal gas

$$U_0 = \sqrt{\gamma \frac{p_0}{\rho_0}} \quad (1.5)$$
where $\gamma$ is the ratio of principal specific heats, $p_o$ is the equilibrium pressure and $\rho_o$ the equilibrium density. If $U(\Omega)$ is the phase speed at angular frequency $\Omega$ then $U_0/U(\Omega)$ is a measure of the dispersion and is given by

$$\frac{U_0}{U(\Omega)} = \frac{\text{Re} k(\Omega)}{k_0}$$

(1.4)

The real part of the complex wavenumber may be expressed as

$$\text{Re}(k) = \frac{2\pi}{\lambda}$$

(1.5)

where $\lambda$ is the (real) wavelength, then with the imaginary part of $k$ given by (1.2), (1.1) becomes

$$\Delta A = \lambda \exp(-ak_0z) \exp i(2\pi z/\lambda - \Omega t)$$

(1.6)

(1.6) shows that the amplitude of the wave decays as $\exp(-ak_0z)$.

The acoustic absorption coefficient is often defined, not as is done here by equation (1.2), but in terms of the decrease in intensity of the sound wave with distance. To correlate the two definitions suppose that $J(z)$ is a time average of the energy flux density due to a sound wave travelling in the $z$ direction. The energy flux is proportional to the square of a local hydrodynamic variable such as pressure and therefore decays as $\exp(-2ak_0z)$ hence

$$J(z) = J(0) \exp(-2ak_0z)$$

(1.7)

where $J(0)$ is the energy flux density at $z=0$. As $J(z)$ is a time average
quantity it does not contain a phase factor. From (1.7)

$$\alpha = \frac{1}{2k_o^2} \ln \left[ \frac{J(0)}{J(z)} \right]$$

(1.8)

(1.8) or an equation like it, often serves as a definition of the acoustic absorption coefficient.

1.3. Dispersion relationships

A key objective in the theory of sound propagation is the prediction of complex dispersion relationships linking \( \Omega \) and \( k \). Except in extreme physical conditions the relationship for a gas may be written as a function of \( \Omega/p_o \). Frequently the acoustic dispersion law arises from a secular equation of the form

$$F(\Omega/p_o, k^2) = 0$$

(1.9)

which is a polynomial in both \( \Omega/p_o \) and \( k^2 \). In general there will be a number of roots and with \( \Omega \) as the independent variable, two of these represent sound propagation.

It is often more convenient to express the dispersion relationship as a power series in \( (i\Omega/p_o) \),

$$\frac{k}{k_o} = 1 + d_1(x_1, T_0)(i\Omega/p_o) + d_2(x_1, T_0)(i\Omega/p_o)^2 + d_3(x_1, T_0)(i\Omega/p_o)^2 + \ldots$$

(1.10)

where \( T_0 \) is the equilibrium temperature and the coefficients \( d_1, d_2, d_3 \ldots \) etc. are real. (1.10) refers to a binary gas mixture. \( x_1 \) and \( x_2 \) are the mole fractions of the components of the mixture but only one of these is independent since \( x_1 + x_2 = 1 \). The composition dependence of the coefficients is expressed in terms of \( x_1 \). Using (1.4) the real part of this series is related to the phase speed,
and, using (1.2), the imaginary part is related to the acoustic absorption coefficient,
\[ \alpha = d_1(x_1,T)(\alpha/p_0) - d_3(x_1,T)(\alpha/p_0)^3 + ... \]  (1.12)

At low frequencies where terms of higher order than the first can be neglected we have
\[ \alpha = \alpha_K = d_1(x_1,T)(\alpha/p_0) \]  (1.13)

\( \alpha_K \) is a first approximation and is sometimes known as the Kohler absorption coefficient\(^9,10\). It may be calculated by assuming harmonic forms for the hydrodynamic variables and substituting these into the linearized Navier-Stokes system of equations. This procedure leads to a set of linear homogeneous equations in which the unknowns are amplitudes of hydrodynamic state variables. The condition for finding non-trivial solutions gives a secular equation of the form (1.9) from which \( \alpha_K \) may be identified. This approach will be discussed further in Section 1.5.

The first order acoustic absorption coefficient has also been derived for pure species gases by an alternative method which makes explicit the relationship between sound absorption and the rate of entropy production.\(^11\) In the following section this procedure is generalised to include binary gases whose components have different specific heats. As a preliminary to finding \( \alpha_K \) we shall derive the harmonic solutions of the Euler equations.
1.4. Hydrodynamic theory of acoustic absorption coefficient

1.4.1. Zero order predictions

The Euler equations are the ordinary conservation laws for a fluid written in differential form. Terms representing dissipation effects, energy transfer by velocity dependent forces and heat fluxes, are neglected. For this reason the equations occupy the most elementary level in a hierarchy of hydrodynamic descriptions. At the next level in the hierarchy, the Navier-Stokes level, irreversible processes are governed by first order constitutive relationships. For example viscous stresses are assumed to be proportional to first order velocity gradients and heat fluxes are assumed to be proportional to first order temperature gradients. The acoustic absorption coefficient depends on irreversible processes but initially it will be supposed that these are negligible.

As the long wavelength limit is approached the fluid flow may be regarded as isentropic and governed by the Euler equations. For the case of a binary gas mixture these relationships may be written as follows:

Species mass conservation,

\[ \frac{\partial p_i}{\partial t} + \rho_i \nabla \cdot \mathbf{u} = 0 \quad i = 1,2 \quad (1.14) \]

Momentum conservation,

\[ \rho_i \frac{\partial \mathbf{u}}{\partial t} + \nabla p = 0 \quad (1.15) \]

Energy conservation,

\[ n_i c_v \frac{\partial T}{\partial t} + p \nabla \cdot \mathbf{u} = 0 \quad (1.16) \]

\[ \frac{d}{dt} \] is the substantive derivative given by

\[ \frac{d}{dt} = \frac{\partial}{\partial t} + \mathbf{u} \cdot \nabla \quad (1.17) \]

\( \mathbf{u} \) is the stream velocity of the fluid, \( T \) its local temperature and \( p \) its pressure. \( \rho \) is the total mass density and \( n \) the total number density. The suffix \( i = 1,2 \) refers to individual species. Thus

\[ \rho = \rho_1 + \rho_2 \quad \text{and} \quad n = n_1 + n_2 \quad (1.18) \]
where $\rho_i$ is the mass density of species $i$ and $n_i$ its number density. If $m_i$ is the particle mass of species $i$,

$$\rho_i = m_i n_i \quad (1.19)$$

The specific heat per molecule for the mixture at constant volume, $c_v$, is related to the species specific heats, $c_{v1}$ and $c_{v2}$, by

$$c_v = x_1 c_{v1} + x_2 c_{v2} \quad (1.20)$$

Suppose that the hydrodynamic state variables in (1.14)-(1.16) have a space-time dependence appropriate to a plane harmonic wave travelling in the $z$-direction. Then we may write

$$\begin{align*}
n_i &= n_0 x_i (1 + \tilde{n}_i e^{i\theta}) \\
u &= \tilde{u} U_0 e^{i\theta} \\
T &= T_0 e^{i\theta}
\end{align*} \quad (1.21)$$

with

$$\theta = kz - \Omega t \quad (1.22)$$

where $n_0$ is the total number density at equilibrium. (1.21) defines the dimensionless amplitudes $\tilde{n}_i, \tilde{u}, \tilde{T}$. If departures from equilibrium are small, non-linearities in (1.14)-(1.16) can be neglected. In the case of a harmonic disturbance this implies that products of dimensionless amplitudes can be ignored. Putting the harmonic forms (1.21) into the Euler equations and neglecting non-linear terms gives, in matrix form,
\[
\begin{bmatrix}
-i\Omega & ik & . \\
. & -i\Omega & ik \\
-ikp_0x_1 & ikp_0x_2 & -i\Omega p_0 & ikp_0 \\
. & . & ikp_0 & -i\Omega c_v n_o T_o
\end{bmatrix}
\begin{bmatrix}
\hat{n}_1 \\
\hat{n}_2 \\
\hat{\xi} \\
\hat{\eta}
\end{bmatrix}
= 0
\] (1.23)

where we have used (1.18)(1.19) and the ideal gas equation of state.

For non-trivial solutions the determinant of the matrix of coefficients is zero, a condition which gives

\[
\Omega^2 [c_v p_0 \Omega^2 - k^2 p_0 (c_v + k_B)] = 0
\] (1.24)

where \(k_B\) is Boltzmann's constant. Applying the relationships between principal specific heats,

\[
c_p - c_v = k_B \quad \text{and} \quad \gamma = \frac{c_p}{c_v},
\] (1.25)

(1.24) becomes

\[
\Omega^2 (\Omega^2 - k^2 \frac{\gamma p_0}{p_0}) = 0
\] (1.26)

For two of the roots of this equation \(\Omega=0\). The other two evidently represent sound propagation in the positive and negative \(z\) directions at the Laplacian speed,

\[
\Omega/k = \pm \sqrt{\frac{\gamma p_0}{p_0}}
\] (1.27)

Substituting for \(\Omega\) in (1.23) from (1.27) and solving gives \(\hat{n}_1, \hat{n}_2, \hat{\xi} \& \hat{\eta}\) for the case of a sound wave. Absolute values of the amplitudes are often determined from boundary conditions but in the present calculation
they will be expressed in terms of a parameter $\tilde{\alpha}$. If we arbitrarily put $\tilde{n}_1 = \tilde{\alpha}$ and work through to the solution for which the positive sign in (1.27) holds then we find

$$\tilde{n}_1 = \tilde{n}_2 = \tilde{n} = \tilde{\alpha} \quad \text{and} \quad \tilde{\beta} = (\gamma-1) \tilde{\alpha} \quad (1.28)$$

Dimensionless pressure amplitudes $\tilde{p}$ and $\tilde{p}_i$ are defined by

$$p = p_0 (1 + \tilde{p} e^{i\tilde{\theta}}) \quad \text{and} \quad p_i = p_0 x (1 + \tilde{p}_i e^{i\tilde{\theta}}) \quad (1.29)$$

where $\tilde{\theta}$ is given by (1.22). For an ideal gas mixture,

$$p_i = n_i k_B T \quad \text{and} \quad p = p_1 + p_2 \quad (1.30)$$

Hence with $n_i$ and $T$ given by (1.21) we get

$$\tilde{p}_i = \tilde{n}_i + \tilde{T} \quad \text{and} \quad \tilde{p} = x_1 \tilde{n}_1 + x_2 \tilde{n}_2 + \tilde{T} \quad (1.31)$$

where the product $\tilde{n}_i \tilde{T}$ has been neglected. From (1.31) we find that if (1.28) holds,

$$\tilde{p} = \tilde{p}_i = \gamma \tilde{\alpha} \quad (1.32)$$

Thus the Euler equations lead to dimensionless amplitudes, given by (1.28) and (1.32), that are independent of frequency and in phase with one another.

It is worth recording the results that are found when (1.26) is satisfied with $\Omega = 0$. As there are two solutions associated with this,
condition the individual amplitudes cannot be determined in full from (1.23). It is found that

\[ \hat{u} = 0 \quad \text{and} \quad \hat{p} = x_1 \hat{n}_1 + x_2 \hat{n}_2 + \hat{r} = 0 \]  
(1.33)

A disturbance for which (1.33) holds has zero stream velocity and constant pressure but the relative values of \( \hat{n}_1 \) and \( \hat{n}_2 \) are not resolved at this level. The physical significance of these results is discussed further in Section 1.5.

For an acoustic disturbance the Euler equations yield what is in effect the zero order term in the expansion (1.10), the Laplacian speed. Similarly if the pressure amplitude, for example, were expanded as a power series in frequency, (1.32) gives the first term in the series. The zero order amplitudes, (1.28) and (1.32), will be used in calculating the various contributions to the entropy generated by a sound wave.

1.4.2. Sound absorption and entropy production

When acoustic energy is dissipated in a fluid, entropy is generated. In general the entropy gained by an element of fluid is related to the amount of heat which flows into it and the irreversible work done on it. The relationship referred to unit volume is written

\[ TdS = dQ + dW_{\text{irr}} \]  
(1.34)

The symbol \( d \) denotes that the heat \( dQ \), and the irreversible work \( dW_{\text{irr}} \), are not perfect differentials. \( dS \) is the entropy change.

If \( dS \) is due to sound absorption then the right hand side of (1.34) is dominated by the irreversible work term. We shall suppose that the change takes place in a time \( dt \) which is long compared with a period of
oscillation. Then $S$ may be regarded as an average over the time period for one cycle. If $J_\text{p}$ is the mean acoustic energy flux, then the energy dissipated per unit volume in a time $dt$ is given by

$$dW_{\text{irr}} = T_0 dS = - \nabla \cdot J \ dt \quad (1.35)$$

where $T_0$ is the mean temperature.

If $\rho$ is the density of the fluid then putting

$$S = \rho s \quad (1.36)$$

gives

$$T_0 \frac{\partial \rho s}{\partial t} = - \nabla \cdot J \quad (1.37)$$

where $s$ is the entropy specific to unit mass. The superposed bar is used throughout to denote a time cycle average.

In general the balance equation for entropy may be written

$$\frac{\partial \rho s}{\partial t} + \nabla \cdot J = \sigma \quad (1.38)$$

where $J$ is the instantaneous entropy flux and $\sigma$ is the entropy source strength. In the present case $J_s$ is an alternating flux whose time cycle average is zero. Therefore taking the average of (1.38) gives

$$\frac{\partial \rho s}{\partial t} = \sigma \quad (1.39)$$

Comparing (1.37) with (1.39) we find

$$T_0 \sigma = - \nabla \cdot J \quad (1.40)$$

Thus in a region where there are no sources of sound the negative divergence of the wave energy flux is proportional to the rate of entropy production.
Expressions for the entropy source strength in a binary fluid are found from the theory of non-equilibrium thermodynamics. We shall express $\bar{\sigma}$ as a sum of terms, each term being second order in wave amplitude and proportional to a transport coefficient. The divergence of the energy flux is proportional to the acoustic absorption coefficient. Thus (1.40) is used to express the acoustic absorption coefficient in terms of transport coefficients of the mixture.

1.4.3. The Kohler absorption coefficient

Terms may be regarded as ordered with respect to frequency as is implied by the series expansion (1.10)*. In deriving the Kohler absorption coefficient, which is first order in frequency, all higher order contributions will be neglected. This means, for instance, that the energy transferred by viscous forces and heat flux may be neglected in writing the divergence of the acoustic intensity as

$$\nabla \cdot \bar{J} = \nabla \cdot \bar{p}u$$  \hspace{1cm} (1.41)

For a plane harmonic disturbance of (real) frequency $\Omega$ travelling in the z direction $p$ and $u$ have the forms given by (1.29) and (1.21) respectively. In taking a cycle average of $p u$ it is noted that the imaginary part of k can be found from (1.2) and that the phase factor vanishes. We find

$$\bar{p}u = \frac{1}{2} \bar{p}u_p U_0 \exp (-2\alpha k_0 z)$$  \hspace{1cm} (1.42)

*(1.10) is equivalent to a power series expansion in terms of a small dimensionless parameter $\omega$ which is of the order of $\Omega$/particle collision frequency, see Section 3.8.
Thus (1.41) becomes, at \( z = 0 \),

\[-[\nabla J(z)]_{z=0} = \alpha k_o \beta \hat{p} \rho_o \rho_o \tag{1.43}\]

There is no loss of generality in considering the point \( z = 0 \) since the origin of the coordinate system is arbitrary. It simply means that we do not have to carry forward the decay factor \( \exp(-2\alpha k_o z) \).

Let us now consider the left hand side of (1.40). The entropy source strength for a binary fluid in bilinear form is given by

\[ S_o = -\pi \cdot \nabla u - q \cdot \nabla T - \frac{T}{2} \sum_i J_i \cdot \frac{g_i}{\rho_i} \tag{1.44} \]

where \( \pi \) is the viscous stress tensor, \( q \) is the heat flux and \( g_i \) the partial specific Gibbs free energy of species \( i \). \( J_i \) is the mass diffusion flux of species \( i \) relative to the centre of mass motion,

\[ J_i = \rho_i (u_i - u) \quad i = 1,2 \tag{1.45} \]

where \( u_i \) is the stream velocity of species \( i \) in the lab frame and \( \rho_i \) is its density. The velocity of the centre of mass flow is given by

\[ \rho u = \rho_1 u_1 + \rho_2 u_2 \tag{1.46} \]

where \( \rho = \rho_1 + \rho_2 \)

It is useful to express the mass fluxes in terms of the diffusion velocity \( w \), given by:

\[ w = u_1 - u_2 \tag{1.47} \]

Using this definition together with (1.45) and (1.46) gives

\[ J_1 = \frac{\rho_1 \rho_2}{\rho} \quad w = - J_2 \tag{1.48} \]

In an ideal gas mixture \( g_i \) may be considered to be a function of \( p_i \) and \( T \) only. In other words \( g_i \) is assumed to be independent of the state
of species $j$ ($i\neq j$). Then

$$
\frac{\partial g_i}{\partial T} = \frac{\partial (g_i/T)}{\partial p_i} T \frac{\partial p_i}{\partial T} + \frac{\partial (g_i/T)}{\partial T} \frac{\partial T}{p_i} \tag{1.49}
$$

Using the ideal gas expressions for $g_i^{13}$ it can be shown that

$$
\frac{\partial (g_i/T)}{\partial p_i} T = \frac{1}{\rho_i T} \tag{1.50}
$$

and

$$
\frac{\partial (g_i/T)}{\partial T} \frac{\partial T}{p_i} = -\frac{h_i}{T^2} \tag{1.51}
$$

where $h_i$ is the partial specific enthalpy of species $i$. Substituting $\frac{g_i}{T}$ in the last term of (1.44) and using (1.48) - (1.51) gives

$$
T_0 = -\tau \cdot \nabla u - g \cdot \nabla T/T - p \frac{d_{12}}{p} \cdot \nabla + \Sigma h_i J_i \cdot \nabla T/T \tag{1.52}
$$

where $d_{12} = \frac{\rho_1 \rho_2}{p} \left( \frac{\nabla p_1}{\rho_1} - \frac{\nabla p_2}{\rho_2} \right)$ \tag{1.53}

The fluxes in (1.52) are eliminated using linear constitutive relationships. These may be inferred from the bilinear expression for the entropy source strength, the Onsager reciprocal relationships and spatial symmetry conditions. They may be written as follows\textsuperscript{12},

Diffusion,

$$
\Gamma = -\nabla \cdot \nabla u - g \cdot \nabla T/T - p \frac{d_{12}}{p} \cdot \nabla + \Sigma h_i J_i \cdot \nabla T/T \tag{1.54}
$$

Heat conduction,

$$
q = -\lambda \nabla T + p k_T \nabla + \Sigma h_i J_i \tag{1.55}
$$

Viscosity,

$$
\eta = -2\eta_0 \nabla u - \eta \nabla \cdot \left( \nabla u \right) \tag{1.56}
$$

$\nabla u$ is a traceless symmetrized tensor. In this notation

$$
\frac{\partial \Gamma}{\partial T} = \frac{1}{T} \left( \frac{\partial \Gamma}{\partial T} + \Gamma \frac{\partial T}{T} \right) - \frac{1}{3} \left( \frac{\partial \Gamma}{\partial T} \right) \nabla \tag{1.57}
$$
\[ A \] is a second rank unit tensor and \( A^\dagger \) is the transpose of \( A \). In (1.54) \( D_{12} \) is the binary diffusion coefficient and \( k_T \) the thermal diffusion ratio. In (1.55) \( \lambda \) is the thermal conductivity. In (1.56) \( \eta \) is the coefficient of shear viscosity and \( \eta_v \) the coefficient of volume or bulk viscosity.

Transforming (1.52) using (1.54) - (1.56) gives

\[
T_0 = 2\eta \nabla^2 u + \eta_v (V \cdot u)^2 + \lambda (V \cdot T)^2 / T + \frac{D_{12} \rho}{x_1 x_2} (d_{12} + k_T \nabla \eta T)^2
\]

Substituting the harmonic forms (1.21) and (1.29) into (1.58) and taking a cycle average gives, at \( z=0 \),

\[
T_0(0) = \frac{1}{4} k_o^2 \left[ \frac{4}{3} \eta \left( \frac{\rho_0}{m_1} \right)^2 + \eta_v \left( \frac{\rho_0}{m_2} \right)^2 + \lambda T_0 \right] + \frac{D_{12} \rho_0}{x_1 x_2} \left[ \frac{\rho_0}{m_1} - \frac{\rho_0}{m_2} \right] + k_T \eta T^2
\]

As terms of lowest order are the only ones to be kept, \( k_0 \) has replaced \( k \) in getting (1.59). \( \rho_{i0} \) is the equilibrium density of species \( i \).

By equating (1.43) and (1.59) in accordance with (1.40) the acoustic absorption coefficient is expressed in terms of linear transport coefficients. As the relationship is a first order approximation it involves the Kohler absorption \( a_K \),

\[
a_K = \frac{1}{2} \left( \frac{\rho_0}{m_1} \right)^2 \left( \frac{\rho_0}{m_2} \right)^2 \left[ \frac{\rho_0}{m_1} - \frac{\rho_0}{m_2} \right] + k_T \eta T^2
\]

With the dimensionless amplitudes given by (1.28) and (1.32) we get

\[
a_K = \frac{1}{2} \left( \frac{\rho_0}{m_1} \right)^2 \left( \frac{\rho_0}{m_2} \right)^2 \left[ \frac{\rho_0}{m_1} - \frac{\rho_0}{m_2} \right] + k_T \eta T^2
\]

For the case of binary monatomic gas mixtures \( \gamma = \frac{5}{3} \) and the volume
Viscosity is zero. (1.61) then becomes

\[ \alpha_K = \frac{2}{3} m_1 \frac{\lambda T}{\rho_0 U_o} \frac{2.5}{6} D_{12} \rho_0 x_1 x_2 \left( \frac{m_2}{m_1} \frac{x_1}{x_2} + \frac{m_1}{m_2} \frac{x_2}{x_1} \right) \left( \frac{k_T}{\rho_0 U_o} \right)^2 \]

(1.62)

in agreement with Kohler's result.\textsuperscript{9,10}

The acoustic absorption coefficient can be calculated from (1.62) using experimental values of the transport coefficients for the mixture, but as these are not always known it is usual to compute the viscosity and thermal conductivity from pure species transport coefficients. In order to carry out this calculation a suitable interatomic potential is chosen since the mixture formulae for \( \eta \) and \( \chi \) depend on the form of the potential. Experimental results for binary mixtures of helium with other rare gases have corroborated the Kohler absorption predictions.\textsuperscript{15,16} When it is assumed that the particles are Maxwell molecules, the mixture formulae and (1.62) yield results which overestimate the absorption coefficient at intermediate concentrations by a small amount, typically of the order of 10%.\textsuperscript{17} However Law, Koronaios and Lindsay\textsuperscript{16} have shown that very good agreement can be obtained in He-Ar and He-Kr if a Lennard-Jones interatomic potential is assumed.

1.5. Hydrodynamic modes in monatomic gas mixtures

The search for solutions of the linearized Euler equations for a harmonic disturbance reduces to solving a 4 x 4 matrix equation (1.23). This is in the form of an eigenvalue problem in which components of an eigenvector are the dimensionless amplitudes \( \tilde{n}_1, \tilde{n}_2, \tilde{u} \) and \( \tilde{\tau} \). The eigenvalues were found in the usual way from a secular equation, (1.24). This is a fourth order polynomial in \( \Omega \) in which two of the roots correspond to sound propagation and two roots vanish.
In this section a similar calculation is outlined in which our starting point is the hydrodynamic equations at the Navier-Stokes level. Again two roots corresponding to sound propagation are found plus two other roots associated with longitudinal motion of the fluid. As none of the eigenvalues vanish four longitudinal dynamical modes are predicted. A discussion of the hydrodynamic modes in binary fluids has been given by Cohen, Sutherland and Deutch.

When taking account of irreversible effects the conservation laws for a binary monatomic gas mixture may be written as follows:

Species mass conservation,
\[ \frac{d\rho_i}{dt} + \rho_i \nabla \cdot \mathbf{u} = 0 \] (1.63)

Momentum conservation,
\[ \rho \frac{d\mathbf{u}}{dt} + \nabla \cdot \mathbf{p} + \nabla \cdot \mathbf{u} = 0 \] (1.64)

Energy conservation,
\[ nc \frac{dT}{dt} + \nabla \cdot \mathbf{p} \mathbf{u} + \mathbf{u} \cdot \nabla \mathbf{p} + \mathbf{u} \cdot \nabla \mathbf{q} - \frac{3}{2} k_B T \sum_{i=1}^{2} \frac{\nabla \cdot \mathbf{J}_i}{m_i} = 0 \] (1.65)

where \( c_v = \frac{5}{2} k_B \). To obtain a closed system of equations we use (1.54) - (1.56) specialised to monatomic gases. In a mixture of monatomic ideal gases the volume viscosity is zero and the specific enthalpy of species \( i \) is given by
\[ h_i = \frac{5}{2} k_B T/m_i \] (1.66)

With these changes (1.54) - (1.56) become
\[ \omega = - \frac{D_{12}}{x_1 x_2} \frac{\rho_2}{\rho} \frac{\nabla p_1}{\rho_1} - \frac{\nabla p_2}{\rho_2} \] (1.67)
\[ \dot{q} = -\lambda \nabla T + \frac{5}{2} k_B T \sum_{i=1,2} \frac{J_i}{m_i} \]  

(1.68)

\[ \overline{u} = -2n \nabla u \]  

(1.69)

In (1.67) and (1.68) terms representing the thermal diffusion effect have been neglected. These have only a small influence on the behaviour of the gas mixture in this context and for the sake of simplicity have been omitted.

The solutions to be considered are assumed to involve small perturbations of the fluid so that non-linearities can be neglected. Linearized version of (1.63) - (1.69) may be transformed to give

\[ \frac{\partial n_1}{\partial t} + n_0 x_1 \nabla u + n_0 x_1 \xi_2 \nabla w = 0 \]  

(1.70)

\[ \frac{\partial n_2}{\partial t} + n_0 x_2 \nabla u - n_0 x_2 \xi_1 \nabla w = 0 \]  

(1.71)

\[ \rho_o \frac{\partial u}{\partial t} + \nabla p - 2n \nabla \cdot (\nabla^2 u) = 0 \]  

(1.72)

\[ n_o c \frac{\partial T}{\partial t} + p_o \nabla u - \lambda \nabla^2 T + p_o x_1 x_2 \left( \frac{m_2 - m_1}{m_1 x_1 + m_2 x_2} \right) \nabla w = 0 \]  

(1.73)

with

\[ \xi_i \text{ is the mass fraction of species } i \text{ given by,} \]

\[ \xi_i = \frac{\rho_i}{\rho_o} \quad i = 1, 2 \]  

(1.75)

\[ J_1 \] and \[ J_2 \] have been eliminated in favour of \( w \) using (1.48)

As with the Euler equations in the previous section we seek harmonic solutions for a plane disturbance travelling in the z direction. u, T, n_1 and n_2 are assumed to have the harmonic forms given by (1.21). The z component of diffusion velocity is assumed to vary in the same way.
The suffix \( z \) refers to the longitudinal direction and we shall temporarily attach the same suffix to the dimensionless stream velocity amplitude associated with longitudinal modes. This distinction is made since transverse modes will also be discussed. With the above harmonic forms (1.70) - (1.74) become

\[
\begin{align*}
- \imath \omega n_1 + \imath k U_0 \tilde{v}_z + \imath k \zeta_2 U_0 \tilde{w}_z &= 0 \\
- \imath \omega n_2 + \imath k U_0 \tilde{v}_z - \imath k \zeta_1 U_0 \tilde{w}_z &= 0 \\
- \imath \omega p_0 \tilde{v}_z + \imath p_0 p/U_0 + \frac{4}{3} \eta k^2 \tilde{w}_z &= 0 \\
- \imath \omega \frac{c_T}{D_{12}} + \imath p_0 U_0 \tilde{v}_z + \lambda k^2 T_0 \tilde{w}_z + \imath k x_1 x_2 p_0 U_0 \left( \frac{m_2 - m_1}{m_1 x_1 + m_2 x_2} \right) \tilde{w}_z &= 0
\end{align*}
\]  

(1.77) - (1.80)

with

\[
U_0 \tilde{w}_z = -\imath k \frac{D_{12}}{x_1 x_2} \frac{\rho_0 \rho_0}{\rho_0 \rho_0} \left( \frac{\tilde{v}_1}{m_1} - \frac{\tilde{v}_2}{m_2} \right)
\]  

(1.81)

By substituting for \( \tilde{w}_z \) in (1.77) - (1.80) using (1.81), and eliminating pressure amplitudes with (1.31), the number of unknown dimensionless amplitudes is reduced to four. In this way (1.77) - (1.81) may be transformed into a 4 x 4 homogeneous matrix equation. This again is in the form of an eigenvalue problem for \( \Omega \). By equating the determinant of the matrix of coefficients to zero we get a fourth order polynomial equation in \( \Omega \) from which four non-vanishing roots are found. The results obtained in this way are based on first order constitutive relationships which means that they are only accurate to order \( k^2 \). Neglecting terms of order \( k^3 \) and above leads to the following eigenvalues:

\[ \omega \]
\[ \Omega_T = \pm kU_0 - ik^2 \Gamma \]  
(1.82)

\[ \Omega_D = - ik^2 D_{12} \]  
(1.84)

where

\[ \Gamma = \frac{1}{2\rho_0} \left[ \frac{4\nu T_0}{U_0^2} + \frac{5}{3} D_{12} \rho_0 x_1 x_2 \left( \frac{m_2 - m_1}{m_1 x_1 + m_2 x_2} \right)^2 \right] \]  
(1.85)

\( \Gamma \) is related to the Kohler absorption coefficient, (1.62), by

\[ \alpha_K = \frac{\Omega}{U_0^2} \Gamma \]  
(1.86)

(1.82) is the complex dispersion relationship for sound waves travelling in the positive and negative \( z \) directions. Apart from two sound modes there are two highly damped longitudinal modes. By substituting each eigenvalue back into the original linear equations the amplitudes associated with each of these can be found. It can be shown that (1.83) is a complex dispersion relationship for the relaxation of harmonic perturbations of the temperature and (1.84) governs the relaxation of a harmonic perturbation of the species concentrations. These are referred to as the thermal mode and the diffusion mode respectively. We shall see in Chapter 2 that in the low frequency limit perturbations in the species number densities are in antiphase for the diffusion mode, whilst the total pressure and temperature are uniform and constant. If initial conditions were to be specified such that \( k \) were real, then according to (1.84) \( \Omega_D \) would be imaginary. The dispersion relationship then refers to a disturbance in which the concentrations vary sinusoidally in space, are in antiphase and decay exponentially towards their equilibrium values with a time constant \( (i/\Omega_D) \). When thermal diffusion is present thermal conduction and diffusion effects...
do not decouple at the low frequency limit. This more complicated situation is discussed by Boon and Yip\(^1\).

Let us return to the linearized hydrodynamic equations, (1.70) - (1.74), and consider transverse components of stream velocity, \(u_x\) and \(u_y\). For a plane perturbation giving rise to gradients in the \(z\) direction the \(x\) and \(y\) components of (1.72) decouple from the rest of the equations to give

\[
\begin{align*}
\rho_o \frac{\partial u_x}{\partial t} - \eta \frac{\partial^2 u_x}{\partial z^2} &= 0 \\
\rho_o \frac{\partial u_y}{\partial t} - \eta \frac{\partial^2 u_y}{\partial z^2} &= 0
\end{align*}
\]

(1.87)

Harmonic solutions of these equations have the forms

\[
\begin{align*}
u_x &= \hat{u}_x u^* \exp i (kz - \Omega t), \\
u_y &= \hat{u}_y u^* \exp i (kz - \Omega t)
\end{align*}
\]

(1.88)

where \(\hat{u}_x\) and \(\hat{u}_y\) are dimensionless amplitudes. From (1.87) the complex dispersion relationships associated with transverse oscillations are given by

\[
\Omega_x = -i k^2 \frac{\eta}{\rho_o}, \quad \Omega_y = -i k^2 \frac{\eta}{\rho_o}
\]

(1.89)

The heavy damping represented by (1.89) corresponds to the fact that shear waves are not propagated in fluids.

A simple illustration of the characteristics of the dispersion laws for hydrodynamic modes is given in Figure 1.1. The locus of \(k\) is plotted on an Argand diagram as the (real) frequency increases from zero. For non-propagating modes the real and imaginary parts of \(k\) are equal at low frequencies, hence the locus of \(k\) bisects the real and imaginary axes. In contrast the complex wavenumber for an acoustic mode is largely
real. Although complex dispersion relationships can be followed to higher frequencies using the Navier-Stokes system of equations, predictions beyond second order in $k$ are inaccurate\textsuperscript{20}. In Chapter 2 we develop equations to investigate high frequency behaviour in disparate mass gases. First some of the work that has been done on this topic is reviewed.

1.6. Sound propagation in disparate mass mixtures

In disparate mass binary gas mixtures ($m_1 << m_2$) the rate at which energy is exchanged between species is much slower than in mixtures where the particle masses are of the same order. For small perturbations from equilibrium the rate of relaxation of the mean kinetic energy difference is characterised by an inverse relaxation time, $\nu_\Delta$ say.
It is usual to define a kinetic temperature, $T_i$, of species $i$, as proportional to its mean translational kinetic energy. Therefore $\nu_\Delta$ can also be regarded as the inverse relaxation time for the temperature difference, $\Delta = T_1 - T_2$. If we compare $\nu_\Delta$ with the self collision frequency, $\nu_i$, for species $i$, then $^{21} \nu_\Delta \sim \delta \nu_2 \sim \delta^2 \nu_1$ where $\delta = (m_1/m_2)^{\frac{1}{2}}$ and $\delta \ll 1$.

Clearly if the state of a disparate mass gas mixture changes rapidly it may be necessary to allow for the fact that the components have different local temperatures. A number of authors$^{22-24}$ have developed generalised hydrodynamic equations to account for two temperature effects taking as their starting point the coupled Boltzmann equations of gas kinetics. An important motivation for this work is the need to overcome the limitations of the Chapman-Enskog theory as exemplified by its application to initial value problems. If the state of the gas is specified at $t=0$, the theory is only applicable, in general, after a time much greater than the longest characteristic relaxation time of the medium. In a disparate mass mixture this implies that it is generally valid for $t \gg \frac{1}{\nu_\Delta}$. A correct two-temperature hydrodynamic theory on the other hand is valid for $t \gtrsim \frac{1}{\nu_\Delta}$. Once the two-temperature hydrodynamic equations have been derived it is a straightforward matter to determine harmonic solutions in the linear approximation.

Predictions of sound propagation characteristics in disparate mass binary gas mixtures have been made by Tsendin. He considers component gases which are not necessarily monatomic and derives hydrodynamic equations from model Boltzmann equations for the mixture with individual species temperatures. An analytical expression for the first coefficient in the series $(1.12)$ is obtained which agrees with the Kohler absorption except for a term containing a cross-collision frequency
and a factor $(\gamma_1 - \gamma_2)^2$, $\gamma_1$ being the specific heat ratio for species $i$. However in the derivation of the Kohler absorption coefficient, given in Section 1.4, a general binary mixture was considered in which the specific heat ratios of the components were not necessarily equal and yet no similar term was found. It may be that the extra contribution to the absorption coefficient in Tsendin's expression (Equation 8b of reference 26) is an artifact of the kinetic model he has used.

Absorption and dispersion of ultrasonic waves in binary disparate mass mixtures has also been discussed by Goldman based on a two fluid generalised hydrodynamics developed in collaboration with Sirovich. The theory is applicable to monatomic mixtures and is consistent with the Kohler absorption at low frequencies. Goldman's predictions of absorption coefficient in He-Ar have been compared with the results of experiment by Prangsma, Jonkman and Beenakker. Outside the frequency range where the Kohler absorption is accurate, agreement is satisfactory at some but not all concentrations.

More recently Huck and Johnson have calculated the absorption and dispersion characteristics of He-Xe gas mixtures from linearized thirteen-moment equations. The calculation takes account of the temperature difference between species, assumes the particles interact as Maxwell molecules, and makes use of disparate mass approximations. As this work is particularly relevant to the present study the results will be summarised in detail.

We saw in Section 1.5 that in seeking harmonic solutions of linearized hydrodynamic equations in one dimension a number of complex dispersion relationships are found, two of which are characteristic of sound propagation. Similarly, in using generalised hydrodynamic equations the condition that non-trivial harmonic solutions may be found leads to
an implicit polynomial relationship, \( F(\frac{\Omega}{P_0}, k^2) = 0 \), which has a number of roots. Suppose that \( \Omega \) is known and that the \( n \) roots of this expression can be written as

\[
k_j = k_j \left( \frac{\Omega}{P_0}, x_1 \right) \quad j = 1, 2, \ldots, n \quad (1.90)
\]

that is, as functions of the frequency-pressure ratio and concentration. Huck and Johnson\(^{29}\) have reported that at a finite frequency, \( \Omega_c \), called the critical frequency, and at a critical concentration, \( x_c \), two of the roots coincide. If \( k_s \) and \( k_D \) are the two complex roots involved then this means that

\[
k_s \left( \frac{\Omega}{P_0}, x_c \right) = k_D \left( \frac{\Omega}{P_0}, x_c \right) \quad (1.91)
\]

The critical frequency is of the same order of magnitude as the inverse relaxation time \( \nu_\Lambda \) but the coincidence of roots does not depend on the relaxation of the temperature difference \( \Delta \). When the calculations are repeated using a single fluid temperature the critical quantities, though changed, are of the same order of magnitude.

From its low frequency behaviour, one of the roots in (1.91), \( k_s \) say, evidently represents ordinary sound propagation. It is significant that at low frequencies the number-density amplitudes corresponding to the other root, \( k_D \), are in antiphase\(^{30}\). This strongly suggests that the second root represents the diffusion mode whose low frequency dispersion relationship is given by (1.84).

In the critical region, around \( (\Omega_c, x_c) \), the absorption and dispersion characteristics of the \( s \) and \( D \)-modes change rapidly for small changes in concentration and there is a suggestion of "interference" between the roots. The authors claim that the sound root undergoes a qualitative change of behaviour as the concentration passes through the critical value\(^{31}\) and that above the critical frequency two propagating modes are
found, an effect referred to as "double sound". In the present study
these theoretical predictions will be re-examined and the results of
experiments on He-Xe are reported, covering the critical region
discussed by Huck and Johnson.
2.1. Harmonic disturbances in a model binary gas

2.1.1. Governing equations

Our principal aim in this Chapter is to calculate the characteristics of sound propagation in binary monatomic gases using moment equations derived with the aid of kinetic theory. As the equations for gas mixtures are rather complicated, we shall first consider a simple model fluid in which the only dissipative process is diffusion. The model is used to illustrate how the roots of a generalised dispersion relationship vary with frequency and to show that under certain conditions the acoustic root and the diffusion root can coincide.

Suppose that a gas mixture with two components, 1 and 2, is described by the following hydrodynamic equations:

Conservation of species number density,

\[
\frac{d_i n_i}{dt} + n_i \nabla \cdot u_i = 0 \quad i = 1, 2
\]  
(2.1)

Species momentum balance equation,

\[
\rho_i \frac{d_i u_i}{dt} + \nabla p_i = K_{ij}(u_j - u_i) \quad i \neq j
\]  
(2.2)

\(\frac{d_i}{dt}\) is the material derivative of species \(i\),

\[
\frac{d_i}{dt} = \frac{\partial}{\partial t} + u_i \cdot \nabla
\]  
(2.3)

\(K_{ij}(u_j - u_i)\) is the force per unit volume acting on species \(i\) due to \(j\) where \(K_{ij}\) depends on the frequency of encounters per unit volume between \(i\) and \(j\) particles. The cross collision frequency is proportional to the product of the particle number densities therefore \(K_{ij}\) can be written as,

\[
K_{ij} = \rho_i \rho_j A
\]  
(2.4)

where \(A\) depends on the cross-collision cross-section and the particle masses. An interspecies force of the form \(\rho_i \rho_j A(u_j - u_i)\) is in agreement...
Small perturbations from equilibrium will be considered for which non-linearities in (2.1) and (2.2) can be neglected. In addition it will be assumed that the fluid remains at a constant temperature $T_{o}$, hence the species pressure gradients may be written as $\nabla p_{i} = k_{b}T_{o} \nabla n_{i}$. With these changes (2.1) and (2.2) become

$$\frac{\partial n_{i}}{\partial t} + n_{0} x_{i} \nabla u_{i} = 0$$  \hspace{1cm} (2.5)$$

$$\rho_{i0} \frac{\partial u_{i}}{\partial t} + k_{b}T_{o} \nabla n_{i} = \rho_{i0} \rho_{j0} A(u_{j} - u_{i}) \hspace{1cm} i \neq j$$  \hspace{1cm} (2.6)$$

It is more convenient to write the hydrodynamic equations in terms of the centre-of-mass stream velocity $u$, defined by (1.46) and the diffusion velocity $w$, defined by (1.47). Transforming velocity variables gives

$$\frac{\partial n_{1}}{\partial t} + n_{0} x_{1} (\nabla u + \xi_{2} \nabla w) = 0$$  \hspace{1cm} (2.7)$$

$$\frac{\partial n_{2}}{\partial t} + n_{0} x_{2} (\nabla u - \xi_{1} \nabla w) = 0$$  \hspace{1cm} (2.8)$$

where $\xi_{i} = m_{i} x_{i} / (m_{1} x_{1} + m_{2} x_{2})$

Adding the two equations represented by (2.6) gives the equation for fluid momentum conservation,

$$\rho_{o} \frac{\partial u}{\partial t} + k_{b} T_{o} (\nabla n_{1} + \nabla n_{2}) = 0$$  \hspace{1cm} (2.9)$$

Dividing (2.6) by $\rho_{10}$ and subtracting two such equations gives,

$$\frac{\partial w}{\partial t} + k_{b} T_{o} \left( \frac{\nabla n_{1}}{\rho_{10}} - \frac{\nabla n_{2}}{\rho_{20}} \right) = -\rho_{o} Aw$$  \hspace{1cm} (2.10)$$

In a gas mixture left to relax towards a steady state $\frac{\partial w}{\partial t}$ becomes small compared with $-\rho_{o} Aw$ after a time interval which is large compared with the relaxation time $\frac{1}{\rho_{o} A}$. Similarly in the presence of steady
oscillations of angular frequency $\Omega$ such that $\Omega \ll \rho_0 A$ the first term in (2.10) is negligible. When $\frac{\partial W}{\partial t}$ is neglected and isothermal conditions prevail (2.10) becomes equivalent to the constitutive equation for diffusion velocity, (1.54), and we can make the identification

$$D_{12} = \frac{k_B T_0}{n_0 m_1 m_2 A}.$$

(2.11)

2.1.2. Longitudinal harmonic disturbances

The solutions of (2.7)-(2.10) to be considered are those associated with plane longitudinal disturbances in the z-direction. It is assumed that the hydrodynamic state variables have the forms

$$\begin{align*}
n_1 &= n_0 \chi (1 + \hat{n}_1 \text{e}^{i\theta}) \quad \text{A} \\
u &= u_0 \hat{v} \text{e}^{i\theta} \quad \text{B} \\
w &= u_0 \hat{w} \text{e}^{i\theta} \quad \text{C}
\end{align*}$$

(2.12)

with $\theta = kz - \Omega t$

The dimensionless amplitudes $\hat{u}$ and $\hat{w}$ are slightly different from corresponding terms in Chapter 1 since we have chosen to use a new scaling speed $u_0$, given by

$$u_0 = (2k_B T_0/\mu)^{1/2}.$$  

(2.13)

where $\mu$ is the reduced mass

$$\mu = \frac{m_1 m_2}{(m_1 + m_2)}.$$  

(2.14)

It is convenient to introduce the dimensionless angular frequency $\omega$, and the dimensionless wavenumber $\kappa$, defined by

$$\begin{align*}
\omega &= \frac{\Omega}{n_0 \sigma_0 u_0} \quad \text{A} \\
\kappa &= \frac{k}{n_0 \sigma_0} \quad \text{B}
\end{align*}$$

(2.15)

where $\sigma_0$ is a scaling parameter with the dimensions of a cross-section defined by
\[ \sigma_{00} u_0 = m_0 A \]  
\[ \text{where } m_0 = m_1 + m_2 \]

Substituting the harmonic forms (2.12), into the hydrodynamic equations (2.7)-(2.10) and using (2.15) gives the following dimensionless equations for the amplitudes,

\[
\begin{align*}
- i \omega vn_1 + i \kappa (\hat{u} + \zeta_1 \hat{w}) &= 0 \\
- i \omega vn_2 + i \kappa (\hat{u} - \zeta_1 \hat{w}) &= 0 \\
- i \omega 2m_{12} \hat{u} + i \kappa m_{10} m_{20} (x_1 \hat{n}_1 + x_2 \hat{n}_2) &= 0 \\
- i \omega \hat{w} + i \kappa \left( \frac{m_{10} m_{20}}{2} \left( \frac{\hat{n}_1}{m_{10}} - \frac{\hat{n}_2}{m_{20}} \right) \right) &= - m_{12} \hat{w}
\end{align*}
\]

(2.18)

where

\[ m_{j0} = \frac{m_j}{m_0} \]  
(2.19)

and

\[ m_{12} = m_{10} x_1 + m_{20} x_2 \]  
(2.20)

We shall consider the case of a disparate mass gas mixture where the mass ratio, \( \delta^2 = \frac{m_1}{m_2} \ll 1 \), and the molar concentrations are of comparable magnitude, i.e. \( x_1 \sim x_2 \). The small parameter \( \delta \) is defined in this way since terms containing a factor \( (m_1/m_2)\frac{1}{2} \) are encountered later, though not in the present calculation. It will be assumed that the frequency of the disturbance is much less than the inverse relaxation time for diffusion velocity. In terms of dimensionless quantities this implies that \( \omega \ll m_{12}^{-1} \) and that the first term in (2.18)D is negligible. Using this and the disparate mass approximations,

\[ m_{10} = \delta^2, \quad m_{20} = 1, \quad m_{12} \approx x_2, \quad \zeta_1 \approx \delta^2 \frac{x_1}{x_2}, \quad \zeta_2 \approx 1 \]

(2.18) becomes, in matrix form
or

\[
\begin{bmatrix}
\gamma & 0 & -1 & -1 \\
0 & \gamma & -1 & \delta^2 x_1 / x_2 \\
-\delta^2 x_1 / 2x_2 & -\delta^2 / 2 & \gamma & 0 \\
\omega / 2x_2 & -i\omega \delta^2 / 2x_2 & 0 & \gamma
\end{bmatrix}
\begin{bmatrix}
\tilde{n}_1 \\
\tilde{n}_2 \\
\tilde{u} \\
\tilde{w}
\end{bmatrix}
= 0 \tag{2.22}
\]

where \( \gamma = \omega / \kappa \) \tag{2.23}

2.1.3. Harmonic modes

(2.22) has non-trivial solutions if the determinant of the matrix of coefficients is zero. From this condition we get a complex dispersion relationship in implicit form,

\[
y^4 - \frac{1}{2x_2} (\delta^2 - i\omega) y^2 - i\omega \delta^2 / 4x_2 = 0 \tag{2.24}
\]

Solving for \( y^2 \) gives

\[
y^2 = \frac{1}{4x_2} (\delta^2 - i\omega) \pm \sqrt{\frac{1}{16x_2^2} (\delta^2 - i\omega)^2 + i\omega \delta^2 / 4x_2} \tag{2.25}
\]

The physical significance of the roots becomes clear if we examine the behaviour of the solution at low frequencies such that \( \omega \ll \delta^2 \). When the positive sign in (2.25) holds, and terms of second order in \( \omega / \delta^2 \) are neglected, we get

\[
\omega / \kappa^+ = \pm \left( \frac{\delta^2}{2x_2^2} \right)^{1/2} (1 - i\omega x_1 / 2\delta^2) \tag{2.26}
\]

The + suffix refers to the + alternative in (2.25). In the limit as \( \omega \to 0 \), (2.26) gives the dimensionless phase speed
which defines \( \kappa_{+o} \); the low frequency limit of the dimensionless wave-number. To restore the dimensions to (2.27) it is multiplied by the scaling factor \( u_0 \). In the disparate mass approximation \( u_0 = (2K_B T_0 / m_1)^{\frac{1}{2}} \) therefore the phase speed represented by (2.27) is \( (K_B T_0 / m_2 x_2)^{\frac{1}{2}} \). This is the isothermal speed of sound in a gas mixture in which species 2 makes the dominant contribution to the density.

The absorption coefficient can be found by applying the definition of \( \alpha \), equation (1.2),

\[
\alpha_+ = \frac{\text{Im} \ k_+}{\kappa_{+o}} = \frac{x_1}{2\delta^2} \omega
\]

\[
= (x_1 / 2n_0 m_1 A) \Omega \tag{2.28}
\]

where (2.15) and (2.16) have been used. Substituting for \( A \) from (2.11) gives

\[
\alpha_+ = \frac{1}{2} D_{12} n_0 m_2 x_1 \left( \frac{\Omega}{\rho_0} \right) \tag{2.29}
\]

(2.29) corresponds to the Kohler\(^9\) approximation of the acoustic absorption coefficient in that it is to first order in frequency.

Clearly \( \kappa_+ \) is the dimensionless complex wavenumber of an acoustic disturbance propagating isothermally.

Let us now consider the mode associated with the negative sign in (2.25). When \( \omega \ll \delta^2 \) we get

\[
(\omega / \kappa_-)^2 = -i\omega/2
\]

\[
\therefore \omega = -i\kappa_-^2/2 \tag{2.30}
\]

Expressing (2.30) in terms of \( \Omega \) and \( k \) using (2.13) - (2.16) gives

\[
\Omega = -i \frac{K_B T_0}{n_0 m_1 m_2 A} k^2 \tag{2.31}
\]

By eliminating \( A \) using (2.11) we get

\[
\Omega = -i k^2 D_{12} \tag{2.32}
\]
(2.32), like (1.84), represents the complex dispersion relationship for a diffusion mode. A relationship for the number density amplitudes of this mode can be found by subtracting (2.18)B from (2.18)A and eliminating \( \dot{\omega} \) using (2.18)D. This gives

\[-i\omega(\ddot{n}_1 - \ddot{n}_2) + \kappa^2 n_1/2x_2 = 0\]  

(2.33)

where low frequency \((\omega \ll \omega_1)\) and disparate mass approximations have been used. With \( \kappa \) given by (2.30), equation (2.33) implies that

\[x_1\ddot{n}_1 + x_2\ddot{n}_2 = 0\]  

(2.34)

This result is characteristic of the diffusion mode at low frequencies for it shows that the total number density is constant and harmonic perturbations in the species number densities are in antiphase.

2.1.4. The coincidence of roots

An important feature of (2.25) is that for a particular critical angular frequency \( \omega_c \), and a particular composition \( x_{ic} \), the acoustic root and the diffusion root coincide. This occurs when the term under the square root sign in (2.25) vanishes. That is, when

\[\frac{1}{16x_2^2}(\delta^2 - i\omega)^2 + i\omega\delta^2/4x_2 = 0,\]  

(2.35)

\( \omega = \omega_c \) and \( x_i = x_{ic} \). From the imaginary part of (2.35) we find that

\[x_{1c} = x_{2c} = 0.5\]  

(2.36)

Figure 2.1 shows the loci of \( \kappa_+ \) and \( \kappa_- \) for the critical composition of the mixture as \( \omega \) varies. The points on each curve are at intervals of 0.2 in \( \omega/\delta^2 \). In accordance with (2.30), the real and imaginary parts of \( \kappa_- \) are equal in the low frequency limit whereas the acoustic wave-number approaches the real axis. When
Figure 2.1: Loci of $\kappa_+$ and $\kappa_-$ at the critical composition. P is the critical point and OP bisects the angle that OQ makes with the real axis.
\[ \omega = \omega_c = \delta^2 \]  

(2.37)

(2.35) is satisfied for the critical composition of the mixture and the wavenumbers are coincident at P with a critical value \( \kappa_c \), which may be found from (2.25),

\[ \kappa_c = 2^{\frac{1}{2}} e^{\frac{i \pi}{8}} \delta \]  

(2.38)

The dispersion and the absorption coefficients have been calculated for both acoustic and diffusion modes from

\[ \alpha_\pm = \frac{\text{Im} \kappa_\pm}{\kappa_\pm^*} \]  

A

and

\[ \frac{U_0}{U_\pm} = \frac{\text{Re} \kappa_\pm}{\kappa_\pm^*} \]  

B

(2.39)

with \( \kappa_\pm \) given by (2.25). (2.39) extends the definitions (1.2) and (1.4) to include the diffusion mode. Figure 2.2 shows the harmonic mode characteristics for three compositions, including the critical composition, Figure 2.2(b).

It is evident from the thirteen moment theory which follows that our chosen scaling frequency, \( n_0 m_A \), is of the same order of magnitude as the self collision frequency of the light particles. Therefore if \( \nu_1 \) is this self collision frequency in dimensionless form, \( \nu_1 \sim 1 \). In comparison the dimensionless inverse relaxation time for the temperature difference, \( \nu_\Delta \) is of the order of \( \delta^2 \nu_1 \sim \delta^2 \). Thus the critical frequency found using the above model is of the same order of magnitude as the inverse relaxation time for \( \Delta \), i.e. \( \omega_c \sim \nu_\Delta \sim \delta^2 \), in qualitative agreement with the thirteen moment prediction for \( \omega_c^{29} \). The critical composition found from the model \( (x_{1c} = x_{2c} = 0.5) \) is roughly the same as that found by Huck and Johnson for He-Xe \( [0.450 < x_{1c}(\text{He}) < 0.475] \).
Figure 2.2: Dispersion and absorption in a model fluid

(a) $x_1 = 0.4$

(b) $x_1 = x_c = 0.5$

(c) $x_1 = 0.6$
The results summarised in Figure 2.2 should not be regarded as quantitative predictions but they suggest that sound propagation characteristics in a binary gas mixture can be influenced by the presence of the diffusion mode. Also the way in which the phase speed varies with frequency may be very different depending on whether $x_1$ is greater than or less than the critical value. [Compare Figure 2.2(a) with Figure 2.2(c)]. This qualitative behaviour is confirmed by the thirteen moment theory.

2.2. The Boltzmann equation

A central problem of kinetic theory is the calculation of velocity distribution functions. The one particle distribution function, $f(r,v,t)$, is defined such that $fdrdv$ is an ensemble average of the number of particles in an element, drdv, of a six dimensional phase space. In special cases the boundary conditions imposed on $f$ make it discontinuous but in the main it is a smooth function of its variables. Taking an ensemble average implies that local spontaneous fluctuations have been averaged out.

It is generally held that in monatomic gases at moderate or low pressures the evolution of $f$ is governed by the Boltzmann equation. In the absence of external forces this may be written

$$\frac{\partial f}{\partial t} + v \cdot \nabla f = \int d\Omega g(\theta,g) [f f'_1 - ff_1]$$  \hspace{1cm} (2.40)

The prime and the suffix 1 refer to velocity variables. For example $f'_1 = f'_1(r,v'_1,t)$. The right hand side of (2.40) represents the rate of change of the distribution function due to collisions. $v$ and $v'_1$ are particle velocities prior to an encounter. After a collision these become $v^*$ and $v'^*$. Relationships between velocities are usually assumed to be governed by the laws of classical mechanics. A well-known consequence of the classical laws is that the relative velocity of the two
particles has the same magnitude before and after an elastic collision. Thus if

\[ g = v - v_1 \quad \text{and} \quad g' = v' - v'_1 \] (2.41)

then

\[ |g| = |g'| = g \] (2.42)

The differential cross-section, \( \sigma \), is a function of the relative speed, \( g \), and the scattering angle \( \theta \), between \( g \) and \( g' \) in the laboratory frame. Hence

\[ g \cdot g' = g^2 \cos \theta \] (2.43)

\( \Omega \) is a solid angle and \( d\Omega = \sin \theta d\theta d\phi \) where \( \phi \) is an azimuthal angle in the plane perpendicular to \( g \). A number of textbooks on kinetic theory include a derivation of Boltzmann's equation and a discussion of its mathematical properties. A recent account has been given by Cercignani.

In deriving (2.40) a number of assumptions are made concerning the nature of particle collisions. It is assumed that the rate at which \( f \) changes due to collisions is determined by binary encounters only. Also the distance between the centres of particles at the point of closest approach has been neglected, an approximation that the Enskog equations seek to correct in the case of particles which behave as hard elastic spheres. Finally it is assumed that molecular chaos prevails. This hypothesis has generated a great deal of debate ever since Burbury first pointed out that it is a condition on which the H-theorem is based. It may be stated as follows. If \( P_1(r_1,v)dr_1dv \) is the probability of finding a particle in an elemental phase volume at \((r_1,v_1)\) and \( P_2(r_2,v_2)dr_2dv_2 \) is the probability of finding one at \((r_2,v_2)\) incident on the first, then the simultaneous probability of finding particles at \((r_1,v_1)\) and \((r_2,v_2)\) is \( P_1P_2dr_1dr_2dv_1dv_2 \). This implies that the events are statistically independent. If the probabilities are defined with respect to an ensemble of equivalent systems of particles then
\[ P_1 = \frac{f(r_1, v_1, t)}{n(r_1)} \] (2.44)

where \( n(r_1) \) is the particle number density at \( r_1 \). Thus molecular chaos implies that particles approaching collision with each other are drawn randomly from the local distribution function.

More generally the two particle probability density \( P_{12}(r_1, v_1, r_2, v_2) \) may be defined such that \( P_{12} dr_1 dr_2 dv_1 dv_2 \) is the simultaneous probability of finding particles at \( (r_1, v_1) \) and \( (r_2, v_2) \). If correlations occur in the sense that

\[ P_{12} - P_1 P_2 \neq 0 \] (2.45)

then the implications of these are neglected.

A test of the predictions derived from Boltzmann's equations are, in part, a test of the above assumptions. Unfortunately exact solutions are only available in special cases and a harmonic perturbation is not one of these. In making predictions of sound propagation characteristics using the moment method we shall find it necessary to make additional approximations.

2.3. The thirteen-moment method

2.3.1. Expansion of the distribution function

Before proceeding to the calculation of sound propagation characteristics using the thirteen moment equations for binary gas mixtures, a brief outline will be given of the moment method as applied to single-species gases. Further details can be found in accounts by the originator of the thirteen moment method, Harold Grad \(^{7,36}\), and in the extensive treatment of moments given by Burgers \(^{37}\).

The method takes advantage of the fact that in many practical non-equilibrium situations the distribution function is a fairly smooth function of particle velocity. If this is the case, then it may be adequately represented by the first few terms of a polynomial expansion.
in velocity about a local Maxwellian distribution. It proves convenient to use three dimensional Hermite polynomials in the expansion and to introduce the dimensionless velocity variable $\xi$, defined by

$$\xi = \left(\frac{m}{k_B T_0}\right)^{1/2} C$$  \hspace{1cm} (2.46)

where $C$ is the peculiar velocity,

$$C = v - u$$  \hspace{1cm} (2.47)

$v$ is the particle velocity and $m$ the particle mass. In kinetic theory the stream velocity $u$ may be defined in terms of the velocity distribution function as

$$nu = \int dv \, v f$$  \hspace{1cm} (2.48)

The expansion of the distribution function is written

$$f(C,r,t) = f^{(0)}(C,r,t) \left[ 1 + a_\alpha(r,t)H^{(1)}_\alpha + a_{\alpha\beta}(r,t)H^{(2)}_{\alpha\beta}/2! + a_{\alpha\beta\gamma}(r,t)H^{(3)}_{\alpha\beta\gamma}/3! + \ldots \right]$$  \hspace{1cm} (2.49)

Greek suffices refer to a Cartesian coordinate system in velocity space and the summation convention of repeated indices is implied. Three dimensional Hermite polynomials are defined by

$$H^{(j)}_{\alpha\beta\gamma\ldots}(\xi) = (-1)^j \frac{1}{\omega(\xi)} \frac{\partial^j}{\partial \xi_\alpha \partial \xi_\beta \partial \xi_\gamma \ldots} \omega(\xi)$$  \hspace{1cm} (2.50)

where $\omega(\xi) = (2\pi)^{-3/2} \exp\left(-\xi^2/2\right)$  \hspace{1cm} (2.51)

The local Maxwellian $f^{(0)}$ is given by

$$f^{(0)}(v-u,r,t) = n(r,t) \left[ \frac{m}{2\pi k_B T(r,t)} \right]^{3/2} \exp\left\{ -\frac{m[v-u(r,t)]^2}{2k_B T(r,t)} \right\} A \hspace{1cm} (2.52)$$

or

$$f^{(0)} = n \left( \frac{m}{k_B T} \right)^{3/2} \omega(\xi) \hspace{1cm} B$$
At present there are more undetermined parameters in (2.49) and (2.52) than are necessary for a general solution. As befits a local Maxwellian in which \( n, T \) and \( \mathbf{u} \) represent the local particle number density, temperature and stream velocity, we require

\[
n = \int dv \, f = \int dv \, f^{(0)}
\]  
(2.53)

\[
n\mathbf{u} = \int dv \, \mathbf{v} f = \int dv \, \mathbf{v} f^{(0)}
\]  
(2.54)

and

\[
p = n k_B T = \int dv \, \frac{1}{3} m c^2 f = \int dv \, \frac{1}{3} m c^2 f^{(0)}
\]  
(2.55)

The expansion coefficients \( a_\alpha \) and \( a_{\alpha\alpha} \) are determined by (2.54) and (2.55). From (2.47), (2.53) and (2.54) \( d\mathcal{C} = dv \) and

\[
\int d\mathcal{C} \, \mathcal{C} f = 0
\]  
(2.56)

One way of evaluating this integral is to change variable using (2.46) and then express the series expansion for \( f \) in terms of differential operators acting on the weighting function, \( \omega(\xi) \), using (2.50). The \( \eta \) component of (2.56) then leads to

\[
\int d\xi \, \xi_\eta \left[ 1 - a_\alpha \frac{\partial}{\partial \xi_\alpha} + \frac{a_\beta}{2!} \frac{\partial}{\partial \xi_\alpha} \frac{\partial}{\partial \xi_\beta} - \ldots \right] \omega(\xi) = 0
\]

The first term makes no contribution to the integral since \( \xi_\eta \) is an odd function and \( \omega(\xi) \) is even in each Cartesian component. As \( \omega(\xi) \) and its derivatives vanish on a spherical surface at infinity in velocity space successive partial integrations can be carried out without having to retain surface integrals. In this way we get

\[
a_\eta \int d\xi \omega(\xi) = 0
\]

and, as the integral is non-zero

\[
a_\eta = 0
\]  
(2.57)
Starting with (2.55) a similar procedure is followed. The
equation is rewritten as

$$\int d\xi \ C^2(f-f^{(o)}) = 0$$  \hspace{1cm} (2.58)

Transforming velocity variables as before gives

$$\int d\xi \ \xi^2 \left( \frac{a_{\alpha \beta}}{21} \frac{\partial}{\partial \xi \alpha} + \ldots \right) \omega(\xi) = 0$$

where (2.57) has been used. Integrating by parts gives

$$a_{\alpha \alpha} \int d\xi \ \omega(\xi) = 0$$

\Rightarrow \quad a_{\alpha \alpha} = 0  \hspace{1cm} (2.59)

According to (2.59) the trace of the second rank tensor, \(a_{\alpha \beta}\), is zero

2.3.2. General form of the transport equations

Our problem now amounts to finding \(n\), \(T\), \(u\) and the \(a\)'s as functions
of space and time. These quantities are moments of the distribution
function, that is they are averages of functions of velocity taken
over \(f\). In order to show this in the case of the \(a\)'s the orthogonality
property of three dimensional Hermite polynomials is used\(^{32}\),

$$\int d\xi \omega(\xi) H^{(N)}_{\alpha_1 \alpha_2 \ldots \alpha_N}(\xi) H^{(M)}_{\beta_1 \beta_2 \ldots \beta_M}(\xi) = \delta^{(N)}_{\alpha \beta}$$  \hspace{1cm} (2.60)

\(\delta^{(N)}_{\alpha \beta}\) can only be non-zero if \(N = M\). It is a tensor of rank \(2N\) whose
components may be expressed in terms of Kronecker-deltas e.g.

$$\delta^{(1)}_{\alpha \beta} = \delta_{\alpha_1 \beta_1}  \hspace{1cm} (2.61)$$

$$\delta^{(2)}_{\alpha \beta} = \delta_{\alpha_1 \beta_1} \delta_{\alpha_2 \beta_2} + \delta_{\alpha_1 \beta_2} \delta_{\alpha_2 \beta_1} + \delta_{\alpha_1 \alpha_2} \delta_{\beta_1 \beta_2}$$

The \(2N\) suffices are attached in pairs to a product of \(N\) Kronecker deltas.
The components of the tensor is then formed from the sum of these products.
for all distinct permutations of the suffices. Hence $\delta^{(N)}_{\alpha \beta}$ is zero unless suffices referring to the same Cartesian coordinate can be paired off. Using the orthogonality property of the Hermite polynomials we find from (2.48) that

$$a^{(j)}_{\alpha \beta \gamma \cdots} = \frac{1}{n} \int dC f^{(j)}_{\alpha \beta \gamma \cdots} \quad (2.62)$$

In general if $A$ is a function of particle velocity then its moment is given by

$$\overline{A} = \int dC f(C,r,t) A(C) \quad (2.63)$$

The evolution of a moment is governed by Maxwell's transport equation. This may be found by multiplying Boltzmann's equation, (2.40), by $A(v)$ and integrating over velocity. In the absence of external forces we get

$$\frac{\partial \overline{A}}{\partial t} + \nabla \cdot \overline{A} = Q_A \quad (2.64)$$

where $Q_A$, known as the collision moment of $A$, is given by

$$Q_A = \int dv dv_1 \int d\Omega g\sigma(g,\theta) A(v) [f^\ast f_1^\ast - f f_1] \quad (2.65)$$

A transformation of (2.65) which is familiar from the usual derivation of the Boltzmann equation leads to a useful alternative expression:

$$Q_A = \frac{1}{4} \int dv dv_1 \int d\Omega g\sigma(g,\theta) [A^\ast + A_1^\ast - A - A_1] [f^\ast f_1^\ast - f f_1] \quad (2.66)$$

Clearly the collision moment of $A$ vanishes, no matter what the distribution function is, if $A = \phi$, where $\phi$ has the property

$$\phi^\ast + \phi_1^\ast = \phi + \phi_1 \quad (2.67)$$

A function which satisfies (2.67) is known as a summational invariant of the collision. Independent functions which fulfil this requirement are
m, mv, and \( \frac{1}{2} mv^2 \), corresponding to the usual conservation laws for particle collisions. When \( A = \rho \) (2.64) becomes

\[
\frac{\partial \tilde{\rho}}{\partial t} + \nabla \cdot \tilde{\rho} \mathbf{v} = 0
\]

(2.68)

(2.68) is of the form of a conservation law for the fluid. In particular if \( \rho = m \) it becomes the law of mass conservation. Similarly putting \( \rho = mv \) leads to the law of momentum conservation and with \( \rho = \frac{1}{2} mv^2 \) we get an equation representing conservation of fluid energy. Moment equations for functions of particle velocity which are not summational invariants will contain a source term on the right hand side, as in (2.64).

2.3.3. The thirteen-moment approximation of the distribution function

As the series expansion, (2.49) has an infinite number of terms there are an infinite number of unknowns obeying a set of simultaneous equations of the form (2.64). These are coupled through the divergence terms, \( \nabla \cdot \tilde{\mathbf{v}} \), so that an equation for the Nth order moment includes a term containing a moment of order N+1. To get an explicit solution the infinite series is terminated at some point so that there is a finite number of coupled differential equations to be solved. The number of moments we choose to include is, in a formal sense, arbitrary. It will depend on such factors as the demands of the problem and the desired accuracy.

The attraction of using the thirteen independent moments \( n, u, T, \tilde{\mathbf{u}}, \tilde{\mathbf{q}} \) is that these have familiar physical interpretations, yet the moment equations which govern their evolution are expected to have a wider range of validity than the hydrodynamic equations at the Navier-Stokes level. In order that the distribution function contains only the above thirteen moments the third rank tensor \( a_{\alpha \beta \gamma} \) is contracted and higher order terms neglected. Taking note of the fact that \( a_\alpha = 0 \) and \( a_{\alpha \beta} \) is traceless,
\( f \) is of the form

\[
f = f^{(0)} [1 + \frac{a_{\alpha\beta}}{2} H_{\alpha\beta}^{(2)} + b_{\beta} H_{\beta}^{(3)}]
\]  

(2.69)

where

\[
H_{\alpha\beta}^{(2)}(\xi) = \xi_{\alpha} \xi_{\beta} \quad \alpha \neq \beta
\]

and

\[
H_{\beta}^{(3)}(\xi) = -\xi_{\beta} (5-\xi^2)
\]

(2.70)

The pressure deviator \( \pi \) and the heat flux \( q \) may be identified with terms in (2.69). Their components are defined in continuum mechanics as momentum and heat flux densities. The equivalent definitions in particle kinetics are

\[
\pi = m \int dC C^0 C f
\]

(2.71)

and

\[
q = \frac{1}{2} m \int dC C C^2 f
\]

(2.72)

Substituting for \( f \) from (2.69) and carrying out the integrations gives

\[
a_{\alpha\beta} = \frac{\pi_{\alpha\beta}}{p} \quad \text{and} \quad b_{\beta} = \frac{1}{5} \frac{q_{\beta}}{p} \left( \frac{m}{k_B T} \right)^{\frac{1}{2}}
\]

(2.73)

Hence (2.69) may be written as

\[
f = f^{(0)} [1 + \frac{1}{2p} \left( \frac{m}{k_B T} \right) \pi : C C - \frac{1}{p} \left( \frac{m}{k_B T} \right) q \cdot C (1 - \frac{m C^2}{5k_B T})]
\]

(2.74)

The pure-species thirteen moment equations for a general interatomic force law can now be derived. With appropriate functions of velocity, \( A(C) \), the integrations in (2.64) are carried out using the approximate expression for the distribution function (2.74). As our primary concern is not with the equations governing a pure-species gas we turn our attention instead to the case of binary mixtures.

2.4. Thirteen-moment equations for a binary gas mixture

It will be assumed that the distribution function for each species
in a binary gas mixture is governed by a Boltzmann equation which
takes account of both self collisions and collisions between particles
of different species. The coupled equations which describe the
evolution of these distribution functions are given by

\[ \frac{\partial f_i}{\partial t} + v_i \cdot \nabla f_i = Q_{ii}[f_i, f_i] + Q_{ij}[f_i, f_j] \quad (2.75) \]

where

\[ Q_{ij}[f_i, f_j] = \int dv_j \int d\Omega \sigma_{ij}(g, \theta)[f_i f_j - f_i f_j] \quad (2.76) \]

\[ Q_{ii} \text{ is given by a similar expression with } i=j. \quad Q_{ii} \text{ and } Q_{ij} \text{ are non-linear} \]
collision operators for self collisions and cross collisions respectively.

\[ \sigma_{ii} \text{ and } \sigma_{ij} \text{ are the corresponding differential cross-sections. (2.75) is} \]
of course, based on similar assumptions to those used in deriving the
Boltzmann equation for a single species gas.

We seek a solution not of the coupled Boltzmann equations but of a
system of transport equations derived from them using approximate
expressions for the distribution functions. The general form of these
transport equations is obtained by taking a general moment of (2.75),

\[ \frac{\partial A_i}{\partial t} + v_i \cdot \nabla A_i = Q_{Aii} + Q_{Aij} \quad (2.77) \]

where

\[ A_i = \int dv_i f_i A(v_i) \]

and

\[ Q_{Aii} = \int dv_i A_i Q_{ii} \]

\[ Q_{Aij} = \int dv_i A_i Q_{ij} \quad (2.78) \]

In order to evaluate collision moments for a mixture in which the
particles have an unspecified interatomic force law, explicit expressions
for the distribution functions are needed. Although one can choose to
expand these about local Maxwellians with a common temperature, or even
a common flow velocity, this is unnecessarily restrictive. The full
potential of the thirteen moment method is exploited only if thirteen
moments are retained for each species. The obvious way of doing this is to use a local Maxwellian for each species containing a species temperature as well as a species stream velocity. Thus, as a generalisation of the single species case, (2.74), we write

\[ f_1(C_i, r, t) = f_1^{(0)}(C_i, r, t) \left[ 1 + \frac{1}{a_i^2 p_i} \right] - \frac{1}{5} \frac{1}{a_i^2 p_i} q_i \cdot C_i (5 - \frac{2C_i^2}{a_i^2}) \quad i = 1, 2 \]  

(2.79)

where \( a_i = (2k T_i / m_i)^{\frac{1}{2}} \)  

(2.80)

and with \( v_i \) as the particle velocity of species \( i \),

\[ C_i = v_i - u_i \]  

(2.81)

The partial pressure, \( p_i \), and the local temperature, \( T_i \), of species \( i \), are given by

\[ p_i = n_i k T_i = \int dv_i \frac{1}{3} m_i C_i^2 f_i \]  

(2.82)

\( u_i \) is the stream velocity of species \( i \) where

\[ n_i u_i = \int dv_i v_i f_i \]  

(2.83)

The local Maxwellian for species \( i \) is given by

\[ f_1^{(0)}(v_i - u_i, r, t) = n_i(r, t) \left[ \frac{m_i}{2\pi k T_i(r, t)} \right]^{3/2} \exp\left\{ -\frac{m_i [v_i - u_i(r, t)]^2}{2k T_i(r, t)} \right\} \]  

(2.84)

\( q_i \) is the species heat flux,

\[ q_i = \int dC_i \frac{1}{3} m_i C_i C_i \frac{2}{f_i} \]  

(2.85)

and \( \pi_i \) the species viscous stress tensor,

\[ \pi_i = \int dC_i m_i C_i \cdot C_i f_i \]  

(2.86)

Specific moment equations of the form (2.77) can now be calculated using appropriate functions of velocity \( A_i(C_i) \). Collision moments are evaluated with \( Q_{ij} \) and \( Q_{ii} \) operating on distribution functions of the
form (2.79). Non-linear thirteen moment equations for monatomic gas mixtures have been derived in this way by Burgers\(^{37}\). Linearized versions of these equations are as follows:

Species number density conservation,

\[
\frac{\partial n_i}{\partial t} + n_{i0} \nabla \cdot u_i = 0 \tag{2.90}
\]

Species momentum,

\[
\rho_{i0} \frac{\partial u_i}{\partial t} + \nabla p_i + \nabla \cdot \Pi_i = K_{ij} [(u_j - u_i) + \frac{2 \zeta_{ij}}{\rho_{i0}} \left( \frac{q_i}{\rho_{i0}} - \frac{q_j}{\rho_{j0}} \right)] \tag{2.91}
\]

Species energy,

\[
\frac{3}{2} n_{i0} \frac{\partial (k_B T_i)}{\partial t} + p_{i0} \nabla \cdot u_i + \nabla \cdot q_i = \frac{3}{m_i} K_{ij} k_B (T_j - T_i) \tag{2.92}
\]

Viscous stress,

\[
\frac{\partial \Pi_{ii}}{\partial t} + \frac{4}{5} \nabla \cdot q_i + 2p_{i0} \nabla \cdot u_i = C_{ii} \Pi_i + C_{ij} \Pi_j \tag{2.93}
\]

Heat flux,

\[
\frac{\partial q_i}{\partial t} + \frac{k_B T_i}{m_i} \nabla \cdot \Pi_i + \frac{5}{2} p_{i0} \nabla \left( \frac{k_B T_i}{m_i} \right) = D_{ii} q_i + D_{ij} q_j \tag{2.94}
\]

Zero suffices on hydrodynamic variables implies that they are equilibrium quantities. The coefficients appearing in the above equations are as follows:

\[
K_{ij} = A p_{i0} \rho_{j0} \quad K_{ij} = K_{ji} \tag{2.95}
\]

\[
C_{ii} = -3B_{ii} \rho_{i0} - (2m_{i0} A + 3m_{i0} B) \rho_{j0} \tag{2.96}
\]

\[
C_{ij} = (2A - 3B) m_{j0} \rho_{i0} \tag{2.97}
\]

\[
D_{ii} = -\rho_{j0} [A(3m_{i0}^2 + m_{i0}^2 z_{ij}) + 4Bm_{i0}^2 m_{j0}] - 2B_{ii} \rho_{i0} \tag{2.98}
\]

\[
D_{ij} = \rho_{i0} [A(3 + z_{ij}) - 4B] m_{j0}^2 \quad (i \neq j) \tag{2.99}
\]
The notation here is similar to that used by Goebel, Harris and Johnson in their work on mixtures of Maxwell molecules except that \( z_{ij} \) and \( Z_{ij} \) have been introduced and the definitions of \( A, B \) and \( B_{ii} \) are modified to account for the fact that particle interaction potentials are not restricted to the inverse fourth power law.

\[
A = \frac{16}{3m_0} \Omega_{ij}^{(1)} \tag{2.100}
\]

\[
B = \frac{16}{15m_0} \Omega_{ij}^{(2)} \tag{2.101}
\]

\[
B_{ii} = \frac{8}{15m_i} \Omega_{ii}^{(2)} \tag{2.102}
\]

\[
z_{ij} = 1 - \frac{2}{5} \frac{\Omega_{ij}^{(1)}}{\Omega_{ij}^{(1)}} \tag{2.103}
\]

and

\[
z_{ij}^* = \frac{2}{5} \frac{\Omega_{ij}^{(1)}}{\Omega_{ij}^{(1)}} + 5z_{ij} - \frac{5}{2} \tag{2.104}
\]

The collision integrals, \( \Omega_{ij}^{(\ell)}(r) \), are those used by Chapman and Cowling,

\[
\Omega_{ij}^{(\ell)}(r) = \frac{\alpha_{ij}}{2\pi^2} \frac{\gamma^2}{\alpha_{ij}} \int_0^{\infty} dy \exp(-y^2) \gamma^{2\tau+3} S_{ij}^{\ell} \tag{2.105}
\]

where \( \gamma = g/\alpha_{ij} \)

\[
\alpha_{ij}^2 = 2(m_i + m_j)kT_0 / m_im_j \tag{2.106}
\]

and

\[
S_{ij}^{\ell} = 2\pi \int_0^\pi d\theta \sigma_{ij}(g_1 \theta)(1 - \cos^2 \theta) \sin \theta \tag{2.107}
\]

Note that when \( i \neq j \) \( \alpha_{ij} = u_0 \).

In contrast to the thirteen moment equations for mixtures of Maxwell molecules, those above contain terms which represent the thermal diffusion effect. One of these terms appears in the species momentum equation, (2.91), as a mutual force acting between species 1 and 2:

\[
\frac{2 K_{ij} z_{ij}}{u_o^2} \left( \frac{q_i}{\rho_{i0}} - \frac{q_j}{\rho_{j0}} \right) \tag{2.91}
\]
and the other,
\[ \frac{5}{2} A m_j p_i \rho_j z_{ij} (u_j - u_i), \]
occurs in the heat flux equation of species i. For Maxwell molecules \( z_{ij} = 0 \) and these terms vanish.

2.5. Alternative forms of the linearized moment equations

The thirteen moment equations for a binary mixture may be expressed in terms of the overall stream velocity, \( u \), the diffusion velocity, \( w \), the mean temperature, \( T \), and the temperature difference, \( \Delta \). In the linear approximation the average temperature is given by

\[ T = x_1 T_1 + x_2 T_2 \]

and the temperature difference by

\[ \Delta = T_1 - T_2 \]

\( u \) and \( w \) are defined by (1.46) and (1.47) respectively. In the present section we carry out this change of variables for (2.90) - (2.94) and in the next harmonic solutions of the transformed moment equations are investigated.

The number density conservation laws, (2.90), have already been written in terms of \( u \) and \( w \) but for completeness they are restated.

\[ \frac{\partial n_1}{\partial t} + n_{10} \nabla \cdot u + n_{10} \nabla \cdot v = 0 \]  

\[ \frac{\partial n_2}{\partial t} + n_{20} \nabla \cdot u - n_{20} \nabla \cdot v = 0 \]

In the species momentum balance equation, (2.91), the source term represents the rate at which momentum is transferred from species j to species i. This is equal to the negative of the corresponding source term
in the momentum balance equation for species j. Therefore on
adding these two equations the source terms cancel and we get the
momentum conservation law for the fluid,

$$\rho_o \frac{\partial \mathbf{u}}{\partial t} + n_o \mathbf{v}_B \mathbf{u} T + k_B T_o (\nabla \mathbf{n}_1 + \nabla \mathbf{n}_2) + \nabla \cdot \mathbf{f}_1 + \nabla \cdot \mathbf{f}_2 = 0$$  \hspace{1cm} (2.112)

Dividing (2.91) by the species density and subtracting two such
equations gives a relationship for the evolution of diffusion velocity,

$$\frac{\partial \mathbf{w}}{\partial t} + \frac{k_B T_o}{\rho_{10}} \nabla \mathbf{n}_1 - \frac{k_B T_o}{\rho_{20}} \nabla \mathbf{n}_2 + \frac{1}{\rho_{10}} \nabla \cdot \mathbf{f}_1 - \frac{1}{\rho_{20}} \nabla \cdot \mathbf{f}_2$$

$$+ \frac{m_2 - m_1}{m_1 m_2} k_B \mathbf{v}_T + \left( \frac{x_2}{m_1} + \frac{x_1}{m_2} \right) k_B \nabla \mathbf{A} = -\rho_o \mathbf{A} \left[ \frac{\mathbf{w}}{u_0^2} \right. \frac{2 \mathbf{A}}{\rho_{10}} - \frac{\mathbf{A}^2}{\rho_{20}} \left. \right]$$

$$ \hspace{3cm} (2.113)$$

where (1.47)(2.108) and (2.109) have been used.

Adding species energy equations, (2.92), gives the law of energy
conservation for the fluid,

$$\frac{3}{2} n_o k_B \frac{\partial T}{\partial t} + p_o \left[ \nabla \cdot \mathbf{u} + \frac{m_2 - m_1}{m_1 x_1 + m_2 x_2} x_1 x_2 \nabla \cdot \mathbf{w} \right] + \nabla \cdot (\mathbf{q}_1 + \mathbf{q}_2) = 0$$

$$\hspace{3cm} (2.114)$$

An equation for the evolution of the temperature difference, \( \Delta \), is found
by dividing (2.92) by the number density of species i and subtracting
two such equations. This gives

$$\frac{3}{2} k_B \frac{\partial \Delta}{\partial t} + k_B T_o \nabla \cdot \mathbf{w} + \frac{1}{n_{10}} \nabla \cdot \mathbf{q}_1 - \frac{1}{n_{20}} \nabla \cdot \mathbf{q}_2 = -3 \mathbf{A} n_o k_B \Delta$$

$$\hspace{3cm} (2.115)$$

Transforming the remaining moment equations using (1.46), (1.47),
(2.108) and (2.109) gives

$$\frac{\partial \mathbf{f}_1}{\partial t} + \frac{4}{5} \mathbf{v}_o \mathbf{q}_1 + 2p_{10} (\mathbf{v}_o \mathbf{u} + \zeta_2 \mathbf{v}_o \mathbf{w}) = C_{11} \mathbf{f}_1 + C_{12} \mathbf{f}_2$$

$$\hspace{3cm} (2.116)$$
2.6. Identification of transport coefficients

Thirteen moment mixture equations can be systematically reduced to the Navier-Stokes system of hydrodynamic equations using, for example, the procedure discussed by Kogan for a single species gas\textsuperscript{32}. When this method is applied to mixtures\textsuperscript{23} it becomes possible to identify certain of the coefficients used above with the familiar transport coefficients of first order hydrodynamics. In this way we find that

\[ D_{12} = \frac{a_{12}^2}{2\text{Am} n_o} \]  

or, using (2.100)

\[ D_{12} = \frac{3 k_B T_0}{16 \mu n_o \Omega_{12(1)}} \]  

This agrees with the first Chapman Enskog approximation of the diffusion coefficient\textsuperscript{25}. Experimental values of the diffusion coefficient will be used to define a collision parameter for cross-collisions in our calculation of sound propagation characteristics.

Pure-species viscosities will also be identified since these are used to define self-collision parameters. By reducing (2.116) and (2.117) to their Navier-Stokes form, (1.56) with \( n_v = 0 \), we can make the identification

\[ \eta_i = -p_{i0}/C_{1i} (\rho_{i0} = 0) \]  

(2.122)
where $\eta_i$ is the coefficient of viscosity of species $i$ and $C_{ii}(\rho_j=0)$ is the coefficient $C_{ii}$ with the species $j$ density put equal to zero. Using (2.96) and (2.101) the viscosity coefficients can also be written

$$\eta_i = \frac{5k_B T_0}{8\xi_i(2)}$$

Again this agrees with the first Chapman Enskog approximation $^{25}$. It is well known from elementary kinetic theory that for a pure gas, $\eta_i / p_{10}$ is of the order of the particle collision frequency per unit volume, where $p_{10}$ is now the total pressure of a gas of $i$ particles. Therefore $C_{ii}(\rho_j=0)$ is of the order of the collision frequency in a gas of species $i$ molecules. If we introduce a quantity of species $j$ to form a mixture, keeping the partial pressure of species $i$ constant, then the self collision frequency of $i$ particles remains the same within ideal gas approximations. Hence even in a mixture $C_{ii}(\rho_j=0)$ is of the order of the self collision frequency of species $i$ particles. We shall make use of this fact when comparing relaxation rates in the thirteen moment description.

2.7. Moment amplitude equations

The behaviour of periodic disturbances is investigated by following the same procedure as was used in analysing the model system of Section 2.1. The hydrodynamic state variables are assumed to have harmonic forms and their governing equations are transformed accordingly. This reduces the problem to one of solving a set of homogeneous linear simultaneous equations or an equivalent matrix equation. Starting with the thirteen moment equations for a mixture we obtain a $10 \times 10$ matrix equation for the one dimensional problem. As this is difficult to handle in full analytically, it has been solved using numerical methods.

In the presence of a plane longitudinal disturbance in the $z$ direction the ten hydrodynamic variables in (2.110) - (2.119) are assumed to vary as
\[
\begin{align*}
n_i &= n_0 x_i (1 + n^* e^{i\theta}) & T &= T_0 (1 + n^* e^{i\theta}) \\
\pi_i &= p_0 x_i \pi_1 e^{i\theta} & \Delta &= T_0 \Delta e^{i\theta} \\
q_i &= p_0 u x_i q_1 e^{i\theta} & u &= u_0 \nu e^{i\theta} \\
w &= u_0 \nu e^{i\theta}
\end{align*}
\]

(2.124) defines the complex amplitudes denoted by the tilde. The phase angle \( \theta \) may be written in terms of the dimensionless wavenumber \( \kappa \), and the dimensionless frequency \( \omega \) as

\[
\theta = \kappa n_0 \sigma_o z - \omega n_0 \sigma_o u t
\]

(2.125)

\( \omega \) and \( \kappa \) are defined by (2.15) and \( \sigma_o \) by (2.16). It will be assumed that \( \omega \) is a known real parameter, and the dispersion relationships we seek will express \( \kappa \) as a function of \( \omega \).

Substituting the harmonic forms, (2.124), into the linearized moment equations (2.110) - (2.119) gives

\[
-i\omega \check{n} + i\kappa (\check{u} + \check{\tau}_2 \check{w}) = 0
\]

(2.126)

\[
-i\omega \check{n}_2 + i\kappa (\check{u} - \check{\tau}_1 \check{w}) = 0
\]

(2.127)

\[
-i\omega \check{w} + i\kappa \left[ x_1 \check{n}_1 + x_2 \check{n}_2 + \check{\tau} + x_1 \check{\pi}_1 + x_2 \check{\pi}_2 \right] = 0
\]

(2.128)

\[
-i\omega \check{w} + i\kappa \left[ x_1 \check{n}_1 + x_2 \check{n}_2 + \check{\tau} + x_1 \check{\pi}_1 + x_2 \check{\pi}_2 \right]
\]

(2.129)

\[
-i\omega \check{w} + i\kappa \left[ x_1 \check{n}_1 + x_2 \check{n}_2 + \check{\tau} + x_1 \check{\pi}_1 + x_2 \check{\pi}_2 \right] = 0
\]

(2.130)

\[
-i\omega \check{n}_1 + i\kappa \left[ \frac{m_2}{m_{10}} \check{w} + x_1 \check{w} + x_1 \check{q}_1 + x_2 \check{q}_2 \right] = 0
\]

(2.131)

\[
-i\omega \check{n}_1 + i\kappa \left[ \frac{m_2}{m_{10}} \check{w} + x_1 \check{w} + x_1 \check{q}_1 + x_2 \check{q}_2 \right] = 0
\]

(2.132)
\[-i\omega x_2 \hat{\pi}_2 + i\xi 4^{2+1} \alpha_1 \alpha_2 + x_2 (u-t_1 w) = C_{21}^0 x_1 \hat{\pi}_1 + C_{22}^0 x_2 \hat{\pi}_2 \] (2.133)

\[-i\omega x_2 \hat{\pi}_2 + i\xi m_{20} x_1 \left[ \frac{1}{2} (\hat{T} + x_2 \hat{\Delta}) \right] = 2D_{11}^0 x_1 \hat{\pi}_1 + 2D_{12}^0 x_2 \hat{\pi}_2 + 5m_{20}^2 x_1 x_2 z_{12} \] (2.134)

\[-i\omega x_2 \hat{\pi}_2 + i\xi m_{10} x_2 \left[ \frac{1}{2} (\hat{T} - x_2 \hat{\Delta}) \right] = 2D_{21}^0 x_1 \hat{\pi}_1 + 2D_{22}^0 x_2 \hat{\pi}_2 - 5m_{10}^2 x_1 x_2 z_{12} \] (2.135)

where

\[C_{ij}^0 = C_{ij} / n_0 \sigma u_0 \] (2.136)

and

\[D_{ij}^0 = D_{ij} / n_0 \sigma u_0 \] (2.137)

2.8. Comparison of relaxation rates

The calculation of harmonic solutions was carried out with collision parameters derived from the transport properties of the He-Xe gas mixtures. Although this may be regarded as a disparate mass mixture \((\delta^2 = 0.03)\) the computation did not take advantage of disparate mass approximations. However it is of interest to compare the various relaxation rates in the thirteen moment description of He-Xe in terms of \(\delta\).

As with the model system discussed earlier the dimensionless inverse relaxation time for diffusion velocity which occurs in equation (2.129) is given by

\[\nu_w = m_{12} \] (2.138)

In a disparate mass mixture \((\delta^2 = m_1 / m_2 << 1)\), with scattering cross-sections and number densities of the same order of magnitude, \(\nu_w = x_2 \nu_1\); i.e. the inverse relaxation time for \(w\) is of the same order as the reference frequency. The dimensionless inverse relaxation time for the temperature difference, (2.131), is given by

\[\nu_\Delta = 2m_{10}^m m_{20} \] (2.139)
or, in the disparate mass approximation $\nu_\Delta \approx 2\delta^2 v_\Delta^2$. Results will be
given for values of $\omega$ in the range up to and including $\omega \sim \nu_\Delta \sim \delta^2$. The
validity of thirteen moment predictions in this frequency range will be
discussed in Chapter 3.

Since $C_{ii}(\rho_j=0)$ is of the order of the self collision frequency per
unit volume of species $i$ particles, the dimensionless self collision
frequency, $v_1 \sim C_{ii}^0(\rho_j=0)$. Referring back to the definitions of $C_{ii}$,
(2.96), and the reference parameters, (2.16), we find $v_1 \sim C_{ii}^0(\rho_2=0)\sim 1$
and $v_2 \sim C_{22}^0(\rho_1=0) \sim \delta$. The difference in order of magnitude of the
self collision frequencies is, of course, due to the fact that the
heavy species mean thermal speed is less, by a factor $\delta$, than that of the
light species. With the reference frequency $n_0^0 u_0$ of the order of the
light species self collision frequency and $u_0$ of the order of the light
species thermal speed, $\frac{1}{n_0^0 \sigma_0}$ is of the order of the mean free path for
light particles. As number densities and collision cross-sections are
not dissimilar for the two species, $\frac{1}{n_0^0 \sigma_0}$ is of the same order as the
mean free path for the mixture as a whole. Hence $|\kappa| = k/n_0^0 \sigma_0$ is of
the order of the Knudsen number for a harmonic disturbance.

2.9. Organisation of the computation

2.9.1. Expressing the equations for moment amplitudes in a standard
matrix form.

The moment amplitude equations, (2.126) - (2.135), may be written,
in matrix form as

$$[i \kappa \mathbf{P} - \mathbf{Q} - i \omega \mathbf{U}] \hat{\mathbf{X}} = 0$$

(2.140)

where $\hat{\mathbf{X}}$ is a vector whose ten components are the dimensionless moment
amplitudes. $\mathbf{U}$ is a unit matrix. $\hat{\mathbf{X}}$, $\mathbf{P}$ and $\mathbf{Q}$ are given by
\[
\begin{bmatrix}
\tilde{n}_1 \\
\tilde{n}_2 \\
\tilde{u} \\
\tilde{v} \\
\tilde{w} \\
\tilde{x} \\
\tilde{y} \\
\tilde{n}_1 \\
\tilde{n}_2 \\
\tilde{q}_1 \\
\tilde{q}_2
\end{bmatrix}
\begin{bmatrix}
1 & \zeta_2 & \cdots & \cdots & \cdots & \cdots \\
\cdots & 1 & -\zeta_1 & \cdots & \cdots & \cdots \\
\frac{m_{10}m_{20}}{2m_{12}} & \frac{m_{10}m_{20}}{2m_{12}} & \cdots & \cdots & \cdots & \cdots \\
\frac{m_{20}/2}{2} & \frac{-m_{10}/2}{2} & \cdots & \cdots & \cdots & \cdots \\
\frac{2}{3} & \frac{2}{3} & \cdots & \cdots & \cdots & \cdots \\
\frac{4/3}{2} & \frac{4/3}{2} & \zeta_2 & \cdots & \cdots & \cdots \\
\frac{4/3}{2} & \frac{-4/3}{2} & \zeta_1 & \cdots & \cdots & \cdots \\
\frac{5/4}{2} & \frac{m_{20}}{2} & \frac{5m_{20}x_2}{4} & \frac{m_{20}/2}{2} & \cdots & \cdots \\
\frac{5/4}{2} & \frac{m_{10}}{2} & \frac{-5m_{10}x_1}{4} & \frac{m_{10}/2}{2} & \cdots & \cdots \\
\end{bmatrix}
\]

\(\chi = (2.141)\)  

\(P = \)
(2.140) is in the form of an eigenvalue problem with \( i\omega \) in the role of eigenvalue. It is more convenient, even when using numerical methods, to have the unknown, \( \kappa \), or some function of \( \kappa \), say \( \lambda(\kappa) \), as eigenvalue so that the problem is then in the form

\[
[A(\omega) - \lambda(\kappa) \uparrow] \hat{\chi} = 0 \tag{2.144}
\]

What might appear to be an obvious way of doing this is to multiply (2.140) by \( \frac{1}{\kappa} (Q - i\omega \uparrow) \) so that the eigenvalue is \( i\kappa \). For the case considered here however, \( \frac{1}{\kappa} \) is singular, hence some other method must be found. An alternative is to multiply (2.140) by \( \frac{1}{\kappa} (Q - i\omega \uparrow) (Q + i\omega \uparrow) \). This gives

\[
[i(Q - i\omega \uparrow) \frac{1}{\kappa} (Q - i\omega \uparrow) (Q + i\omega \uparrow)] \hat{\chi} = 0
\]

or since \( Q \) commutes with \( \uparrow \)

\[
[i(Q - i\omega \uparrow) \frac{1}{\kappa} (QQ \uparrow + \omega^2 \uparrow)] \hat{\chi} = 0
\]
Multiplying by \((\mathbf{Q} + \omega^2 \mathbf{U})^{-1}\) gives an equation of the form (2.144) with

\[
\lambda = 1/\kappa \tag{2.145}
\]

and

\[
\mathbf{A} = (\mathbf{Q} + \omega^2 \mathbf{U})^{-1}(\mathbf{iQ} + \omega \mathbf{U}) \mathbf{P} \tag{2.146}
\]

(2.144) was solved numerically with the complex matrix \(\mathbf{A}\) given by (2.146).

2.9.2. Reduced collision integrals

Collision coefficients contained in the matrix \(\mathbf{Q}\) depend on interatomic potentials through the collision integrals \(\Omega^{(j)}_{ij}(r)\). When dealing with more than one form of potential it is convenient to organise the calculation of collision coefficients around a reduction scheme for the \(\Omega\)'s. Following Maitland, Rigby, Smith and Wakeham the \(\Omega\)'s are referred to the collision integrals for rigid elastic spheres given by,

\[
\Omega^{(j)}_{ij}(r) = \alpha_{ij} \eta(j,r) \frac{\pi d_{ij}^2}{} \tag{2.147}
\]

with \(\eta(j,r) = \frac{(r+1)!}{4\pi^2} [1 - \frac{1+(-1)^j}{2(1+j)}] \) \(\tag{2.148}\)

\(d_{ij}\) is the distance between centres of i and j particles at the point of impact. Reduced collision integrals, \(\Omega^{(j,r)^*}\), are defined by

\[
\Omega^{(j,r)^*}_{ij}(r) = \alpha_{ij} \eta(j,r) \frac{\pi d_{ij}^2}{\Omega^{(j,r)}} \tag{2.149}
\]

Then in the case of rigid elastic spheres all the \(\Omega^{(j,r)^*}\) are equal to one. When some other interatomic potential is used \(d_{ij}\) represents a characteristic distance and \(\Omega^{(j,r)^*}\) depends only on the form of the potential. For Maxwell molecules, where the interatomic force is written

\[
F_{ij} = \frac{\kappa_{ij}}{r^5} \tag{2.150}
\]

and \(\kappa_{ij}\) is a constant, the collision integrals are given by
The $\alpha_5$ are tabulated constants. If we choose the characteristic length as
\[ 2.153 \]
then (2.151) may be written as
\[ 2.154 \]
Comparing (2.149) with (2.154) we find that for Maxwell molecules the reduced collision integrals are given by
\[ 2.155 \]
Comparing (2.149) with (2.154) we find that for Maxwell molecules the reduced collision integrals are given by
\[ 2.156 \]
Comparing (2.149) with (2.154) we find that for Maxwell molecules the reduced collision integrals are given by
\[ 2.157 \]
As there is no preferred direction in the gas mixture, if $\lambda^*$ satisfies
(2.157), then so does $-\lambda^\prime$. Another consequence of this symmetry is that when $\lambda^\prime + -\lambda^\prime$ the complex amplitudes remain the same except that amplitudes of vector components are phase inverted relative to amplitudes of scalar quantities. Thus each solution may be paired with another of similar character whose wavenumber has the opposite sign. For one pair of roots it is found that $\lambda^2 = 0$. The presence of these roots is a consequence of the fact that $\mathbf{P}$ is singular since this implies that $\mathbf{P}_{\xi}^X = 0$ has non trivial solutions and that (2.140) has solutions in the limit as $|\kappa| \to \infty$. Of the four remaining pairs of roots three are associated with the hydrodynamic modes; sound, diffusion and temperature. We shall sometimes refer to these as the S-, D- and T- modes respectively. In addition the mixture thirteen moment equations yield a temperature difference or $\Delta$-mode.

Characteristic solutions of the eigenvalue problem (2.144), have been computed with input parameters (Table 2.1), corresponding to helium-xenon mixtures at 0°C. Figure 2.3 is an Argand diagram showing the loci of complex wavenumbers for He(0.3)-Xe treated as a mixture of Maxwell molecules. The points shown on each curve are at intervals of 10 MHz.Atm$^{-1}$. For the hydrodynamic modes, S, D and T, the wavenumber vanishes in the low frequency limit but for the $\Delta$ mode it is imaginary and has a magnitude of the order of 1 as $\omega$ goes to zero. Thus a low frequency excitation of the $\Delta$-mode decays exponentially to zero with a decay constant of the order of the mean free path.

### Table 2.1. Transport coefficients at 0°C used in the thirteen moment calculation

<table>
<thead>
<tr>
<th></th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Viscosity of helium</td>
<td>18.65x10$^{-6}$ Pa.s</td>
</tr>
<tr>
<td>Viscosity of xenon</td>
<td>21.07x10$^{-6}$ Pa.s</td>
</tr>
<tr>
<td>Diffusion coefficient of He-Xe</td>
<td>49.6 x10$^{-6}$ m$^2$s$^{-1}$</td>
</tr>
</tbody>
</table>
Figure 2.3: Dimensionless wavenumbers for He(0.3)-Xe treated as a mixture of Maxwell molecules.

The graph shows the real ($\text{Re}(\kappa)$) and imaginary ($\text{Im}(\kappa)$) parts of the dimensionless wavenumber $\kappa$. The modes are labeled as S-mode, D-mode, T-mode, and Δ-mode. The Δ-mode is indicated by an arrow on the graph.
The nature of each mode is most clearly shown by the relative values of the complex amplitudes at low frequencies, illustrated by the phasor diagrams of figure 2.4. \( \hat{X} \) is normalised such that \( \hat{X} \cdot \hat{X}^* = 1 \) and only those components with a magnitude greater than 0.1 are shown. The number density amplitude for the light species (helium) \( \hat{n}_1 \), is used as a phase reference in that it is arbitrarily assumed to be real. Although the species temperatures are not shown it is found that for the \( \Delta \)-mode they are roughly in antiphase and in antiphase with their corresponding species number densities such that the partial pressure amplitude for each species is very small. In fact it is only in the case of the \( S \)-mode that the overall pressure amplitude, calculated according to (1.31), is not small at low frequencies and does not vanish in the low frequency limit.

2.10.2. Wavenumber characteristics

Figures 2.5 to 2.12 show a series of wavenumber characteristics for He-Xe mixtures assuming the interatomic potentials are those of Maxwell molecules. As before the points are at equal intervals of 10MHz.Atms\(^{-1}\).

From figures 2.9 and 2.10 it is evident that a point of coincidence of the \( S \)- and \( T \)- mode wavenumbers occurs where the mode fraction of helium is between 0.487 and 0.488. Associated with the critical point is a discontinuous change in the characteristics. As the helium mole fraction passes through the critical value the wavenumber loci of the \( S \)- and \( T \)- modes are exchanged for frequencies above the critical value (75MHz.Atms\(^{-1}\)).

There is a striking similarity between the thirteen moment wavenumber characteristics close to the critical composition and the loci of \( \kappa \) for the model system shown in Figure 2.1. However there is also a significant difference between the two sets of results. Our model system had only \( S \)- and \( D \)- modes built into it but from the thirteen moment calculations for
Figure 2.4: Moment amplitudes at 5 MHz Atm$^{-1}$ for He(0.3)-Xe
Maxwell molecules we find that interference occurs between the S- and T-modes. Furthermore the T- and D-modes are coincident at approximately 40 MHz-1 atm for a helium mole fraction between 0.42 and 0.43 (Figures 2.6 and 2.7).

The phase relationship between component amplitudes of the S- and T-modes at low frequencies are quite distinct, as shown in Figure 2.13(a) for a composition close to the critical value. As the frequency is increased differences between the phase characteristics for the two modes are reduced until they vanish at the critical frequency (Figure 2.13(c)).

The present calculation confirms an observation made by Huck and Johnson, that at the critical point the phase of the number density, stream velocity and temperature for the light species leads the corresponding complex amplitudes of the heavy species by \( \pi/2 \).

A comparison of the results for rigid spheres (Figures 2.14 to 2.19) with those for Maxwell molecules suggests that wavenumbers of the D- and T-modes are sensitive to the form of interatomic potential above about 30 MHz-1 atm. The S-mode by contrast is influenced much less by the choice of potential. For rigid spheres it is the complex wavenumber of the D-mode which approaches that of the S-mode and becomes coincident with it at a critical point (Figures 2.16 and 2.17). Even though the sound mode interferes with a different elementary solution when the particles are assumed to behave as rigid spheres, the critical parameters are similar to those found when Maxwell molecules are considered:

* It should be emphasised that interference in this sense does not mean the mutual interaction of disturbances due to non-linear effects in the fluid, we have assumed a linear system which implies that harmonic disturbances evolve independently of each other. In the present context the term refers to the relationship between wavenumbers of different modes.
<table>
<thead>
<tr>
<th>Interatomic potential</th>
<th>Critical mole fraction of helium</th>
<th>Critical frequency MHz.Atms.$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Maxwell molecules</td>
<td>0.49</td>
<td>75</td>
</tr>
<tr>
<td>Rigid spheres</td>
<td>0.43</td>
<td>77</td>
</tr>
</tbody>
</table>

2.10.3. Conclusions

In analysing experimental data on the propagation of sound it is often safe to ignore non-acoustic modes since acoustic transducers usually respond to pressure oscillations and at low frequencies the pressure amplitudes of the non-acoustic modes are relatively small. In addition these modes are usually heavily damped. If they were to be excited at a boundary the effects would be dissipated within a short distance. However in the region of the critical composition and frequency the acoustic mode is also highly damped and the pressure components of non-acoustic hydrodynamic modes are substantial (see for example, Figure 2.13). In most cases the acoustic mode determines the signal detected experimentally but it is clear that in the critical region it may be necessary to take account of contributions from other modes.

Acoustic dispersion and absorption are related to the real and imaginary parts of the dimensionless wavenumber through equations (1.4) and (1.2). In Chapter 5 the thirteen-moment predictions are compared with the results of experiments on helium-xenon mixtures. First we shall assess the accuracy of the theory by comparing the order of magnitude of moment amplitudes. In particular we wish to determine the relative magnitude of the terms omitted from the thirteen moment calculation. For this reason harmonic solutions of the Boltzmann equations will be rederived using perturbation theory. Before proceeding to the case of disparate mass mixtures perturbation theory applied to mixture in which \( m_1 \sim m_2 \), will be reviewed.
Figure 2.5: He(0.35)-Xe
Maxwell molecules
T-mode
D-mode
S-mode

Figure 2.6: He(0.42)-Xe
Maxwell molecules
T-mode
D-mode
S-mode
Figure 2.8: He(0.45)-Xe Maxwell molecules

![Graph of Maxwell molecules showing D-mode, T-mode, and S-mode](image-url)
Figure 2.10: He(0.48)-Xe
Maxwell molecules.
Figure 2.12: He(0.60)-Xe

Maxwell molecules.
Figure 2.13: Complex amplitudes at a composition \( x_1 = 0.487 \)
close to the critical composition for the coincidence
of S- and T-mode wavenumbers. Scale 1 cm = 0.2

- **S-mode**
  - **Exitation frequency**
  - (a) 10 MHz.Atms\(^{-1}\)
  - \( \hat{n}_2 \) → \( \hat{n}_1 \)

- **T-mode**
  - \( \hat{n}_2 \) → \( \hat{n}_1 \)

(b) 60 MHz.Atms\(^{-1}\)

(c) **Critical frequency**
  - 75 MHz.Atms\(^{-1}\)

(d) 100 MHz.Atms\(^{-1}\)
Figure 2.15: He(0.40)-Xe

Rigid spheres.
Figure 2.17: He(0.441)-Xe
Figure 2.19: He(0.60)-Xe

Rigid spheres.

Re(\kappa) vs. Im(\kappa)
CHAPTER 3 - SOUND PROPAGATION AS A PERTURBED EIGENVALUE PROBLEM

3.1. Introduction

In Chapter 2 the dispersion relationships for harmonic disturbances in binary monatomic gas mixtures were found from generalised hydrodynamic equations for a mixture. We now examine an alternative method in which normal modes are obtained directly from the linearized Boltzmann equations. The basic approach as applied to single species monatomic gases, was pioneered by Mott-Smith and independently by Wang Chang and Uhlenbeck\textsuperscript{38}. It is postulated that the distribution function has the space-time dependence of a harmonic wave and when this form is substituted into the linearized Boltzmann equation, the resulting relationship has the structure of a perturbed eigenvalue problem.

Perturbation theory was applied to the calculation of sound propagation characteristics in pure monatomic gases by Foch\textsuperscript{20} and later used by Foch, Uhlenbeck and Losa\textsuperscript{5} to determine the acoustic properties of binary monatomic gas mixtures. In order to express the results of their calculation in terms of the familiar first order transport coefficients, Foch, Uhlenbeck and Losa draw a correspondence between the equations they derive and the Chapman-Enskog derivation of hydrodynamics. In the present study perturbation theory as applied to mixtures is reformulated. Rather than pointing out the parallel with Chapman-Enskog theory, expressions for the transport coefficients will be identified by comparing the eigenvalues found from perturbation theory with those of the hydrodynamic modes given in Section 1.5.

Perturbation theory is based on the explicit ordering of a problem in terms of a small parameter, in this case the dimensionless wavenumber $\kappa$. When dealing with a disparate mass gas mixture another small parameter $\delta$, may be defined. We shall consider how the presence of the second small parameter affects the validity of solutions expressed as power series expansions in $\kappa$. Solutions in the form of power series expansions in $\delta$
will be derived and used to determine the accuracy of the linearized thirteen moment equations in the critical region.

3.2. Formulation of the problem.

Our starting point is the coupled Boltzmann equations for a binary monatomic gas mixture of Maxwell molecules. As these particles have a differential scattering cross-section which is inversely proportional to their relative speed prior to collision, $g_{ij}(g, \theta)$ for $i,j=1,2$ may be written as a function of $\theta$ only. However, we shall find it convenient to express this dependence on scattering geometry in terms of half the complementary angle $\chi$ (Figure 3.1), where

$$\chi = (\pi - \theta)/2$$  \hspace{1cm} (3.1)

![Figure 3.1](image)

Instead of the scatter cross sections $\sigma_{ij}$, the functions $B_{ij}(\chi)$ will be used in the collision integrals of Boltzmann's equations, where

$$B_{ij}(\chi) d\chi d\phi = g_{ij} \frac{d\Omega}{\Omega}$$ \hspace{1cm} (3.2)$$

$$i,j=1,2$$

The velocity distribution functions may be written as

$$f_i(x,v_i,t) = f_{i0}(v_i)[1+h_i(x,v_i,t)]$$ \hspace{1cm} (3.3)

where $f_{i0}$ is the equilibrium distribution function for species $i$ given by

$$f_{i0}(v_i) = n_{i0}(m_i/2\pi k_B T_o)^{3/2} \exp(-m_i v_i^2 / 2 k_B T_o)$$ \hspace{1cm} (3.4)
Departures from equilibrium are assumed to be small so that non-linearities can be neglected. Substituting distribution functions of the form (3.3) into the coupled Boltzmann equations (2.40) and neglecting terms of second order in $h_i$ give the linearized equations for Maxwell molecules,

\[
\left( \frac{\partial}{\partial t} + v_i v_j \right) h_i = f d v_i f_{ij} \int d x d \phi B_{ii} (x) (h_i^r + h_j^\ast - h_i^\ast - h_j^r) \\
+ f d v_i f_{ij} \int d x d \phi B_{ij} (x) (h_i^r + h_j^\ast - h_i^\ast - h_j^r) \quad (i,j=1,2, \ i \neq j)
\]

The problem will be cast in dimensionless form in two stages. Firstly we introduce the dimensionless velocity variables $c_i$, given by

\[
c_i = \left( \frac{m_i}{2 k_B T_0} \right)^{1/2} v_i
\]

(3.5) then becomes,

\[
\left( \frac{\partial}{\partial t} + \left( \frac{2 k_B T_0}{m_i} \right)^{1/2} c_i \right) c_i h_i = f d c_i n_{ic} w(c_i) \int d x d \phi B_{ii} (x) (h_i^r + h_i^\ast - h_i^\ast - h_i^r) \\
+ f d c_i n_{ic} w(c_i) \int d x d \phi B_{ij} (x) (h_i^r + h_j^\ast - h_i^\ast - h_j^r) \quad (3.7)
\]

where

\[
w(c) = \pi^{-3/2} \exp (-c^2)
\]

Secondly the space-time dependence of $h_i$ is assumed to have the harmonic form,

\[
h_i (x, c_i, t) = \hat{h}_i (c_i) \exp \left[ i n_{o} \sigma_0 (\kappa - u_o \omega t) \right]
\]

(3.9) reintroduces the dimensionless wavenumber $\kappa$, defined by (2.15)$R$, and the dimensionless angular frequency of the disturbance $\omega$, defined by (2.15)$A$. From (2.16) and (2.100) the scaling parameter $u_o \sigma_0$ is given by

\[
u_o \sigma_0 = \frac{16}{5} \Omega_{12}(1)
\]
If the collision integral, equation (2.107), is written as an integral over the new variable $\chi$, then for Maxwell molecules

$$u_o \sigma_o = 2\pi \int_0^{\pi/2} B_{12}(\chi) (2\cos^2 \chi) d\chi$$ \hspace{1cm} (3.11)

In this form $u_o \sigma_o$ may be compared with similar expression for eigenvalues of the collision integrals defined below. With the harmonic form (3.9) for $h_1$ and $h_2$, (3.7) becomes

$$(-i\omega+i\kappa,_{20} \frac{1}{2} c_{z1}) \hat{h}_1 = (x_1 I_{11}^1 + x_2 I_{11}^2) \hat{h}_1 + x_2 I_{12} \hat{h}_2$$ \hspace{1cm} (3.12)

$$(-i\omega+i\kappa,_{10} \frac{1}{2} c_{z2}) \hat{h}_2 = x_1 I_{21} \hat{h}_1 + (x_2 I_{22}^2 + x_1 I_{22}^1) \hat{h}_2$$ \hspace{1cm} (3.13)

where the $I$'s are linear collision operators given by

$$I_{ii}^1 \hat{h}_i = \int dc_i w(c_i) / d\chi d\phi F_{ii}(x) \left( \hat{h}_i^1 + \hat{h}_i^2 - \hat{h}_{11} - \hat{h}_{11} \right)$$ \hspace{1cm} (3.14)

$$I_{ij} \hat{h}_j = \int dc_j w(c_j) / d\chi d\phi F_{ij}(x) \left( \hat{h}_j - \hat{h}_{11} \right)$$ \hspace{1cm} (3.15)

In order that the equations (3.12) and (3.13) be written in a more compact form a 2x2 matrix of collision operators is defined,

$$I = \begin{bmatrix} x_1 I_{11}^1 + x_2 I_{11}^2 & x_2 I_{12} \\ x_1 I_{21} & x_2 I_{22}^2 + x_1 I_{22}^1 \end{bmatrix}$$ \hspace{1cm} (3.16)

and terms which correspond with inhomogeneities in the gas are represented by another 2x2 matrix,
Then (3.12) and (3.13) become

\[(I - i\kappa G)^n = -i\omega \hat{h}\]  

(3.18)

where \(\hat{h}\) is a two component function-vector,

\[
\hat{h} = \begin{bmatrix} \hat{h}_1 \\ \hat{h}_2 \end{bmatrix}
\]  

(3.19)

(3.18) has the structure of a perturbed eigenvalue problem in which \(i\kappa G\) may be regarded as a perturbation. As \(|\kappa| \) is of the order of the mean free path divided by the wavelength of the disturbance, at sufficiently long wavelengths the perturbation is small.

3.3. The unperturbed eigenvalue problem

In the long wavelength limit instead of (3.18) we have

\[I \cdot \bar{\psi} = \nu \cdot \bar{\psi}\]  

(3.20)

where \(\bar{\psi}\) is a vector with components \(\psi_1(c_1)\) and \(\psi_2(c_2)\). This equation arises in connection with the linearized coupled Boltzmann equations for a homogeneous gas mixture, i.e. (3.7) with \(Vh = 0\). The latter may be written

\[
\frac{\partial h}{\partial t} = \n_0 \sigma_0 u_0 h
\]  

(3.21)

where

\[
h = \begin{bmatrix} h_1(c_1) \\ h_2(c_2) \end{bmatrix}
\]  

(3.22)

If we seek solutions of this initial value problem of the form

\[h = \bar{\psi} \exp (-t/\tau)\]  

(3.23)
where
\[ \tau = -\frac{1}{n_0 \sigma u v} \] (3.24)
then \( \psi \) and the dimensionless inverse relaxation time \( \nu \), are given by (3.20).

It is essential for the stability of the system that eigenvalues of the collision operator matrix are either zero or negative. This can be demonstrated quite generally without the restriction to Maxwell molecules. We shall briefly summarise the properties of \( I \) making use of Dirac notation in the process.

The unperturbed eigenvalue problem is rewritten as
\[ I \mid \psi \rangle = \nu \mid \psi \rangle \] (3.25)
\( I \) is now an operator which acts on vectors in an infinite dimensional function-vector space. The scalar product is defined by
\[ \langle 0 | 1^\ast \rangle = \frac{3 c_1}{d c_1} \phi_1^*(c_1) \psi_1(c_1) + \frac{3 c_2}{d c_2} \phi_2^*(c_2) \psi_2(c_2) \] (3.26)
where \( \phi_i \) and \( \psi_i \) are arbitrary functions of velocity. Then using arguments which are a straightforward generalisation of those applied to single species gases, it can be shown that \( \langle \phi | I | \phi \rangle \) is real and
\[ \langle \phi | I | \phi \rangle \leq 0 \] (3.27)
Also \( I \) has the symmetry property
\[ \langle \phi | I | \phi \rangle = \langle \psi | I | \phi \rangle^* \] (3.28)
If \( |\phi\rangle \) is replaced by the eigenvector \( |\psi\rangle \) in (3.27) we get
\[ \nu \langle \psi | \psi \rangle \leq 0 \]
From the definition of the scalar product, unless \( \psi_i(c_i) \) is zero for all \( c_i \), \( \langle \psi | \psi \rangle \) is real and greater than zero, therefore \( \nu \) is real and
\[ \nu \leq 0 \] (3.29)

In establishing (3.27) the same transformation properties of the collision integrals are used as those employed in proving Boltzmann's H-theorem. The conclusion (3.29), is closely related to this theorem since it implies that any small homogeneous disturbance in a uniform binary gas
is either permanent or decays monotonically towards an equilibrium state.

It should be emphasised that the above properties hold even when $I$ does not refer to Maxwell molecules. However this is the only interatomic force law for which a complete solution of the unperturbed problem is available. The solution is expressed in terms of eigenfunctions and eigenvalues of the individual linear collision operators (3.14). Sirovich has shown that the eigenfunctions of these operators are Burnett functions $\psi_{r,lm}$, given by

$$
\psi_{r,lm}(c) = \frac{4\pi r! \Gamma\left(\frac{3}{2}\right)}{\Gamma(r+l+\frac{3}{2})} c^l L_{r}^{l+\frac{1}{2}}(c^2) Y_{lm}(\theta, \phi) \tag{3.30}
$$

The associated Laguerre polynomials $L_{r}^{l+\frac{1}{2}}(c^2)$, are defined by

$$
L_{r}^{a}(z) = \frac{1}{r!} z^{-a} e^{z} \frac{d^{r}}{dz^{r}} e^{-z} z^{r+a} \tag{3.31}
$$

and $Y_{lm}(\theta, \phi)$ represents spherical harmonics,

$$
Y_{lm}(\theta, \phi) = (-1)^m \frac{2l+1}{4\pi} \frac{(l-m)!}{(l+m)!} P_{l}^{m}(\cos \theta) e^{i m \phi} \tag{3.32}
$$

$p_{l}^{m}(x)$ are associated Legendre polynomials which are defined by

$$
p_{l}^{m}(x) = \frac{(1-x^2)^{m/2}}{2^{l} l!} \frac{d^{l+m}}{dx^{l+m}} (x^2-1)^l \tag{3.33}
$$

The Burnett functions and spherical harmonics are normalised such that

$$
\int d\Omega \ Y_{lm}^{*}(\theta, \phi) Y_{l'm'}(\theta, \phi) = \delta_{ll'} \delta_{mm'}
$$

and

$$
\int dc \ c \ \psi_{r,lm}(c) \psi_{r,l'm'}(c) = \delta_{rr} \delta_{ll'} \delta_{mm'} \tag{3.34}
$$

In calculations involving plane longitudinal disturbances such as a plane sound wave, the distribution functions are axially symmetric in velocity space. We are therefore mainly interested in using Burnett functions which reflect this symmetry. Burnett functions which are symmetrical about the $z$ axis are defined by (3.30) and (3.32) with $m=0$. 
Whenever the linear collision operators act on Burnett functions
we get

\[
\begin{align*}
I_{ii}^i \psi_{\ell m}(c_i) &= \epsilon_{ii,\ell}^i \psi_{\ell m}(c_i) \\
I_{ij}^i \psi_{\ell m}(c_i) &= \epsilon_{ij,\ell}^j \psi_{\ell m}(c_i) \\
I_{ij}^j \psi_{\ell m}(c_j) &= \epsilon_{ij,\ell}^j \psi_{\ell m}(c_i)
\end{align*}
\]

(3.35)

According to Sirovich \(^{39}\)

\[
\begin{align*}
\epsilon_{ii,\ell}^i &= 2\pi \int_0^{\pi/2} F_{ii}(\chi) \left[ \cos^{2r+\ell} \chi P_{\ell}^0(\cos \chi) + \sin^{2r+\ell} \chi P_{\ell}^0(\sin \chi) - 1 - \delta_{\ell 0} \delta_{\ell 0} \right] d\chi \\
\epsilon_{ij,\ell}^j &= 2\pi \int_0^{\pi/2} F_{ij}(\chi) \left[ (1 - 4m \cos^2 \chi) \right] P_{\ell}^0 \left[ \frac{1 - 2m \cos^2 \chi}{1 - 4m \cos^2 \chi} \right] d\chi \\
\epsilon_{ij,\ell}^j &= 2\pi \int_0^{\pi/2} F_{ij}(\chi) (2m \cos^2 \chi) \left[ \cos^{2r+\ell} \chi P_{\ell}^0(\cos \chi) - \delta_{\ell 0} \delta_{\ell 0} \right] d\chi
\end{align*}
\]

(3.36)

Note that the operator \(I_{ij}\) transforms the variable of the function on which it operates from \(c_j\) to \(c_i\). The eigenvalues do not depend on the subscript \(m\) since the collision operators are independent of azimuthal angle. This means that there is at least a \((2\ell+1)\)-fold degeneracy at each eigenvalue. However a plane longitudinal disturbance may be represented in the subspace of axially symmetric vectors in which this particular degeneracy does not arise.

An eigenfunction-vector of \(I\) has the form

\[
\begin{bmatrix}
ar_{\ell} \psi_{\ell m}(c_1) \\
b_{\ell} \psi_{\ell m}(c_2)
\end{bmatrix}
\]

therefore finding \(a_{\ell}, b_{\ell}\) and \(\nu_{\ell}\) in

\[
\begin{bmatrix}
ar_{\ell} \psi_{\ell m}(c_1) \\
b_{\ell} \psi_{\ell m}(c_2)
\end{bmatrix} = \nu_{\ell}
\begin{bmatrix}
ar_{\ell} \psi_{\ell m}(c_1) \\
b_{\ell} \psi_{\ell m}(c_2)
\end{bmatrix}
\]

(3.37)
leads to the solution of the unperturbed eigenvalue problem. Using (3.16) and (3.35), and dropping Burnett indices for the moment, (3.37) becomes

$$\begin{bmatrix} a & \psi \\ b & \psi \end{bmatrix} = \begin{bmatrix} (a\beta_{11} + b\beta_{12}) & \psi \\ (a\beta_{21} + b\beta_{22}) & \psi \end{bmatrix} = \nu \begin{bmatrix} a & \psi \\ b & \psi \end{bmatrix}$$

(3.38)

where

$$\beta_{ii} = x_i e_{ii}^i + x_j e_{ij}^j \quad \text{and} \quad \beta_{ij} = x_j e_{ij}^i$$

(3.39)

(3.38) is satisfied if

$$\begin{align*}
(\beta_{11} - \nu) a + \beta_{12} b &= 0 \\
\beta_{21} a + (\beta_{22} - \nu) b &= 0
\end{align*}$$

(3.40)

and non-trivial solutions are obtained if

$$\begin{vmatrix} \beta_{11} - \nu & \beta_{12} \\ \beta_{21} & \beta_{22} - \nu \end{vmatrix} = 0$$

(3.41)

Expanding the determinant gives a quadratic in \(\nu\) with two roots given by

$$\nu_\pm = \frac{1}{2} (\beta_{11} + \beta_{22}) \pm \sqrt{\frac{1}{4} (\beta_{11} - \beta_{22})^2 + \beta_{12} \beta_{21}}$$

(3.42)

Thus there are two eigenvalues for each Burnett index. The \(\pm\) suffix denotes the alternative signs in (3.42). Substituting this result back into (3.38) and solving gives

$$\begin{align*}
a_\pm &= \frac{\beta_{12}}{[x_1 (\beta_{12})^2 + x_2 (\beta_{11} - \nu_\pm)^2]^{1/2}} \\
b_\pm &= \frac{\nu_\pm - \beta_{11}}{[x_1 (\beta_{12})^2 + x_2 (\beta_{11} - \nu_\pm)^2]^{1/2}}
\end{align*}$$

(3.43)
where the normalisation

\[ x_1^2 + x_2^2 = 1 \]  

(3.44)

has been used. This normalisation condition is related to the way in which the scalar product is defined, (3.26). Suppose that \( \gamma \) denotes the Burnett indices and the \( \pm \) suffix originating with (3.41): \( \gamma = (r, \ell, m, \pm) \). Then (3.25) can be written as

\[ I | \gamma > = \nu_\gamma | \gamma > \]  

(3.45)

If we require \( | \gamma > \) to be normalised such that

\[ < \gamma | \gamma' > = \delta_{\gamma \gamma} \]  

(3.46)

then (3.44) follows.

We can now state the solution to the initial value problem (3.21). If \( h \) can be expanded in terms of eigenfunction-vectors of \( I \) for \( t \geq 0 \), then

\[ h = \sum_\gamma D_\gamma \exp \left( -t/\tau_\gamma \right) \left[ a_\gamma \psi_\gamma(c_1) \right. \left. + b_\gamma \psi_\gamma(c_2) \right] \]  

(3.47)

where

\[ \tau_\gamma = -1/\sigma_0 \nu_\gamma \]  

(3.48)

\( a_\gamma \) and \( b_\gamma \) are given by (3.43), \( \nu_\gamma \) by (3.42) and the expansion coefficients \( D_\gamma \), depend on the initial conditions.

A few examples of axially symmetric eigenvectors of \( I \) are given in Table 3.1.
Table 3.1

Eigenvectors and eigenvalues of $I$

<table>
<thead>
<tr>
<th>$r \xi \pm$</th>
<th>$\begin{bmatrix} a_{r \xi \pm} &amp; \psi_{r \xi}(c_1) \ b_{r \xi \pm} &amp; \psi_{r \xi}(c_2) \end{bmatrix}$</th>
<th>$\nu_{r \xi \pm}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>00-</td>
<td>$x_2^{-\frac{1}{2}} \begin{bmatrix} 0 \ 1 \end{bmatrix}$</td>
<td>0</td>
</tr>
<tr>
<td>00+</td>
<td>$x_1^{-\frac{1}{2}} \begin{bmatrix} 1 \ 0 \end{bmatrix}$</td>
<td>0</td>
</tr>
<tr>
<td>01-</td>
<td>$m_{12}^{-\frac{1}{2}} \begin{bmatrix} \frac{1}{m_{10}} \psi_{01} \ \frac{1}{m_{20}} \psi_{01} \end{bmatrix}$</td>
<td>0</td>
</tr>
<tr>
<td>01+</td>
<td>$\left(\frac{1}{m_{12}x_1x_2}\right)^{\frac{1}{2}} \begin{bmatrix} m_{20}^2x_2\psi_{01} \ m_{10}^2x_1\psi_{01} \end{bmatrix}$</td>
<td>$-m_{12}$</td>
</tr>
<tr>
<td>10-</td>
<td>$\begin{bmatrix} \psi_{10} \ \psi_{10} \end{bmatrix}$</td>
<td>0</td>
</tr>
<tr>
<td>10+</td>
<td>$(x_1x_2)^{\frac{1}{2}} \begin{bmatrix} \frac{1}{x_1} \psi_{10} \ \frac{1}{x_2} \psi_{10} \end{bmatrix}$</td>
<td>$-2m_{10}m_{20}$</td>
</tr>
</tbody>
</table>
3.4. Physical significance of the coefficients of eigenvectors

The perturbed eigenvalue problem may be written in Dirac notation as

\[(I-iK)|\hat{\mathbf{h}}\> = -i\omega |\hat{\mathbf{h}}\> \quad (3.49)\]

For a plane longitudinal disturbance \(|\hat{\mathbf{h}}\>\) can be expanded in terms of those eigenvectors of \(I\) that possess axial symmetry. If we denote the latter by \(|\alpha\>\) then

\[|\hat{\mathbf{h}}\> = \sum_{\alpha} B_{\alpha} |\alpha\> \quad (3.50)\]

Here, as elsewhere, the omission of the Burnett index \(m\), implies that it is zero. The coefficients in the expansion are given by the inversion formula

\[B_{\alpha} = \langle \alpha | \hat{\mathbf{h}} \rangle \quad (3.51)\]

and are closely related to the dimensionless moment amplitudes of Chapter 2. In order to make the physical significance of the present terminology clearer we shall point out some of these relationships.

For example, using the first two eigenvectors from Table 3.1 and our prescription for the scalar product, (3.51) becomes

\[B_{00-} = \frac{x_2}{2} \int dc_2 w(c_2) \hat{n}_2 \]
\[B_{00+} = \frac{x_1}{2} \int dc_1 w(c_1) \hat{n}_1 \quad (3.52)\]

These may be shown to be proportional to the number density amplitudes \(\hat{n}_i (i=1,2)\), equation (2.12). With the distribution functions of harmonic form

\[n_i = n_0 x_i (1+n_i e^{i\theta}) = \int dv_i f_{i0}(v_i) (1+n_i e^{i\theta}) \quad (3.53)\]

Transforming the variable of integration using (3.6) gives

\[\hat{n}_i = \int dc_i w(c_i) \hat{n}_i \quad (3.54)\]

Comparing (3.54) with (3.52) we have
The governing equation for $B_{00+}$ is found by taking the scalar product of $<00+|$ with (3.49). Using the symmetry property of the collision operator (3.28), $I_1^j$ may be made to act on $|00+>$ rather than $|00>$ but as the eigenvalue $v_{00+}$ is zero the collision term vanishes and the equation for $B_{00+}$ takes the form appropriate to a conserved quantity,

$$-i\omega B_{00+} + i\kappa E B <00+|C|\alpha> = 0$$

(3.56) is the equivalent of (2.127)

Similarly other components of $|\hat{\alpha}>$ may be identified with dimensionless amplitudes. The four coefficients of vectors with zero eigenvalue in the expansion (3.50) correspond to the four conserved quantities which arise when a plane longitudinal disturbance in a binary gas is analysed. The conserved quantities are the two particle populations, the longitudinal momentum and the kinetic energy. Of those components associated with non-conserved quantities $B_{10+}$ is of particular interest in disparate mass mixtures. Using the two-component function-vector corresponding to $|10+>$ (Table 3.1), the scalar product (3.51) becomes

$$B_{10+} = (x_1 x_2)^{1/2} \left\{ \int d_1 w(c_1) \psi_{10+}^1 - \int d_2 w(c_2) \psi_{10+}^2 \right\}$$

where $\psi_{10+} = \frac{2}{3} \frac{2}{3} \left( \frac{3}{2} - c^2 \right)$

It is found that $B_{10+}$ is proportional to the temperature difference amplitude. In order to show this, the defining equation for the species kinetic temperature (2.82), is used to express the temperature difference $\Delta$, as

$$k_B \Delta = k_B T_0 \Delta e^{i\theta} = \frac{1}{n_1} \int dv_1 f_1 (\frac{1}{m_1} v_1^2) \frac{1}{n_2} \int dv_2 f_2 (\frac{1}{m_2} v_2^2)$$

where advantage has been taken of the linear approximation to write $v_1$
and $v_2$ in place of the peculiar velocities $C_1$ and $C_2$. Transforming velocity variables using (3.6) and using the harmonic form (3.9), gives

$$\lambda = -\frac{2}{3} \int dc_1 w(c_1) \frac{3}{2} \hat{c}^2 - \int dc_2 w(c_2) \frac{3}{2} \frac{c_2^2}{c_2^2}$$

Comparing with (3.57) we find

$$B_{10^+} = -\left(\frac{3}{2}\right)^{\frac{1}{2}} (x_1^2 x_2^2) \hat{\lambda}$$

Since $B_{10^+}$ and $\hat{\lambda}$ are proportional to one another, the negative of $v_{10^+}$, Table 2.1, and the dimensionless inverse relaxation time for the temperature difference (2.139), are the same. Similarly $B_{01^+}$ is found to be proportional to the diffusion velocity amplitude $\hat{w}$, and $v_{01^+}$ equal to the inverse relaxation time $v_w$ (2.138).

Also note that in the linear approximation the thirteen-moment representation of the distribution functions for binary monatomic gas mixtures can be expressed as an expansion in eigenvectors of $A$. In the case of a plane longitudinal disturbance, the thirteen moments per species reduces to a total of ten which can be completely represented in the subspace spanned by $|00->, |00>, |01->, |01>, |10->, |10>, |02->, |02>, |11->$ and $|11+>$. In Section 3.9 we shall examine the accuracy of a solution confined to the thirteen-moment sub-space.

3.5. Matrix elements of the perturbation

In using Rayleigh-Schrödinger perturbation theory to find an approximate solution of (3.49) we shall need to know the matrix elements of the perturbation operator $C$, given by (3.17), with respect to eigenvectors of the unperturbed operator $I$. With the eigenvectors having the form given in (3.37), matrix element of $C$ are given by
\[ C_{YY'} = \langle \gamma | C | \gamma' \rangle = x_1 \int_{\Omega} d\omega (c_1) a_\gamma^* (m_{20} c_{01} a_\gamma) \psi_{\gamma - 1} x_2 \int_{\Omega} d\omega (c_2) b_{\gamma'}^* (m_{10} c_{02} b_{\gamma'}) \psi_{\gamma'} \]

\[ = (a_\gamma a_{\gamma - 1} m_{20} x_1 + b_{\gamma'} b_{\gamma - 1} m_{10} x_2) \Xi_{\gamma \gamma'} \] (3.62)

where

\[ \gamma \equiv (r, \ell, m, \pm), \quad \gamma' \equiv (\ell', \ell', m', \pm) \]

and

\[ \Xi_{\gamma \gamma'} = \int_{\Omega} d\omega (c) \psi_{\gamma}^* c_{\gamma'} \psi_{\gamma} \] (3.63)

(3.63) may be evaluated with the aid of the recursion relationship

\[ c_{\gamma r,\ell,m} = \left[ \frac{(r+\ell+3/2)(\ell+m+1)(\ell-m+1)}{(2\ell+1)(2\ell+3)} \right]^{\frac{1}{2}} \psi_{r,\ell+1,m} 

- \left[ \frac{r(\ell+m+1)(\ell-m+1)}{(2\ell+1)(2\ell+3)} \right]^{\frac{1}{2}} \psi_{r-1,\ell+1,m} 

+ \left[ \frac{(r+\ell+1)(\ell+m)(\ell-m)}{(2\ell+1)(2\ell-1)} \right]^{\frac{1}{2}} \psi_{r,\ell-1,m} 

- \left[ \frac{(r+1)(\ell+m)(\ell-m)}{(2\ell+1)(2\ell-1)} \right]^{\frac{1}{2}} \psi_{r+1,\ell-1,m} \] (3.64)

A derivation of (3.64) is given in Appendix 3A. Combining (3.63) and (3.64) we get

\[ \Xi_{r,\ell,m,r',\ell',m'} = \left[ \frac{(r+\ell+3/2)(\ell+m+1)(\ell-m+1)}{(2\ell+1)(2\ell+3)} \right]^{\frac{1}{2}} \delta_{r,-r,m,-m} 

- \left[ \frac{r(\ell+m+1)(\ell-m+1)}{(2\ell+1)(2\ell+3)} \right]^{\frac{1}{2}} \delta_{r-1,r,m,m} 

+ \left[ \frac{(r+\ell+1)(\ell+m)(\ell-m)}{(2\ell+1)(2\ell-1)} \right]^{\frac{1}{2}} \delta_{r,r,m,m} 

- \left[ \frac{(r+1)(\ell+m)(\ell-m)}{(2\ell+1)(2\ell-1)} \right]^{\frac{1}{2}} \delta_{r+1,r,m,m} \] (3.65)

Matrix elements with respect to axially symmetric eigenvectors are found from the above relationships by putting \( m = 0 \). Instead of (3.62) - (3.65) we have

\[ C_{\alpha\alpha'} = \langle \alpha | C | \alpha' \rangle = (a_\alpha a_{\alpha - 1} m_{20} x_1 + b_\alpha b_{\alpha - 1} m_{10} x_2) \Omega_{\alpha\alpha'} \] (3.66)
where
\[ \alpha = (r, \ell, \pm), \quad \alpha^\prime = (r^\prime, \ell^\prime, \pm), \]

\[ \Omega_{\alpha\alpha^\prime} = \int \psi_{\alpha} \psi_{\alpha^\prime} \]

and

\[ \Omega_{\ell, \ell, \ell^\prime, \ell^\prime} = (\ell + 1) \left[ \frac{r^{\ell + \frac{3}{2}}}{(2\ell + 1)(2\ell + 3)} \right]^{1/2} \delta_{r, r^\prime} \delta_{\ell, \ell^\prime} - (\ell + 1) \left[ \frac{r}{(2\ell + 1)(2\ell + 3)} \right]^{1/2} \delta_{r, -1, r^\prime} \delta_{\ell + 1, \ell^\prime} + \ell \left[ \frac{r^{\ell + \frac{1}{2}}}{(2\ell + 1)(2\ell - 1)} \right]^{1/2} \delta_{r, r^\prime} \delta_{\ell - 1, \ell^\prime} \]

The first few matrix elements \( \Omega_{\alpha\alpha^\prime} \) are given in Table 3.2.
## TABLE 3.2. Matrix elements of the perturbation

<table>
<thead>
<tr>
<th>r, l, ±</th>
<th>00-</th>
<th>00+</th>
<th>01-</th>
<th>01+</th>
<th>10-</th>
<th>10+</th>
<th>02-</th>
<th>02+</th>
<th>11-</th>
</tr>
</thead>
<tbody>
<tr>
<td>00-</td>
<td>.</td>
<td>.</td>
<td>m\frac{m_{10}^{+}x_{2}^{+}}{2m_{12}}</td>
<td>m\frac{x_{1}^{-}}{m_{12}}</td>
<td>.</td>
<td>.</td>
<td>.</td>
<td>.</td>
<td>.</td>
</tr>
<tr>
<td>00+</td>
<td>.</td>
<td>.</td>
<td>m\frac{m_{10}^{+}x_{2}^{+}}{2m_{12}}</td>
<td>m\frac{x_{2}^{-}}{m_{12}}</td>
<td>.</td>
<td>.</td>
<td>.</td>
<td>.</td>
<td>.</td>
</tr>
<tr>
<td>01-</td>
<td>m\frac{m_{10}^{+}x_{2}^{+}}{2m_{12}}</td>
<td>m\frac{m_{10}^{+}x_{2}^{+}}{2m_{12}}</td>
<td>.</td>
<td>.</td>
<td>m\frac{m_{10}^{+}x_{2}^{+}}{2m_{12}}</td>
<td>.</td>
<td>.</td>
<td>c_{01-,02-}</td>
<td>c_{01-,02+}</td>
</tr>
<tr>
<td>01+</td>
<td>-m\frac{x_{1}^{+}}{m_{12}}</td>
<td>m\frac{x_{2}^{+}}{m_{12}}</td>
<td>.</td>
<td>.</td>
<td>-m\frac{x_{1}^{+}x_{2}^{+}}{3m_{12}}</td>
<td>m\frac{m_{10}^{+}x_{2}^{+}}{2m_{12}}</td>
<td>m\frac{m_{12}^{+}}{3}</td>
<td>c_{01+,02-}</td>
<td>c_{01+,02+}</td>
</tr>
<tr>
<td>10-</td>
<td>.</td>
<td>.</td>
<td>-m\frac{m_{10}^{+}x_{2}^{+}}{3m_{12}}</td>
<td>-m\frac{x_{1}^{+}x_{2}^{+}}{3m_{12}}</td>
<td>m\frac{m_{10}^{+}x_{2}^{+}}{2m_{12}}</td>
<td>.</td>
<td>.</td>
<td>.</td>
<td>c_{10-,11-}</td>
</tr>
<tr>
<td>10+</td>
<td>.</td>
<td>.</td>
<td>.</td>
<td>.</td>
<td>-m\frac{m_{12}^{+}}{3}</td>
<td>.</td>
<td>.</td>
<td>.</td>
<td>c_{10+,11-}</td>
</tr>
<tr>
<td>02-</td>
<td>.</td>
<td>.</td>
<td>c_{02-,01-}</td>
<td>c_{02-,01+}</td>
<td>.</td>
<td>.</td>
<td>.</td>
<td>.</td>
<td>c_{02-,11-}</td>
</tr>
<tr>
<td>02+</td>
<td>.</td>
<td>.</td>
<td>c_{02+,01-}</td>
<td>c_{02+,01+}</td>
<td>.</td>
<td>.</td>
<td>.</td>
<td>.</td>
<td>c_{02+,11-}</td>
</tr>
<tr>
<td>11-</td>
<td>.</td>
<td>.</td>
<td>.</td>
<td>.</td>
<td>.</td>
<td>.</td>
<td>.</td>
<td>.</td>
<td>c_{11-,10-}</td>
</tr>
<tr>
<td>11+</td>
<td>.</td>
<td>.</td>
<td>.</td>
<td>.</td>
<td>.</td>
<td>.</td>
<td>.</td>
<td>.</td>
<td>c_{11+,10-}</td>
</tr>
</tbody>
</table>
3.6. The perturbed eigenvalue problem

Following standard perturbation theory we suppose that when $|\kappa|$ is small a power series expansion in $(-i\kappa)$ exists for both $(-i\omega)$ and $|\psi>$ in a continuous range of $\kappa$. Then

$$-i\omega = \omega^{(0)} + (-i\kappa)\omega^{(1)} + (-i\kappa)^2\omega^{(2)} + (-i\kappa)^3\omega^{(3)} + \ldots$$  \hfill (3.69)

and

$$|\psi> = |\psi^{(0)}> + (-i\kappa)|\psi^{(1)}> + (-i\kappa)^2|h^{(2)}> + (-i\kappa)^3|h^{(3)}> + \ldots$$  \hfill (3.70)

Eventually (3.69) will be used to express $\kappa$ as a power series in $\omega$ for acoustic modes since comparisons with experiment are easier if the frequency is the independent variable. Substituting the expansions into (3.49) and equating coefficients gives a set of equations for successively higher order terms in the perturbation series

\[
\begin{align*}
(I - \omega^{(0)}) |\psi^{(0)}> &= 0 \quad \text{(A)} \\
(I - \omega^{(0)}) |\psi^{(1)}> &= (\omega^{(1)} - C)|\psi^{(0)}> \quad \text{(B)} \\
(I - \omega^{(0)}) |\psi^{(2)}> &= (\omega^{(1)} - C)|\psi^{(1)}> + \omega^{(2)}|\psi^{(0)}> \quad \text{(C)} \\
(I - \omega^{(0)}) |\psi^{(3)}> &= (\omega^{(1)} - C)|\psi^{(2)}> + \omega^{(2)}|\psi^{(1)}> + \omega^{(3)}|\psi^{(0)}> \quad \text{(D)}
\end{align*}
\]

(3.71)

If the suffix $k$ denotes individual independent solutions of (3.71) then a solution of the $n$th order equation $|\psi^{(n)}>$, $n \geq 1$ has a zero order counterpart written as $|\psi^{(0)}>$. At this point $|\psi^{(n)}>$ may have an arbitrary multiple of $|\psi^{(0)}>$ added to it and the sum remains a solution of the $n$th order equation by virtue of (3.71)A. In order to ensure that $|\psi^{(n)}>$ is unique this arbitrary multiple is chosen such that

$$<\psi^{(0)}|\psi^{(n)}> = 0 \quad n \geq 1$$  \hfill (3.72)

By taking the scalar product of $<\psi^{(0)}|$ with the $n$th order equation and using the symmetry property (3.28), the left hand side vanishes in accordance with (3.71)A. Hence the inhomogeneous terms are orthogonal to
corresponding solutions of the homogeneous equation (3.71)A. If an
N-fold degeneracy occurs at zero order such that

\[ \omega_i^{(0)} = \omega_j^{(0)} \quad i = 1, 2, \ldots, j, \ldots, N \]  \hspace{1cm} (3.73)

then this orthogonality condition gives rise to N equations of the form

\[ \langle h_i^{(0)} | \omega_j^{(1)} - \omega_j^{(2)} h_j^{(n-1)} + \omega_j^{(3)} h_j^{(n-3)} \rangle + \]

\[ \cdots + \omega_j^{(n)} \delta_{ij} = 0 \]  \hspace{1cm} (3.74)

where zero order solutions are normalised according to

\[ \langle h_i^{(0)} | h_j^{(0)} \rangle = \delta_{ij} \]  \hspace{1cm} (3.75)

At order n (\( \geq 1 \)) we shall use (3.74) to determine \( \omega_j^{(n)} \) and in the event of an N-fold degeneracy at zero order, to find N-1 of the coefficients in an expansion for \( |h_j^{(n-1)}\rangle \).

For a plane longitudinal disturbance such as a plane sound wave, the solutions may be confined to the subspace of axially symmetric eigenvectors of \( I \). With this restriction there is at zero order an infinite number of non-degenerate elementary solutions for which the unperturbed eigenvalues do not vanish and a four-fold degeneracy with zero eigenvalue (Section 3.3). Identifying \( \omega^{(0)} \) from (3.71)A with the unperturbed or zero order eigenvalues, we find that the first term in the generalised complex dispersion relationship (3.69), vanishes for the degenerate solution \( |\sigma\rangle \) say, where

\[ I |\sigma\rangle = \nu_{\sigma} |\sigma\rangle \]  \hspace{1cm} (3.76)

\( \nu_{\sigma} = 0 \) and \( \sigma \equiv (00^+), (00^-), (01^-), (10^-) \)

These solutions are closely related to the four longitudinal hydrodynamic modes since each hydrodynamic dispersion law, when expressed as a power
A general zero order solution with zero eigenvalue can be expressed as a linear combination of the \( |\sigma> \). Four such linear combinations can be used to construct a new orthonormal basis \( |s> \), in the degenerate subspace,

\[
|s> = \sum D_{s\sigma}^{|\sigma>} \quad s = 1,2,3,4
\]  

(3.77)

An arbitrary basis set of the form (3.77) will satisfy (3.71)A with \( \omega^{(0)} = 0 \) but if the \( |s> \) are to be the correct zero order solutions for the given perturbation, the coefficients \( D_{s\sigma}^{|\sigma>} \) must be such that \( |s> \) satisfies the orthogonality condition (3.74) with \( n=1 \). This condition may be written as

\[
<\sigma^-|\omega^{(1)}_s - C|s> = 0 \quad A
\]

or

\[
<\sigma^-|\omega^{(1)}_s - C|s> = 0 \quad B
\]

(3.78)

where \( \sigma^- \) and \( s^- \) take the same values as \( \sigma \) and \( s \) respectively. With \( |s> \) given by (3.77), (3.78)B becomes

\[
\sum_{\sigma} \left[<\sigma^-|C|\sigma> - \omega^{(1)}_s \delta_{\sigma\sigma^-}\right] D_{s\sigma} = 0
\]

(3.79)

In dealing with the degeneracy we are led to a subsidiary 4x4 eigenvalue problem (3.79), which gives first order contributions to \( \omega \) as well as the zero order solutions in the degenerate subspace. Using the matrix elements \( C_{\sigma\sigma^-} \) from Table 3.2, (3.79) becomes
Setting the determinant of the 4x4 matrix equal to zero gives the secular equation

\[ [\omega(1)]^2 \{ [\omega(1)]^2 - \frac{5m_{10}m_{20}}{6m_{12}} \} = 0 \]  

(3.81)

with roots

\[ \omega_1 = \left( \frac{5m_{10}m_{20}}{6m_{12}} \right)^{1/2}, \quad \omega_2 = -\left( \frac{5m_{10}m_{20}}{6m_{12}} \right)^{1/2}, \quad \omega_3 = \omega_4 = 0 \]  

(3.82)

Substituting these back into (3.79) and solving gives

\[
\begin{align*}
\text{s=1: } & |1\rangle = \left( \frac{3x_2}{10} \right)^{1/2} |00\rangle + \left( \frac{3x_1}{10} \right)^{1/2} |00\rangle + \left( \frac{1}{2} \right)^{1/2} |01\rangle \rightarrow \left( \frac{1}{5} \right)^{1/2} |10\rangle \rightarrow A \\
\text{s=2: } & |2\rangle = -\left( \frac{3x_2}{10} \right)^{1/2} |00\rangle - \left( \frac{3x_1}{10} \right)^{1/2} |00\rangle + \left( \frac{1}{2} \right)^{1/2} |01\rangle \rightarrow + \left( \frac{1}{5} \right)^{1/2} |10\rangle \rightarrow B
\end{align*}
\]  

(3.83)

For \( s = 3,4 \) \( \omega_s^{(1)} = 0 \) and we get

\[ D_{01-,s} = 0 \]  

A

and

\[ \frac{x_2^{1/2}}{\left( \frac{2}{5} \right)^{1/2}} D_{00-,s} + \frac{x_1^{1/2}}{\left( \frac{2}{5} \right)^{1/2}} D_{00+,s} - \frac{1}{\left( \frac{3}{5} \right)^{1/2}} D_{10-,s} = 0 \]  

B

(3.84)

Solutions 1 and 2 represent acoustic disturbances travelling in the
positive and negative z-directions respectively. \( \omega^{(1)}_1 \) may be recognised as the dimensionless Laplacian speed of sound for a binary mixture of monatomic gases. This, and other results given above, are equivalent to what was found from the Euler equations, for example (3.84) may be identified with (1.65). We can anticipate that 3 and 4 are the non-propagating longitudinal hydrodynamic modes, the diffusion mode and the thermal mode.

3.7. Non-propagating modes

3.7.1. The diffusion and temperature modes

Because of the degeneracy at first order (i.e. \( \omega^{(1)}_3 = \omega^{(1)}_4 = 0 \)), \(|3>\) and \(|4>\) are not yet fully defined. However there is a standard procedure\(^{41}\) that usually will remove the remaining degeneracy at second order and determine the components of \(|3>\) and \(|4>\). In addition the procedure yields second order contributions to the eigenvalues for these modes. We find (see Appendix 3B) that

\[
\omega^{(1)}_3 = -\frac{3}{2} \frac{C^{2}}{v_{10+}} = \frac{1}{2} \quad (3.85)
\]

\[
\omega^{(1)}_4 = -\frac{3}{5} \left( \frac{C^{2}}{v_{11-}} + \frac{C^{2}}{v_{11+}} \right) \quad (3.86)
\]

\[
|3> = (x_2)^{\frac{1}{2}} |00> - (x_1)^{\frac{1}{2}} |00> \quad (3.87)
\]

and

\[
|4> = (-\frac{1}{5}) \left( \frac{2x_1}{2} \right)^{\frac{1}{2}} |00> + (-\frac{2}{5}) \left( \frac{2x_2}{1} \right)^{\frac{1}{2}} |00> + (\frac{3}{5})^{\frac{1}{2}} |10> \quad (3.88)
\]

Thus to second order in \( \kappa \)

\[
\omega_3 = -i\kappa^2/2 + O(\kappa^3) \quad (3.89)
\]

and

\[
\omega_4 = i\kappa^2 \frac{3}{5} \left( \frac{C^{2}}{v_{11-}} + \frac{C^{2}}{v_{11+}} \right) + O(\kappa^3) \quad (3.90)
\]
These are dispersion relationships for longitudinal hydrodynamic modes and may be compared with the corresponding equations found from hydrodynamics. The coefficients in (3.87) indicate that mode 3 is a disturbance in which the number density amplitudes are in antiphase at zero order as is the case for the diffusion mode. Restoring the dimensions to (3.89) and identifying it with the dispersion relationship for the diffusion mode, (1.91), implies that

\[ D_{12} = - \frac{3}{2} \frac{C_{10^+,01^+}^2}{v_{01^+}} \left( \frac{u_o}{n_0 \sigma_o} \right) = \frac{u_o}{2n_0 \sigma_o} \]  

(3.91)

Likewise comparing (3.90) with (1.90) shows that

\[ \lambda/k_B = - \frac{3}{2} \left( \frac{C_{11^-,01^-}^2}{v_{11^-}} + \frac{C_{11^+,01^-}^2}{v_{11^+}} \right) \left( \frac{u_o}{n_0 \sigma_o} \right) \]  

(3.92)

Using (3.91) and (3.92) transport coefficient of the mixture can be related to the parameters which define the interatomic potentials.

### 3.7.2. Transverse modes

It would be useful to have available an expression for the coefficient of shear viscosity in terms of matrix elements of the perturbation. One way of deriving this relationship is to take a hint from our derivation of hydrodynamic modes and consider transverse disturbances. As we saw in Chapter 1, these decouple from each other and from the longitudinal hydrodynamic modes. In the present terminology this is a consequence of the axial symmetry of \( I_i C \).

Of the two independent transverse hydrodynamic modes we shall consider the one whose zero order contribution is \( |\pi> \), where \( \pi=(0,1,1,-) \). \( |\pi> \) satisfies

\[ I|\pi> = \nu_\pi |\pi> \]  

(3.93)

with \( \nu_\pi = 0 \)
In order to identify the shear viscosity coefficient it is necessary to determine the dispersion relationship for $\omega$ to second order in $\kappa$.

Because the unperturbed eigenvalue $\nu_\pi$ is zero, the zero order term in (3.69) vanishes for this, as for the other hydrodynamic modes. The first order coefficient is found by applying the orthogonality condition (3.74) with $n=1$, for the particular case where $|h_1^{(0)}>=|h_2^{(0)}>=|\pi>$. This gives

$$\omega^{(1)}_\pi = \langle \pi |C|\pi> = 0,$$

(3.94A)

the matrix element vanishing in accordance with (3.62) and (3.63).

Applying the orthogonality condition (3.74), to the inhomogeneous term in the second order equation (3.71)C, gives

$$\omega^{(2)}_\pi = \langle \pi |C|h_\pi^{(1)}>$$

(3.94B)

If $|h_\pi^{(1)}>$ is expanded in basis vectors and the expansion coefficients found from the first order equation (3.71)B, in the usual way, we get

$$|h_\pi^{(1)}> = \sum_{\gamma} \frac{\langle \gamma |C|\pi>}{\nu_\gamma} |\gamma>$$

(3.95)

Referring to our formulae for the matrix elements, (3.62) and (3.63), we find that only two terms in the summation do not vanish and when the result is substituted into equation (3.94B) we get

$$\omega^{(2)}_\pi = - \frac{\langle 0,2,1,-|C|0,1,1,->^2}{\nu_{02-}} + \frac{\langle 0,2,1,+|C|0,1,1,->^2}{\nu_{02+}}.$$ 

(3.96)

or in terms of matrix elements with respect to axially symmetric vectors,

$$\omega^{(2)}_\pi = - \frac{3}{4} \left[ \frac{c_{02-,01-}^2}{\nu_{02-}} + \frac{c_{02+,01-}^2}{\nu_{02+}} \right].$$ 

(3.97)

Thus the dimensionless dispersion relationship for hydrodynamic shear modes is
Comparing (3.98) and (1.89) we find that the coefficient of shear viscosity is given by

\[
\eta/\rho_0 = -\frac{3}{4} \left[ \frac{C^{2}_{02-,01-}}{v_{02-}} + \frac{C^{2}_{02+,01-}}{v_{02+}} \right] \left( \frac{u_0}{n_0 \sigma_0} \right) 
\]

(3.99)

The viscosity coefficient is thus related to atomic parameters.

3.8. Dispersion and absorption coefficient of the acoustic modes

That solution of the first order equation (3.71)B which is associated with a sound wave propagating in the positive z direction, may be written in the general form

\[
|h_1^{(1)}\rangle = A^{(1)}_{21} |2\rangle + A^{(1)}_{31} |3\rangle + A^{(1)}_{41} |4\rangle + \sum_{\beta \neq \sigma} a^{(1)}_{\beta1} |\beta\rangle 
\]

(3.100)

In view of the orthogonality condition (3.72), |1\rangle is omitted from the expansion. The coefficients in the summation are found by substituting for |h_{\beta}^\langle\rangle in the first order equation, (3.71)B, and taking the scalar product with |\beta\rangle, \beta \neq \sigma.

Thus

\[
a^{(1)}_{\beta1} = -\langle \beta | C | 1 \rangle / \nu_{\beta} \]

(3.101)

The A^{(1)}'s are found from the orthogonality condition on the inhomogeneous term in the second order equation, that is, we consider a special case of (3.74) in which n=2, |h_{1}^{(0)}\rangle = |s\rangle and |h_{j}^{(0)}\rangle = |l\rangle:

\[
<s | \omega^{(1)}_{1} - C | h_{1}^{(1)} \rangle + \omega^{(2)}_{1} \delta_{1s} = 0 
\]

(3.102)

Substituting for |h_{1}^{(1)}\rangle using the general form (3.100) leads to expressions for \omega^{(2)}_{1}, A^{(1)}_{21}, A^{(1)}_{31} and A^{(1)}_{41}, in terms of matrix elements of the perturbation. The matrix elements can then be eliminated in favour of
first order transport coefficients of the mixture using (3.91), (3.92)
and (3.99). These steps are given in detail in Appendix 3C together
with the evaluation of (3.101). The results are as follows:

\[
\omega_1^{(2)} = \left[ \frac{2}{3} \rho_o + \frac{2}{15} \frac{\lambda}{n-o-k_B} + \frac{5}{6} D_{12} x_1 x_2 \left( \frac{m_2-m_1}{m_1 x_1 + m_2 x_2} \right)^2 \right] \frac{n_o \sigma_o}{u_o}
\]
or

\[
\omega_1^{(2)} = \Gamma \frac{n_o \sigma_o}{u_o}
\]

where \( \Gamma \) is given by (1.85)

\[
A_{21}^{(1)} = \left( \frac{2}{3} \right) \rho_o - \frac{2}{15} \frac{\lambda}{n-o-k_B} - \frac{5}{6} D_{12} x_1 x_2 \left( \frac{m_2-m_1}{m_1 x_1 + m_2 x_2} \right)^2 \frac{n_o \sigma_o}{u_o}
\]

\[
A_{31}^{(1)} = \frac{5}{6} D_{12} (x_1 x_2)^{\frac{1}{2}} \left( \frac{m_2-m_1}{m_1 x_1 + m_2 x_2} \right)^{\frac{1}{2}} \frac{n_o \sigma_o}{u_o}
\]

and

\[
A_{41}^{(1)} = - \frac{2\sqrt{3}}{15} \frac{\lambda}{k_B} \frac{\sigma_o}{u_o}
\]

From the evaluation of (3.101)

\[
a_{01+1}^{(1)} = \left( \frac{5}{4} \right)^{\frac{1}{2}} \frac{c_{01+,10-}}{v_{01+}}
\]

\[
a_{02-,1}^{(1)} = - \left( \frac{1}{2} \right)^{\frac{1}{2}} \frac{c_{02-,01+}}{v_{02+}}
\]

\[
a_{01+1}^{(1)} = - \left( \frac{1}{2} \right)^{\frac{1}{2}} \frac{c_{02+,01-}}{v_{02-}}
\]

\[
a_{11-,1}^{(1)} = \left( \frac{5}{4} \right)^{\frac{1}{2}} \frac{c_{11-,10+}}{v_{11-}}
\]

\[
a_{11+,1}^{(1)} = \left( \frac{5}{4} \right)^{\frac{1}{2}} \frac{c_{11+,10-}}{v_{11+}}
\]

This completes the solution of the first order equation. By following
a similar procedure, higher order terms in the perturbation series can be
found. However we shall go no further than the calculation of \( \omega_1^{(3)} \).

This third order coefficient in the series expansion for \( \omega \) is found
from the orthogonality condition on the inhomogeneous term in the third
order equation, (3.74) with \( n=3 \) and \( |h_{1}^{(0)}> = |h_j^{(0)}> = |1> \):

\[
<1|\omega_1^{(1)} - C|h_{1}^{(2)}> + \omega_1^{(3)} = 0
\]

(3.108)
Rather than evaluating this by constructing a series expansion for $|h^{(2)}_1\rangle$, we can eliminate $|h^{(2)}_1\rangle$ in favour of $|h^{(1)}_1\rangle$. Reversing the roles of $|1\rangle$ and $|h^{(2)}_1\rangle$ in (3.108) and substituting for $(\omega^{(1)}_1-C)|1\rangle$ using the first order equation, (3.71)B, gives

$$<h^{(2)}_1|I|h^{(1)}_1\rangle + \omega^{(3)}_1 = 0$$

(3.109)

Taking advantage of the symmetry property of $I$, (3.28), and substituting for $I|h^{(2)}_1\rangle$ from the second order equation, (3.71)C, gives

$$\omega^{(3)}_1 = -<h^{(1)}_1|\omega^{(1)}_1 - C|h^{(1)}_1\rangle$$

$$= (2[A^{(1)}_{21}]^2 + [A^{(1)}_{31}]^2 + [A^{(1)}_{41}]^2 - \frac{1}{\Sigma} \frac{\Sigma C|1\rangle)^2}{\Sigma C|1\rangle^2}$$

$$+ \Sigma \Sigma \frac{\Sigma C|1\rangle^2}{\Sigma C|1\rangle^2}$$

(3.110)

$\beta, \alpha \neq \sigma$

The summations are evaluated using an identity for $C|1\rangle$, equation (3C.2) of Appendix 3C. By referring to Table 3.2, non-vanishing terms in the double summation can easily be identified. Also formulas (3.104), (3.105) and (3.106) for the $A^{(1)}$'s are used to get

$$\frac{u_o^2}{n_o \sigma_o} \frac{2}{n_o \rho_o} \frac{\omega^{(1)}_1}{\omega^{(1)}_1} = \frac{2}{2} \frac{n_o}{5} - \frac{2}{15} \frac{\lambda}{n_o k_B} - \frac{5}{6} \frac{1}{n_o k_B} \frac{m_x - m_o}{x_2} \left(\frac{m_x}{x_1 + m_x x_2}\right)^2$$

$$+ \frac{5}{6} \frac{p^2}{12} \frac{x_2}{x_2} \left(\frac{m_x - m_o}{x_1 + m_x x_2}\right)^2 \left[1 \frac{5}{3} \frac{m_x}{x_1 + m_x x_2} \right] + 4 \frac{\lambda}{75} \left(\frac{\lambda}{n_o k_B}\right)^2$$

$$- \left\{ \frac{1}{2} \frac{C^{22,-01}}{\nu_{02}} + \frac{C^{22,+01}}{\nu_{02}} - \frac{C^{11,-10}}{\nu_{11}} + \frac{C^{22,+10}}{\nu_{11}} \right\} \frac{u_o^2}{n_o \sigma_o}$$

$$- \left\{ \frac{5}{2} \frac{C^{01,+10}}{\nu_{01}} - \frac{C^{01,+02}}{\nu_{02}} - \frac{C^{02,-01}}{\nu_{02}} - \frac{C^{02,-02}}{\nu_{02}} - \frac{C^{02,+01}}{\nu_{02}} \right\}$$

$$+ \left\{ \frac{5}{2} \frac{C^{02,-01}}{\nu_{02}} - \frac{C^{02,-11}}{\nu_{11}} + \frac{C^{02,-11}}{\nu_{11}} + \frac{C^{02,-11}}{\nu_{11}} + \frac{C^{02,+11}}{\nu_{11}} + \frac{C^{02,+11}}{\nu_{11}} \right\} \frac{u_o^2}{n_o \sigma_o} \omega^{(1)}_1$$

(3.111)
(3.111) gives us the third coefficient in the power series expansion, (3.69), for $\omega$ in terms of $\kappa$ for the case of an acoustic mode. Experimentally it is usually $\omega$ that is known, therefore comparison with experiment is more readily made with $\kappa$ written as a power series in $\omega$.

Noting that $\omega^{(0)} = 0$ the inverted series is

$$\kappa = \omega/\omega^{(1)} + i\left[\frac{\omega^{(2)}}{[\omega^{(1)}]^3}\right] \omega^2 - \left[\frac{2[\omega^{(1)}]^2 - \omega^{(1)} \omega^{(3)}}{[\omega^{(1)}]^5}\right] \omega^3 + \ldots$$

(3.112)

The sound absorption coefficient is related to the imaginary part of $\kappa$,

$$\alpha = \frac{\text{Im} \kappa}{\kappa_o} = \frac{\omega^{(2)}}{[\omega^{(1)}]^2} \omega + \ldots$$

(3.113)

where $\kappa_o = \omega/\omega^{(1)}$, is the dimensionless wavenumber in the low frequency limit. Using (3.103) we find that the first term in the series expansion for $\alpha$ agrees with the Kohler\textsuperscript{9,10} absorption coefficient for binary mixtures of monatomic gases in the absence of thermal diffusion,

$$\alpha_K = \frac{\omega^{(2)}}{[\omega^{(1)}]^2} = \left\{ \frac{2}{3} \frac{n}{\rho_o} + \frac{2}{15} \frac{\lambda}{n_0 k_B} + \frac{5}{6} D_1 12 x_1 x_2 \left( \frac{m_2 - m_1}{m_1 + m_2} \right)^2 \frac{n}{\rho_o} \right\}^2$$

(3.114)

Dispersion in the mixture is given by

$$\frac{U_o}{U} = \frac{\text{Re} \kappa}{\kappa_o} = 1 - \left\{ \frac{2[\omega^{(2)}]^2 - \omega^{(1)} \omega^{(3)}}{[\omega^{(1)}]^4} \right\} \omega^2 + \ldots$$

$$= 1 - \left\{ 2n^2 - \left( \frac{U_o}{n_o \sigma_o} \right)^2 \omega^{(1)} \omega^{(3)} \right\} \left( \frac{\sigma_o}{U_o} \right)^2 + \ldots$$

$$= 1 - \left\{ \frac{1}{3} \frac{n}{\rho_o} \left[ 2n + \frac{4}{3} \frac{\lambda}{n_0 k_B} + \frac{25}{3} D_1 12 x_1 x_2 \left( \frac{m_2 - m_1}{m_1 + m_2} \right)^2 \right] \right\}$$

$$+ \frac{1}{3} \frac{\lambda}{n_0 k_B} \left[ D_1 12 x_1 x_2 \left( \frac{m_2 - m_1}{m_1 + m_2} \right)^2 - \frac{2}{25} \frac{\lambda}{n_0 k_B} \right]$$

$$+ \frac{5}{6} D_2^2 12 x_1 x_2 \left( \frac{m_2 - m_1}{m_1 + m_2} \right)^2 \left[ 5 x_1 x_2 \left( \frac{m_2 - m_1}{m_1 + m_2} \right)^2 + \frac{5}{3} \left( \frac{m_1 + m_2}{m_1 + m_2} \right)^2 - 1 \right]$$
This expression should agree with the corresponding result given by Foch, Uhlenbeck and Losa when their equation is specialised to Maxwell molecules [equation (5.2) of reference 5]. Although we have not demonstrated that the two equations are algebraically equivalent numerical checks have been carried out which confirm that they give the same values of phase speed.

3.9. Perturbation theory for disparate mass gas mixtures

If the particle mass ratio $m_1/m_2 \sim 1$ and $|\kappa| \ll 1$, harmonic disturbances in a binary gas may to a good approximation be described by the first few terms in the perturbation expansions (3.69) and (3.70). In a disparate mass gas, where $\delta = (m_1/m_2)^{1/2} \ll 1$ and $\kappa \sim \delta$, these are no longer well-ordered series. For example as $\omega_1^{(1)} \sim \delta$, (3.81), the first term in the expansion (3.69) is of the order $|\kappa| \delta$. Inspection of the second term reveals that it is of the order $|\kappa|^2$ since $\omega_1^{(2)} \sim 1$. Therefore when $|\kappa| \sim \delta$ the second term in the series is of the same order as the first. Clearly the fact that $\kappa$ is a small parameter is no longer a guarantee that successive terms in the expansions are smaller.
For a disparate mass gas mixture the structure of the Boltzmann equations with respect to the small parameters it contains demands a reformulated perturbation theory. The term that we previously regarded as the perturbation (3.17), makes a contribution which is of a different order in the light species equation (3.12), to what it is in the heavy species equation (3.13). In addition a fully ordered formulation of the problem would have to take account of the effect of a small mass ratio on the magnitude of collision integrals.

Rather than starting from the beginning again with a reordering of the coupled Boltzmann equations, advantage can be taken of our knowledge of the eigenvalues $v_\gamma$ and the matrix elements $C_{\gamma \gamma'}$ to make mass factors explicit. For example, it is a straightforward matter to show that, apart from $v_{10+}$ which is of the order $\delta^2$, non-zero unperturbed eigenvalues are either of order $\delta$ or of order $\delta^0 = 1$. The decisive factors determining the order of $v_{r1+}$ and $v_{r1-}$, where $(r,\xi) \neq (0,0)(0,1)(1,0)$, may be traced via (3.42) and (3.36) to $B_{11}(x)/u_0\sigma_0$ and $B_{22}(x)/u_0\sigma_0$ respectively in equation (3.14). $B_{ij}(x)$ has the characteristic form for Maxwell molecules

$$B_{ij}(x) = \kappa_{ij} \frac{\mu_{ij}}{\mu_{ij}} f(x) \quad i,j = 1,2 \quad (3.116)$$

where

$$\mu_{ij} = m_i m_j / (m_i + m_j),$$

$\kappa_{ij}$ is a force constant defined by (2.150) and $f(x)$ is a function independent of particle parameters. From (3.11) the scaling parameter $u_0\sigma_0$ depends on $B_{12}(x)$, therefore

$$v_{r1+} \sim \frac{B_{11}(x)}{u_0\sigma_0} \sim \frac{\mu_{12}^{1/2}}{\mu_{11}} \sim 1$$
whereas
\[ v_{r1} \sim B_{22}(x)/u_0 \sigma_0 \sim \left( \frac{\mu_{12}}{\mu_{22}} \right)^{1/2} \sim \delta \]

The magnitudes of the unperturbed eigenvalues reflect the fact that the relaxation of a disparate mass gas is predominantly governed by three time scales. The inverse relaxation time of the species temperature difference \( v_{10+} \) determines one of these, the heavy species self collision frequency \( v_{r1-} \) determines another and the third is related to the light species collision frequency \( v_{r1+} \), where \( (r,1) \neq (0,0),(0,1),(1,0) \).

The fact that the eigenvalues may be put into three groups according to their magnitude suggests that the operator \( I \) may be split into three ordered subsidiary operators \( I^{(j)} \), \( j = 0,1,2 \), whose eigenvectors are the same as those of \( I \). Thus,

\[ I = I^{(0)} + \epsilon I^{(1)} + \epsilon^2 I^{(2)} \quad (3.117) \]

where \( \epsilon = 1 \) denotes a term of order \( \delta^n = \left( \frac{m_1}{m_2} \right)^n/2 \), \( n=0,1,2 \ldots \). \( I^{(2)} \) has a single non-zero eigenvalue, \( v_{10+} \). Non-zero eigenvalues of \( I^{(0)} \) are denoted by \( v_{r} \) where \( r \equiv (r,l,+{\text{}}) \) excluding \( (0,0,+{\text{}}) \) and \( (1,0,+{\text{}}) \). Non-zero eigenvalues of \( I^{(1)} \) are \( v_{l} \) where \( l \equiv (r,l,-{\text{}}) \) but excluding \( (0,0,-{\text{}}) \), \( (0,1,-{\text{}}) \), \( (1,0,-{\text{}}) \).

In order to take account of the presence of two small parameters we make use of a procedure similar to that suggested by Darrozes. The regime where \( |\kappa| \sim \delta \) is considered, and consequently the term representing inhomogeneities of the gas may be written as \( (\kappa \epsilon)C \). Expanding as a power series in \( \epsilon \) we get

\[ (\kappa \epsilon)C = \kappa C^{(1)} + \epsilon C^{(2)} + \epsilon^2 C^{(3)} + \ldots \]
The subsidiary operators $C^{(j)}$ $j = 1, 2, 3, \ldots$ are defined through their matrix representations with respect to the vectors $|\gamma\rangle$, which we write as $\gamma^{(j)}$. If a matrix element $C_{\gamma\gamma'}$ is of order $n$ then it is allocated in full to $C^{(n+1)}$, whilst corresponding elements of the other matrices $C^{(j)}$ $j \neq n+1$ are zero. Details of this analysis are given in Appendix 3D.

Substituting for $(eic)C$ from (3.118) and for $I$ from (3.117) in (3.49) gives

$$[\hat{I}(\omega) + \epsilon(I^{(1)}) - i\kappa C^{(1)} + \epsilon^2(I^{(2)}) - i\kappa C^{(2)} + \epsilon^3(-i\kappa C^{(3)}) + \ldots + i\omega] |\tilde{h}\rangle = 0$$

(3.119)

(3.119) has a structure which makes it amenable to analysis using perturbation theory. Solutions are sought in the form of power series expansions in $\epsilon$,

$$\omega = \omega^{(0)} + \epsilon \omega^{(1)} + \epsilon^2 \omega^{(2)} + \epsilon^3 \omega^{(3)} + \ldots$$

(3.120)

$$|\tilde{h}\rangle = |h^{(0)}\rangle + \epsilon |h^{(1)}\rangle + \epsilon^2 |h^{(2)}\rangle + \epsilon^3 |h^{(3)}\rangle + \ldots$$

(3.121)

Substituting for $\omega$ and $|h\rangle$ in (3.119) and equating coefficients of $\epsilon$ gives a set of equations for successively higher order terms in the perturbation expansions. Following standard procedure elementary solutions representing hydrodynamic modes are derived in Appendix 3D.

It is found that five solutions of (3.119) are degenerate with zero eigenvalue at both zero order and at first order. If $p$ labels these particular solutions then we get

$$\omega^{(0)}_p = \omega^{(1)}_p = 0 \quad p = 1, 2, 3, 4, 5$$

(3.122)

The vectors $|p\rangle$ which satisfy the zero order equation and are associated with this result have the general form of a linear combination of those basis vectors which span the first order degeneracy. In this case

$$|p\rangle = \sum_{\pi} E_{\pi p} |\pi\rangle \quad \pi = (00-), (00+), (01-), (10-), (10+)$$

(3.123)

At second order the degeneracy is removed and the expansion coefficients $E_{\pi p}$, determined by a 5x5 matrix equation,
\[
\begin{align*}
\begin{array}{c|c|c|c}
\text{ } & \omega(2) & \frac{\kappa c_{00},01-}{p} & \frac{\kappa c_{00},01-}{p} \\
\hline
\omega(2) & -\omega(2) & -\omega(2) & -\omega(2) \\
\kappa c_{01},00- & \kappa c_{01},00- & \kappa c_{01},00- & \kappa c_{01},00- \\
\hline
\frac{i\kappa 2 c_{00},01,C_{01},10-}{\gamma_{01}^{+}} & \frac{i\kappa 2 c_{00},01,C_{01},10-}{\gamma_{01}^{+}} & \frac{i\kappa 2 c_{00},01,C_{01},10-}{\gamma_{01}^{+}} & \frac{i\kappa 2 c_{00},01,C_{01},10-}{\gamma_{01}^{+}} \\
\hline
\frac{i\kappa 2 c_{00},01,C_{01},10-}{\gamma_{01}^{+}} & \frac{i\kappa 2 c_{00},01,C_{01},10-}{\gamma_{01}^{+}} & \frac{i\kappa 2 c_{00},01,C_{01},10-}{\gamma_{01}^{+}} & \frac{i\kappa 2 c_{00},01,C_{01},10-}{\gamma_{01}^{+}} \\
\end{array}
\end{align*}
\]

(3.124)
(3.124) gives the zero order solutions for the four longitudinal hydrodynamic modes and one non-hydrodynamic mode. With reference to (3.61) it is clear that the non-hydrodynamic mode is associated with the relaxation of a harmonic disturbance in the species temperature difference. It is interesting to compare the above subsidiary eigenvalue problem with the 4x4 matrix equation (3.80), used to find zero order solutions where $\kappa$ is the only small parameter. Reordering in terms of $\delta$ has meant that temperature relaxation may be a component in the acoustic modes at zero order. Also terms such as $\kappa C_{00-01-}$, which are first order in $\kappa$, are now considered second order in $\delta$ when $\kappa \approx \delta$, since $C_{00-01-} \approx \delta$ (Table 3.2)

We have not been able to factorize the secular equation from (3.124) and therefore explicit analytical solutions cannot be given. However formal solutions can be stated in terms of the $|p>$ vectors. For the hydrodynamic and temperature difference modes we find at first order that

$$|h^{(1)}_p> = \kappa \left[ \frac{<01+|C^{(1)}|p>}{\nu_{01+}} |01+> + \frac{<11+|C^{(1)}|p>}{\nu_{11+}} |11+> + \frac{<02-|C^{(2)}|p>}{\nu_{02-}} |02-> \right]$$

$$+ \frac{<11-|C^{(2)}|p>}{\nu_{11-}} |11->$$

(3.125)

Notice that $|p>$ and $|h^{(1)}_p>$ contain components of $|00->$, $|00+>$, $|01->$, $|10+>$, $|02->$, $|11>$ and $|11+>$ only. An arbitrary linear combination of these vectors plus $|02+>$ is equivalent to the proposed solution in the linear thirteen moment theory for longitudinal modes. As no additional approximations are made, the thirteen moment solutions, like $|p> + \epsilon |h^{(1)}_p>$, are correct to first order in $\delta$ for $\kappa \approx \delta$

The absence of $|02+>$ in (3.124) and (3.125) implies that the light species stress tensor is of negligible order in the thirteen moment
calculation of longitudinal hydrodynamic modes. Components of $|11+\rangle$ and $|11-\rangle$, representing the light and heavy species heat flux amplitude, are found at first order together with contributions from the heavy species viscous stress and the diffusion velocity, equation (3.125). The temperature difference amplitude on the other hand is a zero order term, equation (3.124).

The original perturbation theory for harmonic disturbances in binary monatomic gas mixtures due to Foch, Uhlenbeck and Losa\textsuperscript{5}, does not lead to well ordered results if $\delta \ll 1$ and $\kappa \sim \delta$. By restructuring the problem it is possible to apply perturbation theory where two small parameters are involved. The results show among other things, that terms omitted from thirteen moment predictions are of the order $\delta^2$. 
APPENDIX 3A  An identity for $c_z \psi_{r \ell m}$.

The Burnett functions $\psi_{r \ell m}$ are given by

$$\psi_{r \ell m} = q_{r \ell m} c_r^{\ell+\frac{1}{2}} (c^2)^{\ell} P_{\ell}^m(\cos \theta) e^{im\phi} \quad (3A.1)$$

where normalisation factors are lumped together in the constant $q_{r \ell m}$.

$$q_{r \ell m} = (-1)^m \frac{\Gamma(\frac{3}{2})}{\Gamma\left(r+\frac{3}{2}\right)} \frac{1}{(\ell+\frac{1}{2}) (\ell-m)!}$$

(3A.2)

Applying the recurrence relation for associated Legendre polynomials,

$$(2\ell+1) x P_{\ell}^m(x) = (\ell+m) P_{\ell-1}^m(x) + (\ell-m+1) P_{\ell+1}^m(x) \quad (3A.3)$$

we find that $c_z \psi_{r \ell m}$ can be written as

$$c_z \psi_{r \ell m} = \frac{q_{r \ell m}}{2\ell+1} c_r^{\ell+1} L_{\ell+\frac{1}{2}}^m (c^2) [(\ell+m) P_{\ell-1}^m(\cos \theta) + (\ell-m+1) P_{\ell+1}^m(\cos \theta)] \quad (3A.4)$$

By using the recurrence relations for associated Laguerre polynomials

$$Z L_{r}^{\alpha}(Z) = (r+\alpha) L_{r+1}^{\alpha}(Z) - (r+1) L_{r+1}^{\alpha-1}(Z) \quad (3A.5)$$

and

$$L_{r}^{\alpha}(Z) = L_{r+1}^{\alpha}(Z) - L_{r-1}^{\alpha}(Z), \quad (3A.6)$$

a linear combination of Burnett functions can be constructed on the right hand side of (3A.4). It then becomes

$$c_z \psi_{r \ell m} = \frac{q_{r \ell m}}{2\ell+1} \left[ c_r^{\ell+1}(\ell-m+1) L_{\ell+\frac{3}{2}} L_{\ell}^m (c^2) P_{\ell+1}^m(\cos \theta) 
- c_r^{\ell+1}(\ell-m+1) L_{\ell-1}^m (c^2) P_{\ell+1}^m(\cos \theta) 
+ c_r^{\ell-1}(\ell+m) L_{\ell+1}^\frac{1}{2} L_{\ell}^m (c^2) P_{\ell-1}^m(\cos \theta) 
- c_r^{\ell-1}(\ell+m) (r+\frac{1}{2}) L_{\ell+1}^\frac{1}{2} L_{\ell}^m (c^2) P_{\ell+1}^m(\cos \theta) \right]$$
or

\[ c_{z}^{\gamma} r \ell m = \left( \frac{r + \ell + \frac{3}{2}}{2 \ell + 1} \right) \frac{(\ell + m + 1)(\ell - m + 1)}{(2 \ell + 1)(2 \ell + 3)}^{1/4} \psi_{r, \ell + 1, m} - \frac{r(\ell + m + 1)(\ell - m + 1)}{(2 \ell + 1)(2 \ell + 3)}^{1/4} \psi_{r - 1, \ell + 1, m} \]

\[ + \left( \frac{(r + \ell + 1)(\ell - m)(\ell + m)}{(2 \ell + 1)(2 \ell - 1)} \right)^{1/4} \psi_{r, \ell - 1, m} - \left( \frac{(r + 1)(\ell + m)(\ell - m)}{(2 \ell + 1)(2 \ell - 1)} \right)^{1/4} \psi_{r + 1, \ell - 1, m} \]

(3A.7)

This is a generalisation of the identity for \( c_{z}^{\gamma} r_{1} (m=0) \) given by Foch and Ford.3
In Section 3.6 we found that the four fold degeneracy at zero order for longitudinal hydrodynamic modes was only partly removed at first order by solving a subsidiary 4x4 eigenvalue problem. Here we show how the degeneracy may be eliminated at second order following a method discussed by Schiff$^{41}$. In the present case it involves setting up a further subsidiary eigenvalue problem using two orthonormal but otherwise arbitrary vectors, $|q_3\rangle$ and $|q_4\rangle$ say, in the two dimensional subspace of the first order degeneracy. Let

$$|q_3\rangle = (x_2)^{\frac{1}{2}} |00\rangle + (x_1)^{\frac{1}{2}} |00\rangle$$

and

$$|q_4\rangle = \left(\frac{2x_1}{5}\right)^{\frac{1}{2}} |00\rangle + \left(\frac{2x_2}{5}\right)^{\frac{1}{2}} |00\rangle + \left(\frac{3}{5}\right)^{\frac{1}{2}} |10\rangle$$

The zero order solutions we seek are linear combinations of $|q_3\rangle$ and $|q_4\rangle$:

$$|t\rangle = B|q_3\rangle + (1-B^2)^{\frac{1}{2}}|q_4\rangle$$

The coefficients have been chosen so that $|t\rangle$ is normalised. $B$ is found from the orthogonality condition on the inhomogeneous term in the second order equation, a special case of (3.74) in which $n=2$ and $|h_i^{(0)}\rangle = |q_i\rangle$:

$$<q_i | w_t^{(1)} - C | h_t^{(1)} \rangle + w_t^{(2)} <q_i | t \rangle = 0$$

In order to evaluate (3B.3) an explicit expression for $|h_t^{(1)}\rangle$ is needed. Because a solution of the first order equation $w_t^{(1)}$ is orthogonal to its zero order counterpart, $|h_t^{(1)}\rangle$ will not include a component of $|t\rangle$. Thus in general
When \( t = 3 \), then \( t' = 4 \) and vice versa. The sum over \( \beta' \) excludes the \( |\sigma> \) since vectors in the degenerate subspace are represented by \( |1>, |2> \) and \( |t'>. \) The coefficients in the summation are found by substituting (3B.4) into the first order equation (3.71)B and taking the scalar product with \( <\beta| \). This gives

\[
a_{\beta t}^{(1)} = -<\beta| C| t>/\nu_{\beta} \tag{3B.5}
\]

where \( \nu_{\beta} \) is found from (3.42) with (3.39) and (3.36). As \( |h_t^{(1)}> \) given by (3B.4) and (3B.5), the pair of relationships represented by (3B.3) become

\[
B\sum_{\beta} \frac{<\beta| C|q_3>^2}{\nu_{\beta}} + \omega_{t}^{(2)} + (1-B^2)\frac{1}{2} \sum_{\beta} \frac{<\beta| C|q_3> <\beta| C|q_4>}{\nu_{\beta}} = 0
\]

and

\[
B\sum_{\beta} \frac{<\beta| C|q_3> <\beta| C|q_4>}{\nu_{\beta}} + (1-B^2)\frac{1}{2} \left[ \sum_{\beta} \frac{<\beta| C|q_4>^2}{\nu_{\beta}} + \omega_{t}^{(2)} \right] = 0
\]

where we have used (3.78)A and the fact that \( \omega_{t}^{(1)} = 0 \).

The degeneracy is removed at second order unless it happens that

\[
\sum_{\beta} \frac{<\beta| C|q_3>^2}{\nu_{\beta}} = \sum_{\beta} \frac{<\beta| C|q_4>^2}{\nu_{\beta}} \tag{3B.7}
\]

and

\[
\sum_{\beta} \frac{<\beta| C|q_3> <\beta| C|q_4>}{\nu_{\beta}} = 0 \tag{3B.8}
\]

(3B.7) and (3B.8) are evaluated using expressions for \( C|q_3> \) and \( C|q_4> \) in terms of basis vectors. Referring to the matrix elements calculated in Section 3.5 we find that

\[
C|q_3> = \sum_{\alpha} <\alpha| C|q_3> |\alpha> = -\left(\frac{3}{2}\right)\frac{1}{2} C_{01^+,10^+}|01^+>
\]

\[
C|q_4> = \sum_{\alpha} <\alpha| C|q_4> |\alpha>
\]

\[
\]
As $|q_3\rangle$ and $|q_4\rangle$ have no components in common, (3B.8) is satisfied. Therefore the other condition, (3B.7), means that if

$$\frac{3}{5} \left( \frac{C_{11-,10-}^2}{\nu_{11-}} + \frac{C_{11+,10-}^2}{\nu_{11+}} \right) + \frac{3}{5} \frac{C_{11+,10+}^2}{\nu_{11+}}$$

the degeneracy is not removed at second order. (3B.11) will only hold at a particular molecular composition. For the present it will be assumed that the degeneracy is removed; then (3B.6) has two distinct solutions.

With $t=3$ say,

$$\omega_3^{(2)} = -\sum_{\beta} \frac{\beta |q_3\rangle^2}{\nu_{11-}^{\beta}} = -\frac{3}{2} \frac{C_{01+,10+}^2}{\nu_{01+}}$$

$$\omega_3^{(2)} = \frac{1}{2}$$

(3B.12)

where $C_{01+,10+}$ and $\nu_{01+}$ are given in Tables 3.2 and 3.1 respectively. For this solution $B = 1$ and

$$|3\rangle = |q_3\rangle = x_2 \vert 00+\rangle - x_1 \vert 00-\rangle$$

(3B.13)

With $t=4$,

$$\omega_4^{(2)} = -\sum_{\beta} \frac{\beta |q_4\rangle^2}{\nu_{11-}^{\beta}} = -\frac{3}{5} \left( \frac{C_{11-,10-}^2}{\nu_{11-}} + \frac{C_{11+,10-}^2}{\nu_{11+}} \right)$$

(3B.14)

and $B = 0$, therefore
Thus the arbitrary choice of $|q_3\rangle$ and $|q_4\rangle$ was fortuitous since these vectors turn out to be the zero order solutions we were seeking.
APPENDIX 3C  The solution of the first order equation for an acoustic mode.

In Section 3.6 we have expressed the solution of the first order equation in the form

\[
|h_1^{(1)}\rangle = A_2^{(1)} |2\rangle + A_3^{(1)} |3\rangle + A_4^{(1)} |4\rangle + \sum_{\sigma} \alpha^{(1)}_{\sigma} |\sigma\rangle
\]  \hspace{1cm} (3.100)

with \( \beta \neq \sigma \)

\[
\alpha_{\beta}^{(1)} = -<\beta|C|1>/\nu_{\beta}
\]  \hspace{1cm} (3.101)

and have pointed out that the \( \alpha^{(1)} \)'s may be found from

\[
<s|\omega_1^{(1)} - C|h_1^{(1)}> + \omega_1^{(2)} \delta_{1s} = 0 \hspace{1cm} s = 1,2,3,4 \hspace{1cm} (3.102)
\]

In this Appendix, explicit expressions for the coefficients in (3.100) will be derived from (3.101) and (3.102).

Reference will be made to identities of the form

\[
C|s\rangle = \omega_s^{(1)} |s\rangle + \sum_{\beta} <\beta|C|s\rangle |\beta\rangle
\]  \hspace{1cm} (3C.1)

\( s = 1,2,3,4 \)  \( \beta \neq \sigma \)

This expansion takes into account that the matrix elements of the perturbation are diagonal with respect to the \( |s\rangle \) within the degenerate subspace. The summation takes care of components outside the subspace. Using equations (3.83), (3.87) and (3.88) together with (3C.1) gives

\[
C|1\rangle = \left(\frac{5m_{10}^{m_{12}}}{6m_{12}}\right)^{1/2} |1\rangle - \left(\frac{5}{4}\right)^{1/2} C_{01+},10-|01\rangle + \left(\frac{1}{2}\right)^{1/2} C_{02-},01-|02\rangle + \left(\frac{1}{2}\right)^{1/2} C_{02+},01-|02\rangle
\]

\[ - \left(\frac{1}{5}\right)^{1/2} C_{11-},10-|11\rangle + \left(\frac{1}{5}\right)^{1/2} C_{11+},10-|11\rangle \]  \hspace{1cm} (3C.2)

\[
C|2\rangle = \left(\frac{5m_{10}^{m_{12}}}{6m_{12}}\right)^{1/2} |2\rangle + \left(\frac{5}{4}\right)^{1/2} C_{01+},10-|01\rangle + \left(\frac{1}{2}\right)^{1/2} C_{02-},01-|02\rangle + \left(\frac{1}{2}\right)^{1/2} C_{02+},01-|02\rangle
\]

\[ + \left(\frac{1}{5}\right)^{1/2} C_{11-},10-|11\rangle + \left(\frac{1}{5}\right)^{1/2} C_{11+},10-|11\rangle \]  \hspace{1cm} (3C.3)
\[ C|3> = -(\frac{3}{2})^\frac{1}{2} C_{01+,10+}|01> \]  
(3C.4)

\[ |C|4> = (\frac{3}{5})^\frac{1}{2} C_{11-,10-}|11->+ (\frac{3}{5})^\frac{1}{2} C_{11+,10-}|11> \]  
(3C.5)

The expansion coefficients, (3.101), can now be given using (3C.2):

\[
a^{(1)}_{01+} = (\frac{5}{4})^\frac{1}{2} \frac{C_{01+,10-}}{\nu_{01+}}
\]

\[
a^{(1)}_{02-} = -(\frac{1}{2})^\frac{1}{2} \frac{C_{02-,01-}}{\nu_{02-}}
\]

\[
a^{(1)}_{02+} = -(\frac{1}{2})^\frac{1}{2} \frac{C_{02+,01-}}{\nu_{02+}}
\]

\[
a^{(1)}_{11-} = (\frac{3}{5})^\frac{1}{2} \frac{C_{11-,10-}}{\nu_{11-}}
\]

\[
a^{(1)}_{11+} = (\frac{1}{5})^\frac{1}{2} \frac{C_{11+,10-}}{\nu_{11+}}
\]  
(3C.6)

The remaining coefficients, and also \( \omega_{1}^{(2)} \), are found by substituting the expansion for \( |h_{1}^{(1)}> \) into (3.102) and using (3C.2) - (3C.5). We find, for \( s=1 \),

\[
\omega_{1}^{(2)} = -\frac{\beta |C|1>^2}{\nu_{\beta}} = -\left(\frac{5}{4}\right)^\frac{1}{2} \frac{C_{01+,10-}}{\nu_{01+}} + \frac{1}{2} \frac{C_{02-,01-}}{\nu_{02-}} + \frac{1}{2} \frac{C_{02+,01-}}{\nu_{02+}} + \frac{1}{5} \frac{C_{11-,10-}}{\nu_{11-}} + \frac{1}{5} \frac{C_{11+,10-}}{\nu_{11+}} \]  
(3C.7)

\[
A_{21}^{(1)} = \frac{1}{2\omega_{1}^{(1)}} \sum_{\beta} \frac{<\beta |C|1>^2}{\nu_{\beta}} \frac{C_{01+,10-}}{\nu_{01+}} - \frac{1}{2} \frac{C_{02-,01-}}{\nu_{02-}} + \frac{1}{2} \frac{C_{02+,01-}}{\nu_{02+}} + \frac{1}{5} \frac{C_{11-,10-}}{\nu_{11-}} + \frac{1}{5} \frac{C_{11+,10-}}{\nu_{11+}} \]  
(3C.8)

\[
A_{31}^{(1)} = -\frac{1}{\omega_{1}^{(1)}} \sum_{\beta} \frac{<\beta |C|1>^2}{\nu_{\beta}} \frac{C_{01+,10-}}{\nu_{01+}} = -\frac{1}{\omega_{1}^{(1)}} \left(\frac{15}{8}\right)^\frac{1}{2} \frac{C_{01+,10-}}{\nu_{01+}} \]  
(3C.9)

\[
A_{41}^{(1)} = -\frac{1}{\omega_{1}^{(1)}} \sum_{\beta} \frac{<\beta |C|1>^2}{\nu_{\beta}} \frac{C_{01+,10-}}{\nu_{01+}} = -\frac{1}{\omega_{1}^{(1)}} \left(\frac{25}{2}\right)^\frac{1}{2} \frac{C_{11-,10-}}{\nu_{11-}} + \frac{1}{\omega_{1}^{(1)}} \frac{C_{11+,10-}}{\nu_{11+}} \]  
(3C.10)
By applying (3.91), (3.92) and (3.99) these results may be expressed in terms of the linear transport coefficients of the mixture:

\[ \omega_1^{(2)} = \left\{ \frac{2}{3} \frac{n}{\rho_0} + \frac{2}{15} \frac{\lambda}{n_0 k_B} + \frac{5}{6} D_{12} x_1 x_2 \left( \frac{m_2 - m_1}{m_1 x_1 + m_2 x_2} \right)^2 \frac{n_0 \sigma_0}{u_o} \right\} \]

or

\[ \omega_1^{(2)} = \Gamma \frac{n_0 \sigma_0}{u_o} \]

(3C.11)

where \( \Gamma \) is given by (1.85).

\[ A_{21}^{(1)} = \frac{1}{2} \left\{ \frac{2}{3} \frac{n}{\rho_0} - \frac{2}{15} \frac{\lambda}{n_0 k_B} - \frac{5}{6} D_{12} x_1 x_2 \left( \frac{m_2 - m_1}{m_1 x_1 + m_2 x_2} \right)^2 \frac{n_0 \sigma_0}{u_o} \right\} \]

(3C.12)

\[ A_{31}^{(1)} = \left( \frac{5}{6} \right)^{\frac{1}{4}} D_{12} x_1 x_2 x_2 \left( \frac{m_2 - m_1}{m_1 x_1 + m_2 x_2} \right)^{\frac{1}{4}} \frac{n_0 \sigma_0}{u_o} \]

(3C.13)

and

\[ A_{41}^{(1)} = -\frac{2\sqrt{3}}{15} \frac{\lambda}{k_B} \frac{\sigma_0}{u_o} \]

(3C.14)

These expressions agree with the corresponding equations given by Foch, Uhlenbeck and Losa^5, their (50a), (50b), (50c) and (50d) specialised to Maxwell molecules.
3D.1. Analysis of the operator C into ordered components.

The problem of finding the harmonic modes of a disparate mass gas mixture has been formulated such that two small dimensionless parameters $\kappa$ and $\delta$ are involved. By considering the case where $\kappa \gg \delta$ the problem has been reduced to one of solving the equation (3.119)

$$[1^{(0)} + \epsilon(1^{(1)} - i\kappa C^{(1)}) + \epsilon^2(1^{(2)} - i\kappa C^{(2)}) + \epsilon^3(-i\kappa C^{(3)}) + \ldots + i\omega] |\psi\rangle = 0$$

We shall determine some of the solutions of this equation and briefly indicate how the ordered components $C^{(j)}$ $j=1,2,3...$ are defined with respect to their matrix representation $C^{(j)}$.

Although mass factors do not occur with simple regularity among the matrix elements $C_{\alpha \alpha'}$, some general statements can be made. Usually eigenvalues of the cross-collision operators (3.14)C, are of a higher order than those of the self collision operators (3.14)A.

Specifically

$$\beta_{12, r\ell} \sim \beta_{21, r\ell} \sim 2r+1$$ whereas $\beta_{11, r\ell} \sim 1$ and $\beta_{22, r\ell} \sim \delta$

(3D.1)

Exceptions to this are when $(r, \ell) = (0,0), (0,1)$ or $(1,0)$. Assuming that $4\beta_{12, r\ell} \beta_{21, r\ell} / (\beta_{11, r\ell} - \beta_{22, r\ell}) \ll 1$ then (3.42) may be approximated by

$$\nu_{r\ell+} \approx \beta_{11, r\ell} + \beta_{12, r\ell} \beta_{21, r\ell} / (\beta_{11, r\ell} - \beta_{22, r\ell})$$

and

$$\nu_{r\ell-} \approx \beta_{22, r\ell} - \beta_{12, r\ell} \beta_{21, r\ell} / (\beta_{11, r\ell} - \beta_{22, r\ell})$$

(3D.2)

(3D.1) and (3D.2) can be used to find the order of the coefficients $a_{r\ell \pm}$ and $b_{r\ell \pm}$ from (3.43) and hence the mass ordering of $C_{r\ell \pm, r'\ell' \pm}$ using (3.66) if $(r, \ell)(r', \ell') \neq (0,0), (0,1), (1,0)$. The exceptional cases may be treated on an individual basis; see for example the explicit expressions for some matrix elements given in Table 3.2. We find
<table>
<thead>
<tr>
<th>r&amp;±</th>
<th>00-</th>
<th>00+</th>
<th>01-</th>
<th>01+</th>
<th>10-</th>
<th>10+</th>
<th>02-</th>
<th>02+</th>
<th>11-</th>
<th>11+</th>
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</tr>
</thead>
<tbody>
<tr>
<td>eC₀₀⁻,₀₁⁻</td>
<td>eC₀₀⁻,₀₁+</td>
<td>eC₀₀⁺,₀₁⁻</td>
<td>eC₀₀⁺,₀₁+</td>
<td>eC₁₀⁻,₁₀⁻</td>
<td>eC₁₀⁻,₁₀+</td>
<td>eC₁₀⁺,₁₀⁻</td>
<td>eC₁₀⁺,₁₀+</td>
<td>eC₁₁⁻,₁₁⁻</td>
<td>eC₁₁⁻,₁₁+</td>
<td>eC₁₁⁺,₁₁⁻</td>
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<td>(3D.3)</td>
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</tbody>
</table>
All matrix elements of order $\delta^0$ are allocated to $C^{(1)}$, those of order $\delta$ to $C^{(2)}$ and so on.

3D.2. Perturbation theory applied to the reordered problem

The proposed solutions of (3.119) are in the form of power series expansions of $\omega$ and $|\hat{h}\rangle$ in terms of $\epsilon$, (3.120) and (3.121) respectively. Substituting these expansions into (3.119) and equating coefficients of $\epsilon$ gives a set of equations for successive terms in the perturbation series:

\[
\begin{align*}
(I^{(0)} + i\omega^{(0)})|h^{(0)}\rangle &= 0 \\
(I^{(0)} + i\omega^{(0)})|h^{(1)}\rangle &= - (I^{(1)} - i\kappa C^{(1)} + i\omega^{(1)})|h^{(0)}\rangle \\
(I^{(0)} + i\omega^{(0)})|h^{(2)}\rangle &= - (I^{(1)} - i\kappa C^{(1)} + i\omega^{(1)})|h^{(1)}\rangle - (I^{(2)} - i\kappa C^{(2)} + i\omega^{(2)})|h^{(0)}\rangle \\
(I^{(0)} + i\omega^{(0)})|h^{(3)}\rangle &= - (I^{(1)} - i\kappa C^{(1)} + i\omega^{(1)})|h^{(2)}\rangle - (I^{(2)} - i\kappa C^{(2)} + i\omega^{(2)})|h^{(1)}\rangle - (i\kappa C^{(3)} + i\omega^{(3)})|h^{(0)}\rangle
\end{align*}
\]

(3D.4)

To ensure that a particular solution $|h^{(n)}\rangle$, of the nth order equation is unique we require that it be orthogonal to its zero order counterpart:

\[
\langle h^{(0)}_k | h^{(n)}_k \rangle = 0 \quad n \geq 1
\]

(3D.5)

Inhomogeneous terms in (3D.4) are orthogonal to corresponding zero order solutions with the same zero order eigenvalue. Thus if $\omega^{(0)}_i = \omega^{(0)}_j$, then from the nth order equation

\[
\begin{align*}
\langle h^{(0)}_i | I^{(1)} - i\kappa C^{(1)} + i\omega^{(1)}_j | h^{(n-1)}_j \rangle + \langle h^{(0)}_i | I^{(2)} - i\kappa C^{(2)} + i\omega^{(2)}_j | h^{(n-2)}_j \rangle + \\
\cdots + i\omega^{(n)}_j \delta_{ij} &= 0
\end{align*}
\]

(3D.6)
where zero order solutions are orthonormal:

\[ \langle h_i^{(0)} | h_j^{(0)} \rangle = \delta_{ij} \]  

(3D.7)

(3D.6) and (3D.7) are the equivalent of (3.74) and (3.75) respectively.

From the definition of \( I^{(0)} \) (Section 3.9) the vectors \( |\tau> \) satisfy the zero order equation (3D.4A, with \( \omega^{(0)}_\tau = i\nu \neq 0 \), \( \tau \equiv (r, \ell, \pm) \) but excluding \((0,0,+)\) and \((1,0,+).\) However, since we wish to find the hydrodynamic modes it is the degenerate solutions with zero unperturbed eigenvalue that must be investigated. Following standard procedure these are represented as a linear combination of degenerate basis vectors,

\[ |h^{(0)}_{\lambda \ell}> = \sum_\lambda D_{\lambda \ell} |\lambda> \]

(3D.8)

\( \ell = 1, 2, 3 \) \hspace{1cm} \lambda \neq \tau \ or \ \lambda \equiv (r, \ell, -) \hspace{0.5cm} (0,0,+) \hspace{0.5cm} (1,0,+) \)

The matrix of the coefficients \( D_{\lambda \ell} \) is sought at first order but in this case it turns out that the full generality of (3D.8) is not required since only a few of the off-diagonal terms are non-vanishing. From the orthogonality condition on the inhomogeneous term in the first order equation, (3D.6) with \( n=1 \), we get

\[ \langle X | I^{(1)} - i\kappa C^{(1)} + i\omega^{(1)}_{\ell} | h^{(0)}_{\lambda \ell} \rangle = 0 \]

This immediately simplifies to

\[ \langle \lambda | I^{(1)} + i\omega^{(1)} | h^{(0)}_{\lambda \ell} \rangle = 0 \]

(3D.9)

since all the matrix elements \( C_{\lambda \ell} \), \( \lambda, \lambda' \equiv (r, \ell, -) \hspace{0.5cm} (0,0,+) \hspace{0.5cm} (1,0,+) \) are zero. From the definition of \( I^{(1)} \) (Section 3.9)

\[ I^{(1)} |\lambda> = \nu_{\lambda} |\lambda> \]

(3D.10)

and in the group of eigenvalues \( \nu_{\lambda} \) there are five which are zero as well as those which are non-zero \( \nu_{\lambda} \), \( \nu \equiv (r, \ell, -) \) but excluding \((0,0,-) \hspace{0.5cm} (0,1,-) \)
(1,0,-). If no degeneracies occur among the non-zero eigenvalues then
the $|u>$ are unique characteristic solutions which satisfy (3D.9) with
$\omega^{(1)}_{q} = i\omega_{u}$. This in part resolves the problem of finding the coefficients
in (3D.8) since in most cases we have $|h^{(0)}_{q}> \equiv |u>$ but a five fold
degeneracy remains and therefore five zero order solutions are still to be
found. If $|p>$, p=1,2,3,4,5 represents the unknown zero order solutions
then these may be written in general form as

$$|p> = \sum_{\pi} E_{\pi p}|\pi>$$

(3D.11)

with $\pi \equiv (0,0-),(0,0+),(0,1-),(1,0-),(1,0+)$

where the $|\pi>$ are basis vectors which span the first order degeneracy.

The $|p>$ may be considered as a new basis in the degenerate subspace
replacing those vectors denoted by $|\pi>$. They satisfy the zero order
equation with

$$\omega^{(0)}_{p} = 0$$

(3D.12)

and the orthogonality condition

$$<p|1^{(1)} + i\omega^{(1)}_{p} |p> = 0$$

(3D.13)

from (3D.6), is satisfied with

$$\omega^{(1)}_{p} = 0$$

(3D.14)

Components of $|p>$ are found at second order by solving a 5x5 matrix
equation. In setting up this subsidiary problem we shall need expressions
for the first order solutions $|h^{(1)}_{q}>$. In general these will be a linear
combination of basis vectors. Thus.

$$|h^{(1)}_{p}> = \sum_{q} a^{(1)}_{q p} |q> + \sum_{\tau} a^{(1)}_{\tau p} |\tau> + \sum_{u} a^{(1)}_{u p} |u>$$

(3D.15)

where q=1,2,3,4,5, except that p is excluded from the first summation in
view of (3D.5), therefore \( q \neq p \). Coefficients in the second summation can be found from the first order equation (3D.4), in the usual way.

We get

\[
a^{(1)}_{\tau p} = i\kappa \frac{\langle \tau |C^{(1)}| p\rangle}{\nu_\tau} \tag{3D.16}
\]

Hence

\[
|h^{(1)}_p\rangle = \sum_q A^{(1)}_q |q\rangle + i\kappa \sum_{\tau} \frac{\langle \tau |C^{(1)}| p\rangle}{\nu_\tau} |\tau\rangle + \sum_u a^{(1)}_{vp} |v\rangle \tag{3D.17}
\]

The coefficients in the other summations and the components of the \(|p\rangle\) vectors are found from the orthogonality condition (3D.6), applied to the inhomogeneity in the second order equation. This may be written as

\[
<\lambda|I^{(1)} - i\kappa C^{(1)} + i\omega^{(1)}_p |h^{(1)}_p\rangle + <\lambda|I^{(2)} - i\kappa C^{(2)} + i\omega^{(2)}_p |p\rangle = 0 \tag{3D.18}
\]

With \(|h^{(1)}_p\rangle\) given by (3D.17) and \(|\lambda\rangle\) restricted to \(|\pi\rangle\), (3D.8) becomes

\[
\kappa^2 \sum_{\tau} \frac{\langle \tau |C^{(1)}| p\rangle <\pi|C^{(1)}| p\rangle}{\nu_\tau} + <\pi|I^{(2)} - i\kappa C^{(2)} + i\omega^{(2)}_p |p\rangle = 0 \tag{3D.19}
\]

Substituting for \(|p\rangle\) from (3D.11) gives a 5x5 matrix equation for the coefficients \(E_{\pi p}\).
\[ E_{00}, p \quad E_{00}, p \quad E_{01}, p \quad E_{10}, p \quad E_{10}, p \]

\[ \frac{\alpha_0, 01 - \alpha_{01}, 01}{v_{01}^+} \quad \frac{2 \alpha_{00, 01} + \alpha_{01, 01} - v_{01}^+}{v_{01}^+} \quad \frac{2 \alpha_{01, 01} - v_{01}^+}{v_{01}^+} \quad \frac{2 \alpha_{10, 01} + \alpha_{01, 01} - v_{01}^+}{v_{01}^+} \quad \frac{2 \alpha_{01, 01} - v_{01}^+}{v_{01}^+} \]

\[ \frac{v_{01}^+}{v_{01}^+} \quad \frac{v_{01}^+}{v_{01}^+} \quad \frac{v_{01}^+}{v_{01}^+} \quad \frac{v_{01}^+}{v_{01}^+} \quad \frac{v_{01}^+}{v_{01}^+} \]

\[ -\omega_p (2) \quad \frac{2 \alpha_{00, 01} + \alpha_{01, 01} - v_{01}^+}{v_{01}^+} \quad \frac{2 \alpha_{01, 01} - v_{01}^+}{v_{01}^+} \quad \frac{2 \alpha_{10, 01} + \alpha_{01, 01} - v_{01}^+}{v_{01}^+} \quad \frac{2 \alpha_{01, 01} - v_{01}^+}{v_{01}^+} \]

\[ \frac{v_{01}^+}{v_{01}^+} \quad \frac{v_{01}^+}{v_{01}^+} \quad \frac{v_{01}^+}{v_{01}^+} \quad \frac{v_{01}^+}{v_{01}^+} \quad \frac{v_{01}^+}{v_{01}^+} \]

\[ \frac{v_{01}^+}{v_{01}^+} \quad \frac{v_{01}^+}{v_{01}^+} \quad \frac{v_{01}^+}{v_{01}^+} \quad \frac{v_{01}^+}{v_{01}^+} \quad \frac{v_{01}^+}{v_{01}^+} \]
This subsidiary eigenvalue problem contains the same matrix elements as the 4x4 matrix equation (3.80) plus some additional ones proportional to $\kappa^2$. Also an extra dimension has been added. (3D.20) determines the zero order solutions for the longitudinal hydrodynamic modes plus one non-hydrodynamic mode and gives the first non-vanishing dispersion relationship for these characteristic solutions.

The coefficients $a_{\nu p}^{(1)}$ in (3D.17) are found from (3D.18) by considering those cases where $|\lambda> = |\nu>$. This gives

$$a_{\nu p}^{(1)} = i\kappa <\nu|C^{(2)}|\nu>/\nu$$

(3D.21)

Similarly the $A_{qp}^{(1)}$ may be found by replacing $|\lambda>$ with $|p'>$ in (3D.18), $p'=1,2,3,4,5$. This is a convenient choice because the product of $|p'>$ with $|h_p^{(1)}> = i\omega$ picks out only one of the remaining coefficients, namely $A_{p'p}^{(1)}$, since the $|p>$ are orthogonal. Thus the term containing $A_{p'p}^{(1)}$ is

$$i\omega_p^{(1)} <p'|h_p^{(1)}> = i\omega_p^{(1)} A_{p'p}^{(1)}$$

(3D.22)

However in this case $\omega_p^{(1)}$ is zero. Therefore the $A^{(1)}$'s are arbitrary and without loss of generality may be put equal to zero. (3D.17) then becomes

$$|h_p^{(1)}> = i\kappa [\varepsilon\Sigma <\tau|C^{(1)}|\nu>/\nu + \Sigma <\nu|C^{(2)}|\nu>/\nu]$$

(3D.23)

By examining the matrix elements of $C^{(1)}$ and $C^{(2)}$, see (3D.3), it is found that there are only two possible non-vanishing terms in each summation and (3D.23) becomes

$$|h_p^{(1)}> = i\kappa [<01+|C^{(1)}|01+>/\varepsilon + <11+|C^{(1)}|11+>/\varepsilon + <11-|C^{(2)}|11->/\varepsilon + <02-|C^{(2)}|02->/\varepsilon]$$

(3D.24)

Characteristic solutions of (3.119) are to first order, $|p>+\epsilon|h_p^{(1)}> |p>$ where $|p>$ is given by (3D.11) and (3D.20) whilst $|h_p^{(1)}> = i\kappa [\varepsilon\Sigma <\tau|C^{(1)}|\nu>/\nu + \Sigma <\nu|C^{(2)}|\nu>/\nu]$. 
CHAPTER 4: DESCRIPTION OF THE EXPERIMENTAL APPARATUS.

4.1. Introduction

In order to test the thirteen moment predictions of dispersion and absorption coefficient, the acoustic properties of He-Xe gas mixtures have been measured in the range of frequency-pressure ratio, \( f/p_0 \), up to 100 MHz Atmosphere. As is the usual practice, \( f/p_0 \) was varied by changing the gas pressure whilst keeping the frequency constant. Thin piezo-ceramic discs excited at their resonance frequency of 1.005 MHz were used as source and receiver.

The acoustic transducers were mounted coaxially and their separation was varied by moving the transmitter along their common axis. With a source of constant amplitude, the phase and amplitude of the received signal was measured as a function of transducer separation. The relationship between the phase of the received signal and the distance travelled by the sound wave through the gas was approximately linear and the transmitter displacement which produced a phase change of 360° was equal to the wavelength of sound. Using the signal frequency the phase speed was calculated and the absorption coefficient was found from the variation of signal amplitude with transducer separation.

A point receiver in the field of a continuous plane harmonic sound wave detects a signal which varies as

\[
V(z,t) = \tilde{V} \exp \left(-\alpha k_0 z\right) \exp i \left(\frac{2\pi z}{\lambda} - \omega t\right)
\]

(4.1)

where the z axis is perpendicular to the wavefronts and \( \tilde{V} \) is the signal amplitude at \( z = 0 \). \( \alpha \) and \( \lambda \) may be found by assuming that (4.1) holds for transducers of a finite size and analysing the data accordingly, but in practice diffraction effects can give rise to errors.
One way of reducing the influence of diffraction on the results is to work in the far field, that is at distances from the sound source greater than $a^2/\lambda$ where $a$ is the radius of the source. In the present investigation this was impractical due to the high absorption coefficients involved. However, accurate results can be obtained in the near field, particularly if edge effects can be minimised. By using a receiver of a smaller diameter than that of the transmitter, edge effects were reduced.

From (4.1) both $\ln|V|$ and the phase angle $2\pi z/\lambda$ vary linearly with displacement but if more than one harmonic mode were to make a significant contribution to the received signal then these relationships may not be linear. Clearly it is possible in principle, to infer the presence of an additional mode in the gas from amplitude and phase data. In practice diffraction, standing waves or transducer misalignment could give rise to deviation from the ideal behaviour represented by (4.1) and it is difficult to eliminate all possibilities. The approach adopted in the present investigation was to fit the data on the assumption that one mode was excited, to find the phase speed and absorption coefficient for that mode and to indicate where a single mode fit is poor.

4.2. Test Chamber

It is important to minimise electrical and mechanical cross-talk between transmitter and receiver since the received signals can be very small. In order to reduce electrical cross-talk both transducers were screened using one wavelength thick copper discs (Figure 4.1). This technique was successfully used by Schotte in experiments to measure the absorption and dispersion of sound in pure monatomic gases at very low pressures. The copper and piezoceramic discs were glued together
with epoxy adhesive. Mechanical vibrations were isolated by supporting each copper disc around its circumference in a nodal plane.

Mechanical cross-talk refers to sound vibrations that travel through the walls of the chamber to the receiver via the receiver housing. Its effects were reduced in two ways. Firstly the acoustic path was made very narrow wherever possible. Secondly additional attenuation of cross-talk was achieved as a result of reflections at the interfaces between materials of dissimilar acoustic impedance. The brass receiver housing was mounted on three narrow pins and held in position by thin springs (Figure 4.1). At the end of each pin
was a pointed nylon tip. The acoustic impedance mismatch between nylon and brass plus the small area of contact helped to ensure that the amount of mechanical cross-talk was small.

Cooling water was passed through the transmitter housing both to give some control over the temperature in the sample chamber and to allow more power to be delivered to the transmitter transducer without over-heating it. Twin-core coaxial cable supplied the signal to the transmitter through a hole drilled along the axis of its housing. A vacuum sealed lead-through closed off the end of the hole behind the transducer.

A micrometer screw gauge, reading to 2μm, was used to move the transmitter towards or away from the receiver and to measure displacements (Figure 4.2). A brass bellows provided a flexible coupling between the transmitter housing and the chamber. At one end the bellows was soldered to a brass flange (Figure 4.3) which was sealed round the transmitter housing with a viton 'O' ring. The other end of the bellows was soldered to a brass plate which was bolted to the chamber and again sealed with an 'O' ring.

Small adjustments could be made to ensure that the transmitter and receiver surfaces were in parallel planes. Provision was made to tilt the receiver housing about a horizontal axis using an adjusting screw on the back plate (Figure 4.1). A small amount of rotation about a vertical axis was achieved by loosening two bolts below the chamber body and rotating it about a cylindrical pin inserted into the centre of its base. The location of the transmitter meanwhile remained fixed as the bellows flexed to accommodate changes in the relative position of the chamber body and transmitter housing. With the copper discs almost in contact their alignment could be accurately assessed by eye.

A flexible heating element insulated with glass fibre was wrapped around the chamber body to control its temperature. Power to the heater
Figure 4.2: The test chamber and micrometer screw gauge.
To vacuum pump

Cooling water inlet

Aluminium bearing block

Brass flange

Brass bellows

Viewing port

Chamber

Pre-amplifier housing

Figure 4.3: The test chamber. Scale: full size
was provided by a variable duty-cycle supply, the on-time of the duty cycle being adjusted manually. A miniature bead thermistor (GM472 equivalent) was used to monitor the temperature of the gas.

4.3. The gas handling system

The chamber was evacuated using a water cooled diffusion pump (Edwards type 203D) backed by a single stage rotary pump (Edwards type ES50). As the vacuum pumps were left running continuously for long periods to allow the chamber to outgas, safety features were incorporated in case of service failure. If the cooling water supply was interrupted the diffusion pump would immediately cut-out and remain off until a reset button was pressed. Should the electrical supply have failed, air would have been released into the inlet side of the rotary pump thus preventing the possibility of rotary pump oil being forced out by atmospheric pressure once the rotor had stopped. If this had happened the rest of the system would have remained under vacuum.

The system was evacuated with all but V2 and the pressure regulators open (Figure 4.4). When the pressure in the chamber was less than $5 \times 10^{-5}$Torr the sample gases were introduced through the needle valve V10. Research grade helium (purity 99.9995%) and research grade xenon (purity 99.993%) were used in the experiment. The sample gas pressure was measured using a differential pressure transducer (SE Labs type SE21/V1/15/D) to within 0.2Torr. From the partial pressures of its components the composition of the mixture was found.

The procedure for passing gas into the chamber was as follows:-

1. Referring to Figure 4.4, V6, V8 and V10 were closed and the pressure regulator on the xenon cylinder was opened for a short period then closed again.
Figure 4.4: Schematic of gas handling equipment.
2. V7 was closed and the needle valve V10, gradually opened to allow xenon into the chamber. When the desired pressure had been reached V10 was closed.

3. V6 was opened and unwanted gas between V10 and V6 was pumped out, at first using the rotary pump only. Any residual gas in this region was then removed using the diffusion pump.

4. Helium was passed into the chamber in a similar way with V6 closed. Unwanted helium between V10 and V6 was then removed.

After conditions had stabilised a series of amplitude and phase measurements were made at the initial gas pressure. When these had been completed some of the sample was allowed to escape through V10 until the pressure in the chamber had dropped by the desired amount. A new set of results was then recorded. In a complete run data were obtained at up to nine different pressures, the whole procedure taking about 50 minutes from the time the gases entered the chamber.

It is obviously important that contamination of the gas during this period is negligible. When the chamber was closed off under the best vacuum achieved, \(10^{-5}\) Torr, the pressure rose by \(5 \times 10^{-2}\) Torr per hour. If we assume that the chamber contains the sample gases at the lowest pressure at which data were obtained, (7.6 Torr) and that air enters at the above rate, then after an hour the contamination is about 0.7%. During a run however some of the gas was allowed to escape at intervals. If allowance is made for this, the proportion of air in the test gas was never more than 0.3%.

4.4. Signal detection

In order to measure the amplitude and phase of small signals accurately it is important to minimise interference from noise. A simple way of doing this is to use a narrow bandwidth filter centred
on the signal frequency. Crystal filters have been produced with a bandwidth of less than 100Hz at 1MHz, but it is possible to obtain much greater selectivity using phase rectification techniques.

Figure 4.5 illustrates the principle of the method as applied to a general linear network. The signal to be measured divides and is fed to two phase sensitive detectors (P.S.D.). At one of these, P.S.D.(A), reference A is in phase with the signal. The output of P.S.D.(A) is a smooth d.c. voltage proportional to the signal amplitude and, under steady conditions, independent of its phase. At the other phase sensitive detector, P.S.D.(B), reference B is in quadrature with the signal and the d.c. output is zero. If the phase of the signal changes there is initially a phase error voltage, $v_o$, at the output of P.S.D.(B). The phase delay unit responds to this voltage in such a way as to bring reference B back to quadrature with respect to the signal and $v_o$ back to zero. Thus phase changes in the linear network are matched by the

Figure 4.5 : Schematic of signal detection.
phase delay unit. Actual phase measurements can be made across the delay unit itself with the obvious advantages of using a clean stable signal of constant amplitude. The effective bandwidth of the arrangement is of the same order as its inverse response time; typical values are around 0.1Hz - 10Hz.

A block diagram of the electrical system is shown in Figure 4.6. Output from the power amplifier was transformer coupled to the transmitter transducer to improve impedance matching. As the signal at the receiver was often very small, a pre-amplifier with good low noise characteristics was needed. The pre-amplifier and tuned amplifier, bandwidth 30KHz, together had a voltage gain of 70dB. Circuit details are given in Appendix 4A. Noise at the output of the tuned amplifier was measured and found to be equivalent to a noise spectral density at the input of the pre-amplifier of $1.2nV.Hz^{-1}$. Within the effective bandwidth of the detection system this was more than 55dB down on the smallest signals examined.

Additional amplification of between 0dB and 50dB was provided by the switched gain amplifier (S.G.A.). A meter was used to monitor its output level which could be up to 1Vrms. Diagrams of the S.G.A. and meter drive circuit are given in Appendix 4B. Brookdeal linear gates (type 9415) were used as half-wave phase sensitive detectors. Readings of signal amplitude were obtained from a digital voltmeter at the output of P.S.D.(A).

The phase delay unit was driven by a square wave reference signal from the frequency synthesiser. A circuit diagram of the unit is given in Appendix 4C. The delay, of between 200nsec, and 1300nsec. was determined by a steady phase control voltage, $V_p$, which varied between ±5V. giving an effective phase change of up to 400°. (Figure 4.7).
Figure 4.6: Signal detection system.

Frequency synthesiser, Hewlett Packard type 3325A. Power amplifier, Ailtech type 5001. Phase meter, PSI model 4001.
One of the principal disadvantages of the basic system, Figure 4.5, is that measurements of phase are limited to the range of the phase delay unit. This restriction was overcome by arranging for the control voltage to switch levels at an appropriate point so that the delay was changed quickly by one complete cycle (≈ 1μsec.). For example if \( \phi \) were decreasing due to changes in the transducer separation, \( V_\phi \) would increase until it reached +5V. At this point a comparator in the control unit underwent a transition, which caused \( V_\phi \) to change from +5V. to -4.3V. As can be seen from the delay unit characteristic, Figure 4.7, this changed the phase of the delay unit output by 360°. Similarly when \( V_\phi \) reached -5V. it was reset by the control unit to +4.3V. In this way reference B was maintained in quadrature with the signal and reference A in phase with it over any number of cycles. A circuit diagram of the control unit and a brief description of the way it functions is given in Appendix 4D.
The output of the sine-square converter underwent a transition between ±1V. at zero crossings of its input signal. Its circuit diagram is given in Appendix 4E. The converter ensured that the phase error voltage, \( v_o \), and the dynamical characteristics of the phase locked loop were independent of the signal amplitude. In order to see how this comes about consider the way in which reference B returned to quadrature with respect to the signal after the latter had undergone a sudden phase change. Figure 4.8(a) shows an out of balance feedback loop. In the absence of the low pass filter the output of P.S.D(B) varies with time as shown in figure 4.8(c). This signal is referred to as \( v_1 \).

As the circuit returns to a steady state the phase error, \( \varepsilon \), and the corresponding phase control voltage, \( v_\varepsilon \), approach zero. Suppose that \( \bar{v}_1 \) is the mean value of \( v_1 \) averaged over the time period \( T \) and that the filter is a first order CR network with a characteristic time constant \( \tau_s \), such that \( \tau_s >> T \). Then to a good approximation

\[
\frac{dv_o}{dt} = - \frac{v_o - \bar{v}_1}{\tau_s}
\] (4.2)

where \( v_o \) is the filter output voltage. If \( \tau \) is the time constant of the integrator then \( v_o \) is given by

\[
v_o = - \tau \frac{dv_\varepsilon}{dt}
\] (4.3)

In order to close the system of equations we shall define the relationship between \( \bar{v}_1 \) and \( v_\varepsilon \). As can be seen from Figure 4.8(c), with a phase error \( \varepsilon \), the cycle time average of \( v_1 \) is given by

\[
\bar{v}_1 = - \frac{\varepsilon}{360} A_v V_{in}
\] (4.4)

where \( A_v \) is the voltage gain of P.S.D.(B) and \( V_{in} \) is the peak to peak voltage of the square wave signal at its input (Figure 4.8(b)). We can
Figure 4.8 : The out-of-balance feedback loop.
also write

\[ v_\varepsilon = G \varepsilon \quad (4.5) \]

where \( G \) is the gradient of the phase delay unit characteristic. As this characteristic is slightly non-linear \( G \) depends to some degree on the operating point. From (4.4) and (4.5) we get the required relationship between \( \bar{v}_1 \) and \( v_\varepsilon \):

\[ \bar{v}_1 = \beta v_\varepsilon \quad (4.6) \]

where \( \beta = -\frac{A_v V_{in}}{360G} \)

Note that \( G \) is negative hence \( \beta \) is a positive quantity. Combining (4.2) (4.3) and (4.6) gives

\[
\frac{d^2 v_\varepsilon}{dt^2} + \frac{1}{\tau_s} \frac{dv_\varepsilon}{dt} + \frac{\beta}{\tau \tau_s} v_\varepsilon = 0 \quad (4.7)
\]

As \( \beta \) is roughly constant, (4.7) approximates to an equation for a damped harmonic variation of potential with time.

The experimental measurements were made with the circuit parameters adjusted for critical damping of the phase locked loop. This requires that

\[ \tau = 4\beta \tau_s \quad (4.8) \]

(4.8) was approximately satisfied with \( \beta = 2.2, \tau = 0.1s \) and \( \tau_s = 0.01s \).

Since \( G \) is not precisely constant it means that the damping of the phase lock loop varies somewhat with \( \phi \). This is not a serious problem but measures were taken to linearize the delay unit characteristic as described in Appendix 4C.
4.5. Corrections to the data

In spite of the precautions taken, electrical cross-talk made a small contribution to the received signal. When the chamber was evacuated a residual signal could be detected whose amplitude and phase were independent of transducer separation. Although 140dB down on the voltage applied to the transmitter, it was large enough to have a significant effect on the results, particularly at low gas pressures. Prior to each run the residual signal was recorded so that it could be subtracted from measurements made with gas in the chamber.

A further correction was necessary due to the limitations of the sine-square converter. Ideally it should trigger at the same point on a cycle regardless of the amplitude of the sinusoidal input. Although it was designed to change state at the zero crossing point of the input signal, in practice the triggering point varied by ± 5ns as the input was reduced by 20dB. from its maximum value (1Vrms). In order to correct for this effect, measurements of phase were made for different signal amplitudes. The readings were taken with the phase detection system as shown in Figure 4.6 but with the frequency synthesiser connected to the input of the S.G.A. via an R.F. attenuator. Whilst signal levels were varied using the attenuator, readings from the digital voltmeter (D.V.M.) at the output of P.S.D.(A) and from the phasemeter were noted. The results are plotted in Figure 4.9.

\( v \) is the D.V.M. reading and \( \delta \phi(v) \) is the phase shift introduced by the sine-square converter relative to that which occurs when \( v = 5.0 \) Volts. By implication \( \delta \phi(5.0) = 0 \). A computer programme was written to fit a suitable function; the first five Tchebechev polynomials, to the above results. Corrections to the data were made by calculating \( \delta \phi(v) \) from the fitting function and subtracting the correction from measured phase angles.
4.6. Experimental procedure and data analysis

Electrical equipment was switched on and allowed to stabilise for at least two hours before any measurements were made. After that time the amplitude and phase of the residual signal were recorded whilst the test chamber was still under vacuum. Gas was then allowed into the chamber as described in Section 4.3 and the partial pressures of each constituent noted. After a few minutes had elapsed to allow the gas to reach thermal equilibrium with its surroundings, the resistance of the thermistor in the chamber was recorded.

The amplitude and phase of the signal were measured for the initial transmitter-receiver separation, typically 1.40mm. This distance was reduced by equal increments and the measurements were repeated at each step. When a sufficient number of readings had been taken the gas pressure was reduced and a further set of results obtained. For a complete run data were recorded at up to nine different pressures in the range $4 \times 10^{-2}\text{Atm}$ to $1.0 \times 10^{-2}\text{Atm}$.
The transducer separation $\Delta z$, had to be large enough for the influence of standing wave and boundary layer effects to be negligible. The contribution from standing waves can be estimated from the fact that a disturbance reflected at both transducers travels a distance $2\Delta z$ further than one arriving directly from the transmitter. Assuming perfect reflections and neglecting losses, the relative magnitude of the contribution from reflections is approximately $\exp(-2ak_o\Delta z)$. This factor was kept below 1% by ensuring that $2ak_o\Delta z > 5$ for all measurements.

The precise separation required to reduce boundary layer effects to negligible proportions is not known but it is generally considered to be of the order of several mean free paths. Using (1.2) and (2.15)B, the above restriction can be written as $\Delta z > 5/2 n_o \sigma_o \text{Im}(\kappa)$. From Section 2.10 it is predicted that $\text{Im}(\kappa)$ is at the most a little more than $1/8$ for the region of interest. If we take $1/n_o \sigma_o$ to be a reasonable estimate of the mean free path, then the transducer separation was 20 mean free paths or greater.

A computer programme was written to calculate the absorption coefficient $\alpha$, and the phase speed $U$, from the experimental data. The first step in the calculation was to subtract the phase error, $\delta \phi(v)$, from all measured phase angles. We shall suppose that $\hat{V}_T(z)$ is a complex voltage which represents the phase and amplitude of the signal after this correction has been made. The next step was to subtract the residual signal due to cross-talk, $\hat{V}_R$, from $\hat{V}_T(z)$. If $\hat{V}_O(z)$ is what remains after correcting for cross-talk then

$$\hat{V}_O(z) = \hat{V}_T(z) - \hat{V}_R \quad (4.9)$$

It was assumed that $\hat{V}_O(z)$ corresponds to a signal of the form (4.1), hence
\[ |\vec{V}_o| = |\vec{V}| \exp(-ak_0z) \quad (4.10) \]
where \( k_0 = U_0/\Omega \nabla_0 \frac{\partial}{\partial z} \)

and

\[ \arg V_0(z) - \arg V_0(0) = \phi(z) - \phi(0) = \frac{2\pi z}{\lambda} \quad (4.11) \]

\( \alpha \) was found by fitting a linear relationship to experimental values of \( \ln |\vec{V}_o| \) and corresponding values of \( z \). The optimum fit was determined by a weighted least squares criterion using standard library computer programmes. Similarly the wavelength \( \lambda \) was found by fitting a linear law to the corrected phase-displacement data. The phase speed was then calculated from

\[ U = \frac{2\pi \Omega}{\lambda} \quad (4.12) \]

4.7. Some comments on the electrical system

Experience has taught us that interference from thermal noise and mechanical cross-talk can be overcome without great difficulty. The reduction of electrical cross-talk to acceptable levels on the other hand, proved to be a more serious problem. Evidently screening of the transducers and the suppression of possible sources of radiation has a high priority.

Even in the absence of cross-talk, phase measurements to better than 1\% at 1MHz are difficult to achieve using standard circuit techniques. This, coupled with the high absorption coefficients encountered with gas mixtures, limits the accuracy to which phase velocity can be measured. Opting for a lower frequency has the advantage that phase measurements can be carried out with greater precision but there is a price to be paid. To work at the same frequency-pressure ratio as before the gas pressure must be less, which probably means receiver signals are weaker. The balance to be struck will depend on circumstances but in the present case more accurate results might have been obtained by using a lower signal frequency.
The pre-amplifier, Figure 4.10, is based on a low noise wideband integrated circuit, 2N459, supplied by Ferranti. The I.C. has a gain of 60dB, 3dB down at 15MHz. It was chosen chiefly because of its low effective noise resistance of 40Ω, equivalent to a white noise spectral density of 800pV.Hz\(^{-1}\).

The tuned filter stage provides a further 10dB gain and has a bandwidth of 32KHz centred on the signal frequency, 1.005MHz. It was included in order to limit the noise and interference that might otherwise be transferred to subsequent stages. At the output is a unity gain stage which can handle signal levels of up to 1Vrms without significant distortion.
Figure 4.10

LOW NOISE PRE-AMP.

&

1 MHz TUNED AMP.

FOR

RZT TRANSDUCER.

Av = 70 dB

q = 30

Residual output noise

TRANSDUCER'S LM304A.

(1.24 nV/√Hz).

E.A.W.
PHYSICS DEPT.
1983.
APPENDIX 4B: THE SWITCHED GAIN AMPLIFIER AND METER DRIVE CIRCUIT

CMOS analogue gates, type DG200, are used to switch the negative feedback in each of three amplification stages, Figure 4.11. The gain of the S.G.A. may be changed from 0dB to 50dB in 10dB steps. A wideband response is achieved by using cascode gain stages to limit Miller effects.45

The meter drive circuit, Figure 4.12, consists of a unity gain amplifier, a half wave rectifier and a stage which matches the current through the meter with the mean rectifier current. D1 ensures that under quiescent conditions the base-emitter junction of Tr4 is biased to a point on the knee of its characteristic. When a signal appears at the emitter of Tr3, Tr4 conducts only during the positive half cycle. Thus Tr4 acts as a half wave rectifier which supplies a charging current to the capacitor C. Under steady conditions a discharged current passes through Tr5 equal to the mean charging current so that the potential difference across C is constant and virtually zero. An increase in the charging current would tend to cause a rise in the potential on C but this is counteracted by a current mirror.46 In response to a small change in the potential at its non-inverting input the I.C. drives a greater current through Tr6. This increase is reflected firstly in the discharge current through Tr5 and secondly in the meter current. The trimmer potentiometer in the emitter of Tr7 is used to adjust the meter calibration so that full scale deflection represents 1Vrms at the input to the circuit.
Figure 4.12

**Meter Drive Circuit.**

Meter Circuit
Input from Main Amp. Out.
APPENDIX 4C: THE PHASE DELAY UNIT.

A 1MHz reference signal is delayed by between 200 ns and 1300 ns depending on the value of the phase control voltage, $V^\phi$. After passing through a squarer circuit the reference is delayed by two monostable multivibrators connected in tandem (Figure 4.13). The delay time at the first monostable is the time for capacitor $C_1$ to charge from $-5V$ to $0V$. Its charging current is related to the control voltage via a current mirror circuit. Similarly the delay at the second monostable depends on the time taken for $C_2$ to charge from $-5V$ to $0V$.

If we suppose for the moment that the zener diode and the two parallel resistors at the emitter of Tr1 are replaced by a single resistor then a change in the control voltage gives rise to a proportional change in the emitter current of Tr1. This is reflected in the current sources Tr2 and Tr3 used to charge $C_1$ and $C_2$ respectively. The rate at which these capacitors are charged is inversely proportional to the delay time, therefore the relationship between $V^\phi$ and the phase delay $\phi$ is of the form

$$\phi = \frac{a}{V^\phi + b}$$  \hfill (4C.1)

where $a$ and $b$ are constants. It would have been better had this been a linear relationship since the damping of the phase locked loop depends on $G = \frac{dV^\phi}{d\phi}$, see equations (4.5) - (4.8). A constant $G$ might have been obtained with a redesigned circuit but instead a compromise solution was adopted. A zener diode was connected to the emitter of Tr1 to reduce the non-linearity of the delay units characteristic (Figure 4.7).

After the delay a 500 ns monostable multivibrator restores a 1:1 mark space ratio. The signal then passes to the output labelled $\phi$ via a NOR gate used as a line driver. The quadrature output is also derived from the 500 ns monostable. First the pulse repetition frequency is
doubled to 2MHz, then the transient of the 2MHz signal which occurs one quarter of the way through the original 1MHz cycle is used to initiate the quadrature cycle.
Figure 4.13

**DIGITAL PHASE DELAY UNIT** (1 MHz)

- Control
- 1/2 V₀
- From Phase Control Unit
- 1.005 MHz.
- Ref. from Oscillator
- ½ P 0.1 µF 220 µF

Schematic diagram showing components like transistors (2N3703), resistors (1K, 2.2K), capacitors (0.1 µF, 220 pF), and logic gates (74121, 74128) for phase delay circuitry.

E.A.W.
Physics Dept.,
1983

Quad output circuit

Outputs to P.S.O. Refs.
APPENDIX 4D: THE PHASE CONTROL UNIT

The phase control unit was used to derive the potential, \( V_\phi \), that determined the delay introduced by the phase delay unit. Most of the time the control unit simply acted as an integrator, a function which was carried out by I.C.1 (Figure 4.14). In addition provision was made to reset the output level for each phase change of 360° of the signal at the input of P.S.D.(B). As described in the main text this meant that when \( V_\phi \) reached +5V, it was reset to -4.3V. and when it reached -5V, it was reset to +4.3V. These voltages were the reference levels for four comparitors built around I.C.2, I.C.3, I.C.4 and I.C.5. The output of all the comparitors was normally high and points P and Q in the circuit normally low. Under these conditions the auxiliary inputs to the integrator have no effect since Tr1 and Tr4 are turned off.

Let us consider the way in which \( V_\phi \) was altered once it had reached a limiting value. The reference level for the comparitor containing I.C.2 is +5V., and hence its output went low whenever \( V_\phi \) exceeded this value. When this happened the flip-flop output at P went high turning Tr1 on. As a result the value of \( V_\phi \) fell until it reached the reference level of I.C.3, that is -4.3V. P then went low again turning Tr1 off. A similar process occurred involving I.C.4 and I.C.5 when \( V_\phi \) made the transition from -5V. to +4.3V.
Figure 4.14  PHASE CONTROL UNIT.

Extends dynamic range to compensate for multiple 360° phase shifts via reset action.
A sinusoidal input signal was clipped symmetrically using the limiting diodes D1 and D2. A comparitor (Type LM360) converted the signal to a square wave and a 500 nsec. monostable multivibrator was used to establish a 1:1 mark space ratio. We have used an opto-isolator in the output stage to combat some early problems with earth loops. After some modifications to earth connections elsewhere in the system, the isolator was of marginal benefit.
5.1. Results for helium-xenon mixtures

Data were obtained at a nominal temperature of 25°C for mixtures in which the mole fraction of helium ranged from 0.2 to 0.8. Numerical values of the measured absorption coefficients and phase velocities are given in Appendix 5A and the results are shown graphically in Figures 5.1 to 5.9. The continuous curves on the graphs are the thirteen moment predictions for Maxwell molecules and the dashed curves represent the theoretical results calculated using a rigid sphere model of interatomic potential. As described in Section 2.6, individual species viscosities and the diffusion coefficient of the mixture were used to define collision parameters for the calculations (Table 5.1)

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Viscosity of helium</td>
<td>19.86x10^-6 Pa.s.</td>
<td>47</td>
</tr>
<tr>
<td>Viscosity of xenon</td>
<td>23.05x10^-6 Pa.s.</td>
<td></td>
</tr>
<tr>
<td>Diffusion coefficient of He-Xe</td>
<td>55.4 x10^-6 m²s⁻¹</td>
<td>48</td>
</tr>
</tbody>
</table>

**TABLE 5.1. Transport coefficients at 25°C**

The diffusion coefficient at 25°C is derived from the value obtained by Wahby, Abdel-Rahman and Los at 26°C with a small correction calculated on the assumption that $D_{12} \propto T^s$ where $s$ is a constant.

Reasonable agreement between theory and experiment is found particularly when the proportion of helium atoms is 0.6 or greater. In most cases the choice of interatomic potential makes little difference to the theoretical results except in the region of the critical composition. On the whole it appears that predictions based on the rigid sphere atomic model correspond more closely with the data than those calculated assuming the particles are Maxwell molecules.
5.2. Comparison of the experimental dispersion data with theory

It is evident from the low frequency phase speed data that experimental values of $U$ are about $1\frac{1}{2}$% above what one would expect considering that $U_o/U$ should tend to 1 in the low frequency limit. The origin of this systematic error is not known but it accounts for some of the discrepancy between theory and experiment.

The behaviour of the experimental dispersion results as the mole fraction of helium increases is highly significant. For $x_{He}$ equal to 0.2, 0.3 or 0.4 (Figures 5.1, 5.2 and 5.3) the phase speed is fairly constant at low frequencies but decreases with frequency above $70 \text{MHz.Atms.}^{-1}$. In contrast, for $x_{He}$ in the range 0.6 to 0.8 there is a large increase in phase speed with frequency (Figures 5.6, 5.7 and 5.8). This radical change in the velocity dispersion characteristic with $x_{He}$ is precisely the behaviour expected as the composition of the mixture passes through a critical value. According to the thirteen moment theory the complex wavenumber characteristic of the acoustic mode undergoes a transition at the critical composition. For frequencies above the critical value the imaginary part of the complex wavenumber does not change greatly but the real part does, decreasing suddenly as the critical composition is exceeded (Compare Figure 2.9 and 2.10). Correspondingly theoretical values of $U_o/U$ above the critical frequency are much lower for $x_{He} = 0.6$ say, than for $x_{He} = 0.4$. The experimental results, despite some small discrepancies, clearly support this general trend in the dispersion characteristics thus providing indirect evidence for the coincidence of roots.

At the intermediate composition, where $x_{He} = 0.5$, the functional form given by equation 4.1 did not fit the corrected phase and amplitude data as closely as at other compositions. A possible reason for this is that the distance over which useful results could be obtained was limited by the high absorption coefficients involved. This has contributed to the random errors in $\alpha$ and $U_o/U$, as exhibited by the data plotted in Figure 5.5.
A helium mole fraction of 0.5 is greater than the predicted critical value \( (= 0.45) \) consequently the theoretical dispersion curves, Figure 5.5, show \( U_0/U \) decreasing with frequency over the whole range up to \( 100 \text{MHz} \). However, this does not correspond with the experimental results. Experimental values of \( U_0/U \) fall between the predicted dispersion curves for the acoustic mode and the mode whose wavenumber coincides with that of the acoustic mode at the critical point (Figure 5.9). The identity of the second mode is found by comparing its low frequency behaviour with the known characteristics of the hydrodynamic modes. As with the standard temperature results of Chapter 2 we find that when the atoms are considered as hard spheres it is the diffusion mode whose complex wavenumber approaches that of the acoustic mode and coincides with it at the critical point. In the case of Maxwell molecules it is the thermal mode. The discrepancy between theory and experimental values of \( U_0/U \) when \( x_{\text{He}} = 0.5 \), may have been due to contributions to the received signal from the second mode. In other words the apparent rate of change of phase with transducer separation may have been the result of two harmonic disturbances with different wavenumbers.

As an example of the kind of effects that can occur suppose that the received signal at a certain point close to the transmitter contains two contributions \( \hat{V}_1 \) and \( \hat{V}_2 \), that are in phase. This situation is illustrated by the phasor diagram, Figure 5.10(a). If the phase of \( \hat{V}_1 \) changes more rapidly with transducer separation than that of \( \hat{V}_2 \) then when the transducers are further apart the phase of \( \hat{V}_1 \) is more retarded, Figure 5.10(b). Notice that the resultant signal has undergone a phase change which is intermediate between that of \( \hat{V}_1 \) and \( \hat{V}_2 \). The amplitudes of \( \hat{V}_1 \) and \( \hat{V}_2 \) have decreased with transducer separation due to absorption in the gas but the amplitude of the resultant has decreased to a relatively greater degree as a result of the components moving out of phase. By forcing a single mode fit to the
resultant in this example, we would get an overestimate of the
absorption coefficient and a phase speed intermediate between those
of the two modes involved.

![Phasor diagrams of the receiver signal due to two harmonic modes.](image)

Figure 5.10: Phasor diagrams of the receiver signal due to two harmonic modes.

A helium mole fraction of 0.45 is just below the predicted critical
value for Maxwell molecules (0.48) and slightly above the critical
value found using the rigid sphere model (0.43). This means that the
calculated dispersion relationships differ widely depending on which
of the two atomic models is used. The predictions obtained for Maxwell
molecules, Figure 5.4, correspond more closely with the data than do
those for rigid spheres. However it would be wrong to attach too much
significance to this result since the calculations are very sensitive to
parameters such as $x_{He}$, in the critical region.

5.3. The absorption coefficient of helium-xenon mixtures.

The thirteen moment predictions of absorption coefficient are
consistent with the data in the frequency range up to 100MHz.Atm.$^{-1}$ for
helium mole fractions of 0.2, 0.3, 0.7 and 0.8 (Figures 5.1, 5.2, 5.7,
and 5.8). At intermediate compositions the experimental results show
that the absorption coefficient continues to increase with frequency
beyond the point where the theory predicts a maximum* (Figures 5.3, 5.4

*A similar effect can be seen in the results of Prangsma Jonkman and Beenakker in relation to Goldman's predictions for He-Ar mixtures.
5.5 and 5.6). This is probably due to the limitations of the thirteen moment approximations at the upper end of the frequency range, although multi-mode effects could also be significant in the critical region.

Numerical checks have been carried out which confirm that the thirteen moment predictions are in agreement with the Kohler absorption coefficient at low frequencies. In the Kohler region, that is where $\alpha$ varies linearly with frequency, it is found that predicted absorption coefficients are consistently higher than the corresponding experimental results. As pointed out in Section 1.4 disagreements of this nature and magnitude have been found by other authors\textsuperscript{17,28}. Not only does the theory overestimate the absorption coefficient in the Kohler region, there is a tendency for the predicted values of $U_2/U$ to deviate from 1 by amounts greater than those found experimentally. It would be of interest to discover the extent to which these differences depend on the choice of interatomic potential.

5.4. Conclusions and suggestions for further work

The frequency dependence of the complex wavenumbers of harmonic modes have been determined from the linearized thirteen moment equations for binary monatomic gas mixtures. It is found that in disparate mass mixtures at a critical composition and at a specific critical frequency the complex wavenumber of the acoustic mode is equal to the wavenumber of one other hydrodynamic mode. Associated with the coincidence of roots is a discontinuous change in the wavenumber characteristic of the acoustic mode at the critical composition. This prediction has observable consequences since the real part of the wavenumber is related to the phase speed of sound and the imaginary part determines the acoustic absorption coefficient. According to the theory there is a marked difference in the dispersion characteristic for the acoustic mode depending on whether the mole fraction of the lighter species $x_1$, is
greater than, or less than the critical value \( x_{1c} \). For \( x_1 < x_{1c} \) the theory predicts that the phase speed decreases with frequency \( f \), for \( f > f_c \) where \( f_c \) is the critical frequency. When the composition is such that \( x_1 > x_{1c} \) the phase speed increases with frequency. In the case of helium-xenon mixtures it is predicted that \( x_{1c} = 0.45 \) and \( f_c = 75 \text{MHz} \). Atms^{-1}

Experimental results have confirmed these qualitative trends in the dispersion characteristic thus providing strong circumstantial evidence for the coincidence of roots. It is not possible to get a precise value of the critical parameters from the experimental data but the results are consistent with the above theoretical predictions.

In the main the experimental results were in reasonable quantitative agreement with the thirteen moment predictions for the acoustic mode alone, a notable exception being the dispersion data for a helium mole fraction of 0.5 at frequencies exceeding the critical value. As 0.5 is greater than the critical mole fraction of helium, the theory predicts a rapid decrease in \( U_0/U \) above about \( 70 \text{MHz} \). Atms^{-1} \) (Figure 5.5). In order to account for the disparity it is suggested that hybrid disturbances are detected in the critical region consisting of two or more harmonic modes. If more than one mode is observed then the data cannot be correctly analysed on the assumption that the detected signal varies as \( \exp(-\alpha k_0 z) \exp(i2\pi z/\lambda - \omega t) \) since two and possibly more such terms would be needed. It would be difficult to obtain data of sufficient accuracy for a two mode fit in which \( \alpha \) and \( \lambda \) are found for each mode as free parameters and certainly the results we have obtained are not good enough for this. However, if the problems discussed in Section 4.1 can be overcome, it should be possible to directly observe two mode effects from phase and amplitude data.

In the critical region the two small parameters that we have defined, \( \kappa \) and \( \delta \), are of the same order of magnitude. This special circumstance allows us to analyse harmonic disturbances in a restricted frequency range
as if there was only one ordering parameter, $\delta$ say. Exploiting the small parameters using perturbation theory we have found that the thirteen moment predictions for longitudinal disturbances in mixtures of Maxwell molecules are an exact consequence of the linearized Boltzmann equation to order $\delta$, when $\kappa \sim \delta$.

An outstanding theoretical problem that remains is the calculation of the relative magnitude of each mode from specific boundary conditions. Knowing that linear combination of modes which matches conditions at a boundary source has little practical value when only the acoustic mode is observed but obviously it would be useful to have this information if more than one mode is detected. One might approach the problem by defining an effective boundary value for each complex moment amplitude, the intention being that the correct amplitudes away from the boundary can be calculated on the hypothetical assumption that the modes decay exponentially with distance in the vicinity of the source in the same way as they do in the bulk of the gas. In fact the effective boundary values defined in this way are not equal to those which occur physically since the modes are distorted in the Knudsen layer. In principle effective source amplitudes may be calculated from the Boltzmann equation with suitably chosen boundary conditions on the distribution functions. Although the problem as applied to the thirteen-moment description is very difficult, reasonable estimates could be obtained using simplified treatments, possibly involving model kinetic equations. The relative weight of each mode may be determined from that linear combination which gives the best fit to a given set of boundary values.

Finally it should be noted that the observation of two longitudinal modes is closely related to similar phenomena occurring in fluid saturated porous media. Two compressive modes have been identified in experiments carried out by Plona\textsuperscript{49} on wet saturated fused glass beads using 0.5MHz tone bursts. The results have been analysed by Berryman\textsuperscript{50} using a
theory originally developed by Biot\textsuperscript{51,52}. The important point about this work that shows its relationship with the present study is that the slower of the two predicted longitudinal disturbance is a diffusion mode. This is evident from the fact that the porous frame and the fluid oscillate in antiphase at low frequencies for the slow disturbance, with a dispersion relationship of the form $\Omega = -ik^2D$, where $D$ is a constant.

The similarities between harmonic propagation in disparate mass gas mixtures and fluid saturated porous media would undoubtedly repay further study. In particular it would be interesting to see if physical conditions in porous media can give rise to coincident roots.
Expt.: Run 1 +
Run 2 ×

Theory:
Maxwell molecules
Rigid spheres

$U_0/U$

$f/p_0 \text{ MHz Atms}^{-1}$

0 20 40 60 80 100
Expt. : Run 5 ○  
Run 6 +  
Run 7 ×

Theory : Rigid spheres  
Maxwell molecules

$\frac{U_0}{U}$ vs. $\frac{f}{p_0}$ MHz Atms.$^{-1}$
Expt.: Run 10 x Theory:
Run 11 o Maxwell molecules —
Run 12 + Rigid spheres ——
Expt.: Run 13 ○ Theory: Rigid spheres ———
Run 14 × Maxwell molecules ———
Run 15 +

$U_0/U$

$\alpha$

$f/p_0$ MHz.Atms.$^{-1}$
Expt. : Run 16 ×  Theory : Rigid spheres -----  
Run 17 +  Maxwell molecules ——
Figure 5.8: He(0.8)-Xe

Expt.: Run 18 ×  Theory: Rigid spheres ---
Run 19 +  Maxwell molecules ---

\[
\frac{u_0}{u} \quad \text{and} \quad \alpha
\]

vs.

\[
f/p_o \quad \text{MHz.Atms}^{-1}
\]
Table 5.2: Run 1

He(0.2)-Xe

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<th>$f/p_0$ MHz.Atms.$^{-1}$</th>
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<th>$U_0/U$</th>
<th>Temp $^\circ$C</th>
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<tbody>
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<td>24.5</td>
<td>0.069</td>
<td>0.981</td>
<td>25.5</td>
</tr>
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<td>39.2</td>
<td>0.103</td>
<td>0.980</td>
<td>25.4</td>
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<tr>
<td>54.4</td>
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<td>25.2</td>
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<td>66.7</td>
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<td>0.991</td>
<td>25.2</td>
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<tr>
<td>69.5</td>
<td>0.160</td>
<td>0.989</td>
<td>25.0</td>
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<td>0.988</td>
<td>25.2</td>
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Table 5.3: Run 2

He(0.2)-Xe

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<th>$U_0/U$</th>
<th>Temp $^\circ$C</th>
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<tr>
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<td>0.068</td>
<td>0.986</td>
<td>24.7</td>
</tr>
<tr>
<td>39.2</td>
<td>0.103</td>
<td>0.986</td>
<td>24.6</td>
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<td>54.4</td>
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<td>0.989</td>
<td>24.6</td>
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<td>24.6</td>
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<td>0.987</td>
<td>24.6</td>
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<td>0.998</td>
<td>24.6</td>
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<td>1.000</td>
<td>24.7</td>
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He(0.3)-Xe

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### Table 5.5: Run 4.

He(0.3)-Xe

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<td>°C</td>
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Table 5.6: Run 5.

He(0.4)-Xe

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Table 5.7: Run 6.

He(0.4)-Xe

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Table 5.8: Run 7.
He(0.4)-Xe

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<td>54.4</td>
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Table 5.9: Run 8.
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He(0.45)-Xe

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<th>Temp °C</th>
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He(0.5)-Xe

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<th>Temp °C</th>
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Table 5.12: Run 11

He(0.50)-Xe

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<th>Temp °C</th>
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Table 5.13: Run 12.

He(0.50)-Xe

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<th>Temp °C</th>
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Table 5.14 : Run 13.
He(0.60)-Xe

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Table 5.15 : Run 14.
He(0.6)-Xe

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He(0.6)-Xe

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Table 5.17 : Run 16
He(0.7)-Xe

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He(0.7)-Xe

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<th>Temp °C</th>
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He(0.8)-Xe

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REFERENCES


34. Enskog, D., K. Svensk. Vet.-Akad. Handl. 64, no.4. (1921)


44. NAG Fortran Library Manual Mk.10 (Numerical Algorithms Group, Oxford 1983). F02AKF was used for the eigenvalue problem and E02ADFW was used for curve fitting.


