ON THE APPROACH TO LOCAL EQUILIBRIUM AND THE
STABILITY OF THE UNIFORM DENSITY STATIONARY STATES
OF A VAN DER WAALS GAS

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B.Sc., Case Institute of Technology, 1963
M.Sc., Case Institute of Technology, 1965

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF
THE REQUIREMENTS FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY
IN THE DEPARTMENT
OF
PHYSICS

We accept this thesis as conforming to the required standard

THE UNIVERSITY OF BRITISH COLUMBIA
DECEMBER, 1970
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Date 12/29/1970
ABSTRACT

Some equilibrium and non-equilibrium properties of a gas of hard spheres with a long range attractive potential are investigated by considering the properties of an equation, proposed by deSobrino (1967), for a one-particle distribution function for the gas model considered. The solutions of this equation obey an H-theorem indicating that our gas model approaches local equilibrium. Equilibrium solutions of the kinetic equation are studied; they satisfy an equation for the density $\eta(r)$ for which space dependent solutions exist and correspond to a mixture of gas and liquid phases.

The kinetic equation is next linearized and the linearized equation is applied to the study of the stability of the uniform density stationary states of a Van der Waals gas. A brief asymptotic analysis of sound propagation in dilute gases is presented in view of introducing an approximation of the linearized Boltzmann collision integral due to Gross and Jackson (1959). To first order, the dispersion in the speed of sound at low frequencies is the same as the Burnett and Wang Chang-Uhlenbeck values while the absorption of sound is slightly less than the Burnett value and slightly greater than the Wang Chang-Uhlenbeck value; all three are in good agreement with experiment. Finally, using the method developed in the previous section, an approximation for the linearized Enskog collision integral is obtained; a dispersion relation is derived and used to show that the uniform density states which correspond to local minima of the free energy and traditionally called metastable, are in fact stable against sufficiently small perturbations.
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ACKNOWLEDGEMENT

I wish to thank Dr. L. Sobrino for suggesting this problem and for the many valuable discussions I have had with him.

A University of British Columbia Graduate Fellowship and research grants from the National Research Council of Canada are gratefully acknowledged.
CHAPTER 1. INTRODUCTION

1. INTRODUCTION

Properties of dense gases can be studied by means of fluid mechanics. The validity of this method is restricted; the fluid equations which describe the evolution in time of the local density, velocity and internal energy density are subject to the requirement that these macroscopic quantities be slowly varying functions of space and time i.e. that the ratio of the change in a macroscopic variable to that variable, over a distance of the order of the mean free path and time of the order of the collision time is negligible.

A more fundamental approach is that of kinetic theory which provides a molecular description of the gas and whose validity is not restricted by the above conditions. A kinetic theory of dense gases was first introduced by Enskog (1922); this is a direct extension of the kinetic theory of dilute gases based on the Boltzmann equation. In the derivation of this equation it was assumed that only binary collisions occur and that the molecules have no extension in space. For a dense gas these assumptions no longer hold; Enskog made a first step in the right direction by considering a gas of rigid spheres of diameter \( \sigma \). For such a gas, collisions are instantaneous so that the probability of multiple encounters remains negligible. However a change in the collision frequency \( \lambda \) results from the finite volume of the molecules; this change is made up of an increase in \( \lambda \) due to the decrease in the phase space of the gas and a decrease in \( \lambda \) due
to molecules screening one another from the other oncoming molecules; thus the collision integral on the RHS of the Boltzmann equation is increased by a factor of $\eta$; furthermore the one-particle distribution functions in that integral are evaluated at the center of the colliding molecules. Although closer to reality, Enskog's theory does not allow for the occurrence of ternary and higher order collisions nor is the spherical model a faithful description of the real intermolecular potential.

A rigorous kinetic theory of dense gases based on the Liouville equation was introduced independently by Born and Green, Kirkwood, Bogoliubov, Yvon in 1946. The only assumption in this theory is that the interaction potential is an additive two-particle potential. A set of coupled equations, the so-called B-B-C-K-Y hierarchy, is obtained by integrating the Liouville equation over the phases of $N-s$ molecules, ($N$ is the total number of molecules of a gas and $s=1,2,\ldots N-1$). A method of solving this hierarchy due to Bogoliubov is clearly presented in a review article by E.G.D.Cohen (1968). This approach to the study of dense gases takes into account ternary and higher order collisions; however, although more satisfying than the method of Enskog from a mathematical point of view, Bogoliubov's method has met with some difficulty (due to the divergence of the expansion of the two-particle distribution function in terms of the one-particle distribution function) which prevents its use, at the present time, for the study of the problem of condensation.

DeSobrino (1967) proposed an equation for the one-particle distribution function of a Van der Waals gas obtained from the first
equation of the B-B-G-K-Y hierarchy by rewriting the two-particle distribution function $f_2$ in terms of the one-particle distribution function $f$ and the pair correlation function at contact $\eta$. When $\eta$ is assumed to be velocity independent, this equation reduces to the Enskog equation with an attractive potential taken into account; deSorboino further assumed that $\eta$ is equal to $(\nu - \nu_b)^{-1}$ which is equivalent to stating that the model under consideration is the traditional Van der Waals gas. The problem of determining the stability of uniform density stationary states was investigated using a simple relaxation time approximation for the collision integral.

In this thesis the problem of approach to local equilibrium and of stability of uniform density stationary states are studied in a more accurate manner. We do not use any specific form of $\eta$ which we simply restrict to be a monotonically increasing, continuous function of the density; we also obtain a dispersion relation needed in the study of stability using a more accurate approximation of the kinetic equation along the lines of a method developed by Gross and Jackson (1959) and Sirovich (1965a).

This thesis is divided into two parts; the first part to be found in chapter 2, deals with the approach to local equilibrium and the equilibrium solutions of the kinetic equation (2.10). An $H$ function is defined which, in the equilibrium limit, yields the correct thermodynamic functions of a Van der Waals gas; the corresponding $H$ theorem is proved for a distribution function $f$ which satisfies our kinetic equation; this implies that the gas described by this equation
approaches local equilibrium. Stationary solutions of (2.10) are then found to obey an equation for the density \( n(r) \) which is identical with the equation obtained by Van Kampen (1964) from equilibrium statistical mechanics; the existence of space dependent solutions of this equation has been discussed by Van Kampen (1964) and Strickfaden (1970). This equation also gives excellent agreement with experiment in calculations of surface tension not too close to the critical point (Strickfaden and deSobrino, 1970).

Because of the complicated expression for the Enskog collision integral, a calculation of non equilibrium solutions of the kinetic equation (2.10) is difficult. However, for a gas in a near equilibrium state, this equation can be linearized and the result expanded to first order in gradients \( \nabla_r \) about \( r \). The linearized Enskog collision integral \( \mathcal{L}_e(\mathcal{L}) \) is equal to \( n(\mathcal{L}) + K(\mathcal{L}) \). where \( \mathcal{L} \) is the linearized Boltzmann operator and \( K(\mathcal{L}) \) is the linearized non-local term. Even in this form the linearized kinetic equation does not lend itself readily to practical computations and an approximation must now be introduced. In section 5 a method of approximating \( \mathcal{L}(\mathcal{L}) \) due to Gross and Jackson is introduced in connection with a brief review of the problem of sound propagation in a dilute gas at low frequencies. In section 6 this method is applied to the linearized kinetic equation of a Van der Waals gas in order to investigate the stability of the uniform density stationary states. We verified the conclusion arrived at by deSobrino in his less accurate calculations that states of a Van der Waals gas, traditionally regarded as metastable, are indeed stable against small dynamical perturbations.
CHAPTER 2. APPROACH TO LOCAL EQUILIBRIUM AND EQUILIBRIUM PROPERTIES

2. THE KINETIC EQUATION

In this section we briefly describe the gas model under consideration and derive a kinetic equation for this model.

We consider, inside a cube of side L, a Van der Waals gas of N molecules whose interaction potential is of the form

\[ U(r) = \begin{cases} 
\infty & \text{for } r \leq \sigma \\
V(r) & \text{for } r > \sigma 
\end{cases} \]

where \( r \) is the distance from the center of a given molecule and \( V(r) \) is a weakly attractive potential with a range \( \delta \) satisfying the inequality

\[ \frac{L}{N^{1/3}} \ll \delta \ll L \]

\( L \) is assumed so large that wall effects are negligible. No external force is present.

For this gas model, the following equation for the one particle distribution function \( f(r, \xi, t) \) was obtained by Grad (1958) from integration of the Liouville equation over all coordinates except those of a given molecule.

\[ \frac{\partial f}{\partial t} + \xi \cdot \frac{\partial f}{\partial r} - \frac{1}{m} \int d\xi' \int_{|r-r'|} \frac{\partial V(r-r')}{\partial \xi'} \frac{\partial f}{\partial \xi'} (r, r', \xi', \xi', t) = \]

\[ \int d\xi' \int d\eta \cdot \omega_{\eta} \cdot (\xi') f_t (r, \xi + \eta, \xi', \xi', t) - f_t (r, \xi - \eta, \xi, \xi', t) \]

For convenience, we have adopted deSobrino's notation where \( \omega \) denotes a unit vector; the symbol \( \cap \) indicates integration
over all values of $r$ such that $\mathcal{Q} \cdot \xi > 0$; $\mathcal{Q}$ is equal to $\mathcal{Q} \cdot \xi$ and finally $\mathcal{Q}$ and $\mathcal{Q}'$ are related to $\mathcal{Q}$ and $\mathcal{Q}'$ as follows

$$(2.3) \quad \mathcal{Q} = \mathcal{Q} + (\mathcal{Q} \cdot \xi) \Xi \quad \mathcal{Q}' = \mathcal{Q}' - (\mathcal{Q} \cdot \xi) \Xi$$

To rewrite eq.(2.1) in terms of the one-particle distribution function we introduce the pair correlation function $q$ defined by

$$(2.3) \quad f_s(r', \xi', t) = q(r', \xi', t) \int f(r; \xi, t) f(|r' - \xi|, t)$$

In (2.3) we have assumed that $q$ is not a function of velocity, i.e. that there is no correlation between the velocities of neighbouring particles. Substituting the RHS of (2.3) into the integral on the LHS of (2.1) and integrating over $\mathcal{Q}$ we obtain

$$(2.4) \quad -\frac{1}{m} \int_{|r - r'| > \sigma} \frac{\partial V(|r - r'|)}{\partial r} \frac{\partial}{\partial \mathcal{Q}} f_s(r; \xi, \mathcal{Q}, t) \mathcal{Q} dr' =$$

$$-\frac{1}{m} \int_{|r - r'| > \sigma} \frac{\partial}{\partial r} \{V(|r - r'|)\} q(r; \xi; t) \pi(t) dr'$$

where

$$(2.5) \quad \pi(t) = \int f(r; \xi, t) d\xi$$

The value of $q$ in Fig. 1 is a reasonable approximation to the $q$ of our model. The region where the pair correlation function differs appreciably from unity is very small ($\sigma < |r - r'| < 1.3 \sigma$); therefore the contribution to the integral on the RHS of (2.4) from this region is small; so that it makes little difference
whether, in that region, we write $q$ or $I$. Furthermore, for $|r-r'| > 1.3\sigma$, $q \sim 1$. Finally since $|r-r'| < \sigma$ is very small compared to the range of the attractive potential, the integration is extended over the sphere $|r-r'| < \sigma$. Thus the RHS of (2.4) can be approximated by

$$
(2.6) \quad \frac{1}{m} \frac{\partial}{\partial t} \mathcal{f}(r,s,t) \cdot \int \left\{ \frac{\partial}{\partial r} V(r,-r') \right\} q(r',t) \eta(r,t) dr' d^2 r'
$$

For a gas in equilibrium, it has been shown that, to first order in density gradient, (Lebowitz and Percus, 1963)

$$
(2.7) \quad q(r_1,r_2) = q(m \left( \frac{r_1 + r_2}{2} \right), r_2)
$$

It is reasonable to expect that the non equilibrium behaviour of $q$ will be similar and we shall assume that

$$
(2.8) \quad q(r_1,r_2,t) = q(m \left( \frac{r_1 + r_2}{2} \right), r_2)
$$

Returning to eq.(2.1), we note that the two particle distribution function in this equation, $\mathcal{f}_z$, is evaluated at contact therefore

$$
(2.9a) \quad \mathcal{f}_z(r+r_+ r_-, s_+, s_-', t) = \eta(m(r_+ r_-, t) \mathcal{f}(r, s_+, t) \mathcal{f}(r + r_+, s_-, t))
$$

$$
(2.9b) \quad \mathcal{f}_z(r+r_+ r_-, s_+, s_-', t) = \eta(m(r_+ r_-, t) \mathcal{f}(r, s_+, t) \mathcal{f}(r + r_+, s_-, t))
$$

Where $\eta$ is the pair correlation function $q$ evaluated at contact
Substituting the RHS of eqs. (2.6), (2.9a) and (2.9b) into eq. (2.1) and expanding to first derivatives in \( \tau \) about \( \tau \) we obtain the kinetic equation

\[
\eta \left( \mathbf{r}, \frac{1}{2} \sigma \mathbf{r}, t \right) = \mathcal{Q} \left( \mathbf{r}, \frac{1}{2} \sigma \mathbf{r}, t \right) - \mathcal{Q} \left( \mathbf{r}, \frac{1}{2} \sigma \mathbf{r}, t \right)
\]

where we have used the abbreviations

\[
(2.10) \quad \frac{\partial \mathcal{Q}}{\partial t} + \frac{\xi}{m} \frac{\partial \mathcal{Q}}{\partial \mathbf{r}} - \frac{1}{m} \frac{\partial \mathcal{Q}}{\partial \mathbf{r}} \cdot \frac{\partial}{\partial \mathbf{r}} \int V(\mathbf{r}, \mathbf{r}') n(\mathbf{r}', t) d\mathbf{r}' + \frac{\partial}{\partial \mathbf{r}} \left\{ \eta \left( \mathbf{r}, \mathbf{r}', t \right) \right\} \cdot \frac{\partial}{\partial \mathbf{r}} \int \frac{\partial \mathcal{Q}}{\partial \mathbf{r}} \frac{\partial}{\partial \mathbf{r}} d\mathbf{r}
\]

where we have used the abbreviations

\[
(2.9) \quad \mathcal{Q} = \mathcal{Q} \left( \mathbf{r}, \mathbf{r}', t \right) \quad \mathcal{Q}' = \mathcal{Q} \left( \mathbf{r}, \mathbf{r}', t \right) \quad \mathcal{Q}' = \mathcal{Q} \left( \mathbf{r}, \mathbf{r}', t \right)
\]

Eq. (2.10) is just the Enskog equation with a long range attractive potential taken into account by a self consistent field approximation. The derivation of (2.10) from Grad's equation (2.1) was due to deSobrino (1967). Throughout this thesis, the pair correlation function at contact, \( \eta \), will be left as an undefined increasing function of the density \( n(\mathbf{r}, t) \).
Figure 1. Radial distribution function $g(r)$ vs $\xi = r/\sigma$ for hard discs at $\gamma = \frac{\nu_0}{\nu} = \sigma$, $\nu = N \sigma^2 / \kappa^2$ from an average of four independent calculations of $g$ for a system of 192 discs (W.W. Wood, 1968).
3. THE H-THEOREM

We wish to show that the kinetic equation (2.10) obeys an H-theorem. First we define an H function for a gas of hard spheres. One way of doing this is to find the entropy per unit volume of such a gas in a uniform, equilibrium state and guessing the H-function from this entropy. For an infinite system of hard spheres the pressure is related to the free energy per unit volume $\phi\left(\frac{p}{kT}, n\right)$ by (Ruelle, 1963)

$$h = n^2 \left( \frac{\partial}{\partial n} \left( \frac{\phi}{n} \right) \right) \beta$$

$$= n \phi'(\beta, n) - \phi(\beta, n).$$

On the other hand we have the well known equation

$$P = n k T \left(1 + \eta(n) \right). \quad (\text{We have set } \frac{2}{3} \pi a^3 \text{ s l}).$$

Equating the RHS of (3.1) and (3.2) and integrating the result with respect to $n$, we obtain an expression for the free energy in terms of $\eta$

$$\phi(\beta, n) = k T \left( n^2 n + n \int \eta(n) dn \right) + n G(\beta)$$

where $G(\beta)$ is some, as yet undefined, function of the temperature. The entropy per unit volume follows immediately

$$A(\beta, n) = - \left( \frac{\partial \phi}{\partial T} \right)_n$$

$$= -k \left(n^2 n + \eta \int \eta(n) dn \right) - n G'(\beta) \left( G \frac{\partial G}{\partial T} \right)$$
The RHS of (3.4) is an exact expression for the entropy per unit volume of an infinite system of hard spheres in terms of the density and pair correlation function at contact. (3.4) suggests an H function of the form

\[(3.5) \quad H = \int f \ln f - f + f \int \eta(n) dn \, dw \]

In fact in the case of equilibrium when \( \hat{f} \) is the absolute Maxwellian

\[(3.6) \quad \hat{f}_0 = n \left( \frac{m}{2\pi kT} \right)^{3/2} e^{-\frac{m}{2kT} \left( \frac{\hat{f}}{c} - c \right)^2} \]

we find, after replacing in (3.5) by the RHS of (3.6) and integrating,

\[(3.7) \quad H = n \ln n - n + n \int \eta(n) dn + \frac{3}{2} n \left( \ln \frac{m}{2\pi kT} - 1 \right). \]

From which the entropy per unit volume is

\[(3.8) \quad \Delta(\beta, n) = -KH = -K \left( n \ln n - n + n \int \eta(n) dn \right) - \frac{3}{2} K n \left( \ln \frac{m}{2\pi kT} - 1 \right). \]

Comparison with (3.4) yields

\[(3.9) \quad G'(\beta) = \frac{3}{8} K \left( \ln \frac{m}{2\pi kT} - 1 \right) - K ; \]

whence

\[(3.9a) \quad G(\beta) = \frac{3}{8} K T \ln \frac{m}{2\pi kT} - K T. \]

The H-function defined in eq.(3.5) for a hard sphere gas is also the appropriate H-function for the Van der Waals gas described by the kinetic equation (2.10) since, as we shall see, the self-consistent field term in this equation is non dissipative.
We shall now proceed to the proof of the H-theorem.

Differentiating eq. (3.5) with respect to $t$ we obtain

$$\frac{\partial H}{\partial t} = \int \left( \frac{\partial \mathcal{F}}{\partial t} + \frac{\partial \mathcal{F}}{\partial \mathcal{H}} \right) \, d\mathcal{H} + \left( \eta + \mathcal{H} - 1 \right) \frac{\partial \mathcal{H}}{\partial t},$$

where

$$\mathcal{H} = \int \eta(\mathcal{H}) \, d\mathcal{H}.$$

From equation (2.10)

$$\frac{\partial \mathcal{F}}{\partial t} = -\frac{m}{\varepsilon} \frac{\partial \mathcal{F}}{\partial \varepsilon} + \frac{1}{m} \frac{\partial \mathcal{F}}{\partial \mathcal{H}} \frac{\partial \mathcal{H}}{\partial t} + \int \left( \mathcal{V}(r-r') \eta(r') \, dr' + \eta J + K \right)$$

where

$$J = \int \frac{dS}{\lambda} \int \eta \left( \int \frac{\partial \mathcal{F}}{\partial \varepsilon} + \frac{\partial \mathcal{H}}{\partial \mathcal{H}} \right) \, dr' \, d\mathcal{H},$$

$$K = \frac{2}{m} \int \frac{dS}{\lambda} \int \eta \left( \int \frac{\partial \mathcal{F}}{\partial \varepsilon} + \frac{\partial \mathcal{H}}{\partial \mathcal{H}} \right) \, dr' \, d\mathcal{H}.$$ 

Integrating eq. (3.11) over $\mathcal{H}$ we obtain the conservation of mass equation

$$\frac{\partial \mathcal{H}}{\partial t} = -\frac{\partial \mathcal{F}}{\partial t} \int d\mathcal{H}.$$

In equation (3.10), replacing $\partial \mathcal{F}/\partial t$ by its value in (3.11), we get

$$\frac{\partial H}{\partial t} = -\frac{\partial \mathcal{F}}{\partial t} \int d\mathcal{H} + \int \left( \frac{\partial \mathcal{F}}{\partial \mathcal{H}} \left( \eta J + K \right) \, d\mathcal{H} + \left( \eta + \mathcal{H} - 1 \right) \frac{\partial \mathcal{H}}{\partial t} \right);$$

the term involving the long range potential $\mathcal{V}(r-r')$ vanishes; thus $\mathcal{V}(r)$ is non dissipative.

We have the following identities

$$\frac{\partial \mathcal{F}}{\partial t} \cdot \int \left( \frac{\partial \mathcal{F}}{\partial \varepsilon} + \frac{\partial \mathcal{H}}{\partial \mathcal{H}} \right) d\mathcal{H} = \frac{\partial \mathcal{F}}{\partial t} \cdot \int \left( \frac{\partial \mathcal{F}}{\partial \varepsilon} + \frac{\partial \mathcal{H}}{\partial \mathcal{H}} \right) d\mathcal{H} + \frac{\partial \mathcal{H}}{\partial t} \cdot \int d\mathcal{H} + \frac{\partial \mathcal{H}}{\partial t} \cdot \int d\mathcal{H};$$

$$(\eta + \mathcal{H} - 1) \frac{\partial \mathcal{H}}{\partial t} = -\left( (\eta + \mathcal{H} - 1) \frac{\partial \mathcal{H}}{\partial t} \right) \int d\mathcal{H}. $$
equation (3.13) becomes, taking into account (3.12), (3.14) and (3.15)

\[
\begin{align*}
\frac{\partial H}{\partial t} &= -\frac{d}{dt} \int \left( \frac{f^2}{2} - \frac{f^2}{2} + \eta \frac{\partial f}{\partial x} \right) d\tau + \frac{\partial F}{\partial \tau} \int f^2 d\tau - \eta \frac{\partial^2}{\partial x^2} \int f^2 d\tau \\
&\quad + \int \left( \frac{\partial f}{\partial x} \right)^2 (\eta J + K) d\tau .
\end{align*}
\]

\( F \) is a function of density \( \eta(x,t) \), therefore

\[
\begin{align*}
\frac{\partial F}{\partial \tau} \int f^2 d\tau &= \frac{d}{dt} \int f^2 d\tau - \eta \frac{\partial}{\partial x} \int f^2 d\tau - \eta \frac{\partial^2}{\partial x^2} \int f^2 d\tau \\
&= \eta \left\{ \frac{\partial}{\partial x} \int f^2 d\tau - \eta \frac{\partial^2}{\partial x^2} \int f^2 d\tau \right\} \\
&= \frac{3}{8\pi} \iint_{\eta} d\xi d\eta \left( \frac{\partial f}{\partial x} \right)^2 \left( \frac{\partial f}{\partial x} \right)^2 \left( \frac{\partial f}{\partial x} \right)^2 \left( \frac{\partial f}{\partial x} \right)^2 .
\end{align*}
\]

It is well known that

\[
\begin{align*}
\eta \int (\lambda f^2 + 1) J d\tau &= \frac{3}{16\pi} \iint_{\eta} d\xi d\eta \left( \frac{\partial f}{\partial x} \right)^2 \left( \frac{\partial f}{\partial x} \right)^2 \left( \frac{\partial f}{\partial x} \right)^2 \left( \frac{\partial f}{\partial x} \right)^2 ,
\end{align*}
\]

and one can readily show that

\[
\begin{align*}
\int (\lambda f^2 + 1) K d\tau &= \frac{3}{16\pi} \iint_{\eta} d\xi d\eta \left( \frac{\partial f}{\partial x} \right)^2 \left( \frac{\partial f}{\partial x} \right)^2 \left( \frac{\partial f}{\partial x} \right)^2 \left( \frac{\partial f}{\partial x} \right)^2 \\
&\quad \times \left\{ \eta \left( \frac{\partial f}{\partial x} \right)^2 \left( \frac{\partial f}{\partial x} \right)^2 \left( \frac{\partial f}{\partial x} \right)^2 \left( \frac{\partial f}{\partial x} \right)^2 \right\}.
\end{align*}
\]

Eqs. (3.17), (3.18) and (3.19) are then substituted into eq.(3.16) which becomes, after some rearrangement

\[
\begin{align*}
\frac{\partial H}{\partial \tau} &= \frac{d}{dt} \int \left( \frac{f^2}{2} - \frac{f^2}{2} + \eta \frac{\partial f}{\partial x} \right) d\tau + \frac{\partial F}{\partial \tau} \int f^2 d\tau - \eta \frac{\partial^2}{\partial x^2} \int f^2 d\tau \\
&\quad + \int \left( \frac{\partial f}{\partial x} \right)^2 (\eta J + K) d\tau .
\end{align*}
\]
With the definitions
\[ \chi \equiv \frac{f' f''}{f^2} \quad \delta \equiv \frac{1}{s} \left( \frac{\partial}{\partial s} \frac{f'}{f} \right) \quad \sigma \equiv \frac{1}{s} \left( \frac{\partial}{\partial s} \frac{f'}{f} \right) \]

the RHS of eq. (3.20) becomes

[3.21] \[ \Pi(r, t) = \eta \frac{2}{3} \int_0^1 \left\{ (1 - \chi) \ln \chi + \sigma (1 - \chi + s \ln \chi) + \frac{\varepsilon}{\chi} (1 - \chi + s \ln \chi) \right\} \frac{d^4r}{d^3\Omega} \]

The integrand on the RHS of (3.21) is identical to deSobrino's eq. (3.12). To prove the H-theorem, deSobrino assumed that \( s \) and \( \sigma \) are independent variables. From the definition of \( \chi \), to vary \( \chi \) one must vary the functional form of \( f \); but \( \delta \) and \( \sigma \) are also functions of \( f \); therefore in general \( \delta \) and \( \sigma \) are not independent variables.

We have the equality

[3.22] \[ \Pi(r, t) = \eta \frac{2}{3} \int_0^1 \left\{ (1 - \chi) \ln \chi + \sigma (1 - \chi + s \ln \chi) \right\} \frac{d^4r}{d^3\Omega} \]

so that \( \Pi(r, t) \) reduces to

[3.22a] \[ \Pi(r, t) \equiv \eta \frac{2}{3} \int_0^1 \left\{ (1 - \chi) \ln \chi + \sigma (1 - \chi + s \ln \chi) \right\} \frac{d^4r}{d^3\Omega} \]

Let us set

[3.22b] \[ a(\chi, \sigma) \equiv (1 - \chi) \ln \chi + \sigma (1 - \chi + s \ln \chi) \]

and study the sign and magnitude of \( a(\chi, \sigma) \) as \( \chi \) approaches unity. We are interested in near-equilibrium states therefore we can write

[3.22c] \[ f = f_0 (1 + \eta) \]

with \( |\eta| \ll 1 \). To first order in \( \eta \)

[3.22d] \[ \chi = \frac{f' f''}{f^2} = 1 + \chi_0 + \chi_1 - \chi \quad \sigma = \frac{1}{s} \left( \frac{\partial}{\partial s} \frac{f'}{f} \right) \]
Since $|\alpha| \ll 1$,

$$\ln \chi = \ln (1 + |\alpha|) = |\alpha|$$

$$1 - \chi + \chi \ln \chi = O[|\alpha|^2]$$

$$(1 - \chi) \ln \chi = - |\alpha|^2$$

so that

$$(3.23) \quad \alpha(\chi, \sigma) \sim - (1 - \chi^2) |\alpha|^2$$

We recall that

$$\chi = \frac{\sigma}{r} \frac{\partial}{\partial r} \ln r = \frac{1}{r} \sigma \frac{\partial}{\partial r} \ln r = \frac{\sigma}{r} \frac{\partial}{\partial r}$$

In this form we see that $\chi$ is the ratio of the change in $\sigma$ over the distance of a molecular radius to $r$. $\chi$ does not vary appreciably over such a small distance so that $|\chi| \ll 1$.

Therefore the value of $\alpha(\chi, \sigma)$ given in (3.23) is always less or equal to zero; it is equal to zero when $\chi = 1$, i.e. $\chi = \chi^{(s)}$ (see (3.22a)). Returning to (3.22) we see that $\nabla(\tau, t) < 0$;

\[ \nabla(\tau, t) = 0 \quad \text{when} \quad \chi = \chi^{(s)} \]

Equation (3.20 can be rewritten as follows

$$\begin{align*}
\left(3.24\right) \quad \frac{\Delta H}{\Delta t} &= - \frac{\Delta}{\Delta t} \cdot \int \frac{d}{d\tau} \left( - \theta + \tau^2 \right) d\tau - \frac{\Delta}{\Delta t} \cdot \frac{2}{16\pi} \cdot \int \int d\tau d\theta d\phi \\
\left(3.24\right) &= \left( \frac{\partial f}{\partial r} + f f' \right) \frac{\partial}{\partial r} \frac{\Delta f}{\Delta t} + \nabla(\tau, t)
\end{align*}$$

The physical meaning of this equation is clear. The increase in entropy per unit time in a fixed unit volume located at $r$ at time $t$, $\Delta H/\Delta t$, is equal to the flux of entropy into the unit volume due to fluid flow (first integral on the RHS of (3.24)) plus the flux
of entropy due to the fact molecules are not points but occupy a
finite volume (2nd integral) plus increase in entropy per unit time
per unit volume due to binary collisions, \( \Pi (r,t) \). We note that the
long range potential does not contribute to the increase in entropy.

Integrating eq. (3.24) over the volume of the container we obtain

\[
\text{(3.25)} \quad \frac{d}{dt} \int V \Pi (r,t) \, d^3 \mathbf{r} = \frac{dH_o}{dt} = \int C(r,t) \, d^3 \mathbf{r} \leq 0
\]

\( H \) is bounded from below (Chapman & Cowling, 1958) and for a container
of finite volume \( H_0 \) is also bounded from below, therefore \( H_0 \) cannot
decrease indefinitely but must tend to a limit corresponding to a state
of the gas in which \( \frac{dH_0}{dt} = 0 \) but if \( \frac{dH_0}{dt} = 0 \), then \( \chi = 1 \) and
the distribution is the local Maxwellian

\[
\begin{align*}
\psi (r,t) &= \psi (r,t) \left( \frac{m}{2\pi kT(r,t)} \right)^{3/2} \exp \left( - \frac{m}{2kT(r,t)} \left( \frac{\mathbf{r}}{\mathbf{r}} - \mathbf{c}(r,t) \right) \right).
\end{align*}
\]
4. **EQUILIBRIUM SOLUTIONS**

The H-theorem of section 3 gives a strong indication that the gas described by the kinetic equation (2.10) will approach equilibrium. It is natural to seek the equilibrium (i.e., time independent) solutions of (2.10) among the local Maxwellian solutions of the form

\[
\begin{align*}
\frac{4}{n} & \equiv \langle \xi \rangle = n(r) \left( \frac{m}{2\pi kT(r)} \right)^{\frac{3}{2}} e^{-\frac{m}{2kT} (\frac{\xi}{r} - \xi(r))}.
\end{align*}
\]

To find the functional dependence of \( n, T \) and \( \xi \) on \( r \) we substitute for \( \xi \) the value of \( \langle \xi \rangle \) given in (4.1) into (2.10) and obtain using the summation convention

\[
\begin{align*}
\frac{C^\mu}{n} \frac{\partial n}{\partial r^\mu} & + \frac{\xi}{2} C^\mu \frac{\partial p'}{\partial r^\mu} - \eta \gamma \frac{\partial \gamma}{\partial r^\mu} + \left( (1 + 2\eta) \frac{C^\mu}{n} + \eta \gamma + \frac{1}{2} C^\mu \frac{\partial p'}{\partial r^\mu} + 2 \frac{p'}{n} \gamma \frac{\partial \gamma}{\partial r^\mu} + \frac{2}{3} \frac{p'}{n} \frac{\partial \gamma}{\partial r^\mu} \right) \right) + \left( \frac{\gamma}{n} \frac{\partial \gamma}{\partial r^\mu} \right) \right) = 0,
\end{align*}
\]

where \( w = \frac{\xi}{r} - \xi \), \( \gamma = \partial/\partial r^\mu \), \( j = \sqrt{\gamma} \equiv \sqrt{\gamma} \). Each coefficient of the powers of \( w^\mu \) must vanish separately. The coefficient of \( w^\mu w^\nu w^\alpha \) gives immediately

\[
\begin{align*}
\beta' &= \frac{m}{2kT} = \text{constant}.
\end{align*}
\]

The temperature is uniform.
From the coefficient of \( w'w' \) we obtain the following equation

\[
(1 - \frac{2}{5} \eta)(\partial^\nu c^\nu + \partial^\nu c^\mu) + \frac{2}{5}\eta \partial^\nu c^\lambda \partial^\nu \lambda = 0
\]

For \( \mu \neq \nu \) (4.4) reduces to

\[
\partial^\nu c^\nu + \partial^\nu c^\mu = 0 \quad (\mu, \nu = 1, 2, 3)
\]

For \( \mu = \nu \) \((\mu, \nu = 1, 2, 3)\) we get from (4.4), adding the results

\[
(1 + \frac{1}{5} \eta) \partial^\nu c^\nu = 0
\]

The general solution of (4.5) and (4.6) is

\[
\zeta = u \times r + \zeta_0
\]

where \( u \) and \( \zeta_0 \) are constant. The general motion of a gas in a stationary state is a uniform rotation and a constant translation.

One example of such a motion is a circular helix whose axis is along the \( z \)-direction; then \( \zeta = (-\omega y, \omega x, c_0) \) For a motion described in (4.7) the shear stress tensor is zero to first order in the velocity gradient.

Since \( \beta' = \) constant and using eq. (4.6) we obtain for the coefficient of the zeroth order in \( w' \)

\[
(4.8) \quad c^\mu \frac{\partial u^\mu}{\partial x^\eta} = 0
\]

This means that \( n \) remains constant on the flow line.

From the coefficient of \( w' \) in eq. (4.2) we have

\[
(4.9) \quad 2\beta' c^\nu \partial^\nu c^\mu + (1 + 2\eta) \frac{\partial u^\mu}{\partial x^\eta} + \eta \partial^\mu \eta + \frac{2\beta'}{m} \partial^\mu (\eta v) = 0
\]

when \( \zeta = 0 \) and using the identity

\[
(4.10) \quad \eta \frac{\partial u^\eta}{\partial x^\theta} = \frac{\partial}{\partial x^\eta} \int \eta \eta d\eta
\]

we reduce eq. (4.9) to

\[
(4.11) \quad \partial^\mu (\lambda u^\mu + m \eta + \int \eta d\eta + \frac{\beta'}{m} \int \eta v) = 0
\]
This equation was derived by Van Kampen (1964). It is the condition for an extremum of a function $F(n)$ subject to the requirement that $\int n(r)dr = N$. When this extremum is a minimum $-F/\mu$ can be identified as the free energy of the gas and the constant on the RHS of (4.11a) is then the chemical potential divided by $kT$

$$\text{constant} = \frac{1}{kT} (\mu - \frac{2}{2} kT \ln \frac{m}{\xi kT})$$

where $\mu$ is the part of the chemical potential due to the potential energy of the gas and $-\frac{1}{2} kT \ln \frac{m}{\xi kT}$ is the contribution to the chemical potential from the kinetic energy.

Strickfaden (1970), using for $\eta$ the Padé approximant of Ree and Hoover (1964) and for $V(r)$ the (12,6) Lennard-Jones potential, showed that for $T < T_c$, space dependent solutions of (4.11a) exist which correspond to a mixture of liquid and vapor phases.

For an equilibrium state, eq. (4.11a) becomes

$$(4.12) \quad \frac{\mu}{kT} = -\ln n - n \eta - \int \eta(n) dn - \frac{2}{m} \int Vn - \frac{3}{2} \frac{ln}{\xi kT}$$

from which one easily deduces the free energy per unit volume at $r$

$$(4.13) \quad -\frac{\psi(n(r))}{kT} = n(r) \ln n(r) + n(r) - n(r) \int \eta(n)dn - \frac{3}{2} \frac{n(r) ln}{\xi kT} - \frac{\rho'}{m} \int V(r-r')n(r')dr'$$

The thermodynamic functions of a gas of hard spheres with a long range attractive tail are derived from the definition of the H function given in (3.5). Substituting in (3.5) $\frac{\rho}{m}$ by the local Maxwellian
and carrying out the integration over \( \frac{m}{2\pi kT} \) we get the entropy per unit volume

\[
\lambda (\beta, n) = -k n(r) \{ \rho m n(r) - n(r) \} + \int n \, dn + \frac{3}{2} \left( \frac{m}{2\pi kT} \right) - 1
\]

This is the same equation as (3.8) except that now \( n \) is a function of \( r \).

The internal energy is

\[
\mathcal{U} = \frac{2}{3} N kT + \frac{1}{2} \int \int n_z (r, r') U (|r - r'|) \, dr \, dr'
\]

\[
= \frac{2}{3} N kT + \frac{1}{2} \int \int n(r) n(r') V (|r - r'|) \, dr \, dr'
\]

where \( V \) is the long range part of \( U \).

The free energy is

\[
\mathcal{A} = \mathcal{U} - TS
\]

\[
= \frac{1}{2} \int n(r) n(r') V (|r - r'|) \, dr \, dr' + kT \int (n \rho n - \eta) \, dr + kT \int n^2 \, dr + \frac{3}{2} N kT \rho \left( \frac{m}{2\pi kT} \right)
\]

From (4.15) it follows that the local free energy per unit volume is

\[
\Psi (n(r)) = \frac{1}{2} n(r) \int n(r') V (|r - r'|) \, dr' + kT \int n(r) \rho n(r) - n(r)
\]

\[
+ kT n(r) \nabla (n(r)) + \frac{3}{2} kT n(r) \rho \left( \frac{m}{2\pi kT} \right)
\]

This is the same as equation (4.12) which was obtained directly from the kinetic equation (2.10). For a uniform density the pressure can be readily obtained

\[
p = n^2 \left( \frac{2}{\partial n} \left( \frac{\dot{\rho}}{n} \right) \right) \beta
\]

\[
= kT n \left( u + \eta \right) - \frac{1}{2} n^2 \mathcal{W} \left( \mathcal{W} - \int n(r) \, dr \right)
\]
CHAPTER 3. SOME LINEAR NON-EQUILIBRIUM RESULTS

We have been considering the approach to local equilibrium and the equilibrium solutions of the kinetic equation (2.10). We now investigate some non-equilibrium properties of this equation. The complicated expression on its RHS restricts us from the start to the case of near-equilibrium states where equation (2.10) can be simplified by linearization.

A problem connected with near-equilibrium states is that of determining the stability of the uniform density stationary states of a Van der Waals gas against small perturbations; these uniform density states correspond to the absolute minimum and the local minima of the free energy (Van Kampen, 1964) and are traditionally called the stable and metastable states respectively. For this problem the RHS of the linearized kinetic equation is still unmanageable and an approximation for it must be found. A method due to Gross and Jackson (1959) and later extended by Sirovich (1965a) is used; (the modified linearized kinetic equation will be called the GJS model for convenience). According to this method, the linearized Boltzmann collision integral \( I(h) \) is expanded in terms of the eigenfunctions of the linearized collision operator of a Maxwell gas; the first few terms in the expansion are retained while the remaining terms are approximated by assuming that, as far as these terms are concerned, the gas is Maxwellian and furthermore, that all eigenfunctions have the same eigenvalue.
The GJS model is the only one which yields results on sound propagation in good agreement with experiment over a wide frequency range (Sirovich and Thurber, 1965b); of particular importance is the good agreement with experiment at high frequencies. This implies that this model is valid at high frequencies as well as at low frequencies so that it is particularly suitable to the study of the stability of the uniform density states which, from a mathematical point of view, is closely related to the problem of sound propagation and consists in deriving a dispersion relation $E(\omega, k, V, n) = 0$ for a Van der Waals gas and evaluating $E$ as a function of $\omega$ as $\omega$ increases from $-\infty$ to $\infty$. 
5. **SOUND PROPAGATION AT LOW FREQUENCIES**

In this section, we present the GJS model in connection with an asymptotic analysis of sound propagation in rarefied monatomic gases in order to acquaint the reader with this model which will be applied to the more complicated problem of determining the stability of the uniform density states of a Van der Waals gas. The results of this section will also serve as a means of checking the calculations in the stability problem.

An expansion of the wave number \(k\) for a Maxwell and hard sphere gas up to 3rd power in \(\omega\) is derived using the GJS model in which the first five terms in the expansion of \(L(h)\) are kept intact. This value of \(k\) is compared to those obtained from the Navier-Stokes, Burnett, Super-Burnett, 13-moments and recently Wang Chang - Uhlenbeck approximations. (For these values of \(k\), see Greenspan, 1965; also Foch and Uhlenbeck, 1967).

(a) **The GJS Model**

From the Boltzmann equation the GJS equation for \(\mathfrak{N} = 5\) (\(\mathfrak{N}\) is the number of non-approximated terms in the expansion of \(L(h)\) in eigenfunctions of \(L_{\text{Maxwell}}\)) is now derived.

\[\text{For a GJS model, the collision frequency } \lambda \text{ is velocity independent and it has been shown (Sirovich and Thurber, 1969) that in this case the expansion of } k \text{ in powers of } \omega \text{ does not converge; However, though it is not convergent, the series is asymptotic.}\]
The Boltzmann equation for a one dimensional flow is

\[
\frac{\partial f}{\partial t} + \xi_3 \frac{\partial f}{\partial x} = \iint \mathcal{B}(\theta, \phi, \bar{\xi}) (f' - \bar{f}) \, d\theta d\phi d\bar{\xi}
\]

where

\[ \xi = |\bar{\xi}' - \bar{\xi}|; \quad f' = f(\tau, \bar{\xi}', \xi) \quad \text{etc.} \]

Eq. (5.1) is linearized by writing

\[
f = f_0 (1 + \lambda)
\]

where

\[
f_0 = m_0 \left( \frac{m}{kT_0} \right)^{3/2} \frac{1}{(2\pi)^{3/2}} e^{-\frac{m \bar{\xi}^2}{2kT_0}}
\]

Eq. (5.1) becomes, ignoring terms quadratic in \( \lambda \)

\[
\left( \frac{\partial}{\partial t} + \xi_3 \frac{\partial}{\partial x} \right) \lambda = \iint f_0 \left[ \lambda \right] \mathcal{B}(\theta, \phi, \bar{\xi}) \, d\theta d\phi d\bar{\xi}' = \mathcal{L}(\lambda)
\]

where

\[
\left[ \lambda \right] = \bar{\lambda} + \bar{\lambda}' - \lambda - \lambda
\]

Dimensionless variables are introduced

\[
t' = \lambda t; \quad v' = \frac{\bar{v}}{\sqrt{kT_0/m}}; \quad x' = \frac{x}{\sqrt{kT_0/m}}; \quad \beta' = \frac{\beta}{\lambda}; \quad \xi' = \frac{\xi}{\sqrt{kT_0/m}}
\]

where \( \lambda \) is an undefined constant frequency. In terms of these new variables (5.4) becomes

\[
\left( \frac{\partial}{\partial t'} + \xi_3 \frac{\partial}{\partial x'} \right) \lambda = \iint \mathcal{B}'(\theta, \phi, \sqrt{kT_0/m}) \, w' \left[ \lambda \right] \, d\theta d\phi d\xi' = \mathcal{L}(\lambda)
\]
where

\[ \omega' = \frac{1}{(2\pi)^{n/2}} e^{-v^2/2} \]

\( \mathcal{L}_{r}(x, v, t) \) is expanded in terms of the eigenfunctions \( \psi_{r} \) of the linearized collision operator, \( \mathcal{L}_{M} \), of a Maxwell gas. The double index in \( \psi_{r} \) can be reduced to a single index (Sirovich and Thurber, 1965a).

\[ \psi_{r(l)}(x, v) = \psi_{l} \]

Then

\[ \mathcal{L}_{r}(x, v, t) = \frac{1}{L} \sum_{l=1}^{\infty} a_{l} \psi_{l} \]

where

\[ a_{l} = \int \mathcal{L}_{r} \psi_{l} dv \]

Substituting (5.8) into (5.6) and dropping the prime superscript on \( t' \), \( x' \), \( v' \) and \( \omega' \)

\[ (\frac{\partial}{\partial t} + v_{3} \frac{\partial}{\partial x_{3}}) \mathcal{L}_{r} = L(\mathcal{L}_{r}) = \sum_{l=1}^{\infty} a_{l} \mathcal{L}_{l} \psi_{l} = \sum_{l=1}^{\infty} a_{l} \lambda_{ij} \psi_{j} \]

where

\[ \lambda_{ij} = \int \omega \psi_{i} (\mathcal{L}_{r} \psi_{j}) dv \]

The following approximation of the RHS of (5.10) is due to Sirovich and Thurber (1965a)
This approximation of $L(\hbar)$ is substituted into the RHS of (5.10); one obtains

$$L(\hbar) \approx \sum_{i,j=1}^{N} a_{ij} \lambda_{ij} \Psi_j + \sum_{i=N+1}^{\infty} a_{ii} \Psi_i + \sum_{i=1}^{N} a_{ii} \Psi_i + \lambda_{N+1} \Psi_i$$

This model differs from the one of Wang Chang and Uhlenbeck in that the streaming term which becomes important at high frequencies is not truncated; this may account for the better agreement of this model with experiment at those frequencies (Figures 2 and 3).

Furthermore the expansion of $L(\hbar)$ is not truncated; an approximation for those terms which, in the Wang Chang - Uhlenbeck model, have been neglected is now provided and taken into account. (For a more detailed discussion of the properties of the Wang Chang - Uhlenbeck and GJS models at high frequencies, see Sirovich and Thurber (1967), (1969)).

For $\mathcal{M} = 5$ and for a plane wave perturbation a dispersion relation is derived from eq. (5.13). The wave number $k$ is solved in terms of $\omega$.

The following quantities which are needed in the derivation of the dispersion relation are now written down. The eigenfunctions of
Figure 2. Comparison of theoretical speeds of sound of a Maxwell gas with experiment.

Figure 3. Comparison of theoretical absorption coefficients of a Maxwell gas with experiment.
of the linearized collision operator of a Maxwell gas,

$$\gamma_{r \ell} = -\frac{S_{r \ell}^r \left( \frac{y^2}{5} \right) y^\ell P_\ell \left( \frac{y_3}{y} \right)}{\sqrt{\pi} \ell (\ell + 1) (\ell + 3/2)^{1/2}}$$

where $S_{r \ell}^r$ and $P_\ell$ are the Laguerre and Legendre polynomials respectively. The first five eigenfunctions are

$$\psi_1 \equiv \phi_{10} = 1$$
$$\psi_2 \equiv \phi_{01} = y_3$$

$$\psi_3 \equiv \phi_{10} = y_3^2 \left( 1 - \frac{1}{5} y_3 \right)$$
$$\psi_4 \equiv \phi_{02} = \frac{1}{2} \sqrt{5} \left( y_3^3 - \frac{1}{3} y_3 \right)$$
$$\psi_5 \equiv \phi_{11} = \sqrt{10} \left( 1 - \frac{1}{5} y_3 \right) y_3$$

Substituting these values of $\psi_i$ ($i = 1, \ldots, 5$) into (5.9) one obtains the corresponding coefficients $a_i$

$$a_1 \equiv a_{00} = \int w_h dv \equiv \nu$$

$$a_2 \equiv a_{01} = \int w_h y_3 dv \equiv u_3$$

$$a_3 \equiv a_{10} = -\sqrt{\frac{1}{30}} \left\{ \frac{1}{15} \int w_h v^3 dv - \int w_h dv \right\} \equiv -\sqrt{\frac{1}{5}} \tau$$

$$a_4 \equiv a_{02} = \frac{1}{2} \sqrt{3} \left\{ \int w_h y_3^2 dv - \frac{1}{3} \int w_h v^2 dv \right\} \equiv \frac{1}{2} \sqrt{3} \rho_{33}$$

$$a_5 \equiv a_{11} = -\sqrt{\frac{2}{5}} \left\{ \int w_h v^\tau y_3 dv - 5 \int w_h y_3 dv \right\} \equiv -\frac{1}{2} \sqrt{\frac{5}{3}} S_3$$

$\nu$ and $\tau$ are the dimensionless deviations in density and temperature; $u_3$, $\rho_{33}$ and $S_3$ are the dimensionless velocity, stress tensor and heat vector respectively.
Using the following correspondence between the two ways of indexing

\[
\begin{array}{ccc}
1 & 0 & 0 \\
2 & 0 & 1 \\
3 & 1 & 0 \\
4 & 0 & 2 \\
5 & 1 & 1 \\
\end{array}
\]

we rewrite the matrix \( \lambda_{ij} \) in the form \( \lambda_{r' e'; r e} \)

\[
\begin{pmatrix}
\lambda_{11} & \lambda_{12} & \lambda_{13} & \lambda_{14} & \lambda_{15} \\
\lambda_{21} & \lambda_{22} & \lambda_{23} & \lambda_{24} & \lambda_{25} \\
\lambda_{31} & \lambda_{32} & \lambda_{33} & \lambda_{34} & \lambda_{35} \\
\lambda_{41} & \lambda_{42} & \lambda_{43} & \lambda_{44} & \lambda_{45} \\
\lambda_{51} & \lambda_{52} & \lambda_{53} & \lambda_{54} & \lambda_{55}
\end{pmatrix}
= 
\begin{pmatrix}
\lambda_{00,00} & \lambda_{00,01} & \lambda_{00,10} & \lambda_{00,02} & \lambda_{00,11} \\
\lambda_{01,00} & \lambda_{01,01} & \lambda_{01,10} & \lambda_{01,02} & \lambda_{01,11} \\
\lambda_{10,00} & \lambda_{10,01} & \lambda_{10,10} & \lambda_{10,02} & \lambda_{10,11} \\
\lambda_{02,00} & \lambda_{02,01} & \lambda_{02,10} & \lambda_{02,02} & \lambda_{02,11} \\
\lambda_{11,00} & \lambda_{11,01} & \lambda_{11,10} & \lambda_{11,02} & \lambda_{11,11}
\end{pmatrix}
\]

The normalized values of the matrix elements \( \lambda_{r' e'; r e} \) for a gas of hard spheres are given by Sirovich and Thurber (1965a); it is found that the above matrix for a hard sphere gas is diagonal, thus for \( \mathcal{N} = 5 \), eq. (5.13) is identical for both Maxwell and hard sphere gases.

The matrix elements of \( \mathcal{D}(h) \) defined in (5.4) are written down explicitly; to first order in perturbation they are the same for both Maxwell and hard sphere gases (see Grad, 1949)

\[
\begin{align*}
\wedge_{00;00} &= \wedge_{01;01} = \wedge_{10;10} = 0 \\
\wedge_{02;02} &= -6n_o B_{(2)}^1 \\
\wedge_{11;11} &= -4n_o B_{(2)}^1 \\
\wedge_{03;03} &= -9n_o B_{(2)}^1 
\end{align*}
\]
where for a Maxwell gas

\[ \beta^{(2)}_1 = \frac{2}{15\sqrt{\pi}} \mathcal{I}(\nu) \left( \frac{2V_0}{m} \right)^{1/2} \nu \left( \frac{1}{2} \right) \]

\[ \mathcal{I}(\nu) = \pi \int_0^\infty \sin^3 \theta \cos^2 \theta \sin \theta \, d\vartheta \, db \]

\( V_0 \) is the strength of the potential

\[ \nabla(r) = \frac{V_0}{r^\alpha} \]

\( b \) is related to \( \theta \) by

\[ \theta(b) = \int_0^b \frac{d\theta}{(1 - \beta^2 \frac{b}{b})^{3/2}} \]

\[ 1 - b^2 - \frac{1}{2} \left( \frac{\beta b}{b} \right)^4 = 0 \]

and for a hard sphere gas

\[ \beta^{(2)}_1 = \frac{2\epsilon}{5!} \sigma^3 \sqrt{\pi} \kappa T_0/m \]

For the definition of the dimensionless \( \beta' \) in (5.5) we take

\[ \lambda = \frac{\lambda}{\alpha_{03},03} = \frac{9}{ \kappa_0 \beta_1^{(2)}} \]

Consequently the eigenvalues of the dimensionless operator \( \mathcal{L} \) are

\[ \lambda_{00},00 = \lambda_{01},01 = \lambda_{10},10 = 0 \]

\[ \lambda_{01},02 = \frac{2}{3} \]

\[ \lambda_{10},12 = \frac{1}{4} \]

\[ \lambda_{03},03 = -1 \]

It is now assumed that \( h \) is a plane wave perturbation

\[ h(x',t',t') = h(x) e^{i(k'\delta - \omega t')} \]
where \( x' \) and \( t' \) are the dimensionless length and time defined in (5.5) and \( k' \) and \( \omega' \) the dimensionless wave number and frequency

\[
k' = \frac{k \sqrt{K_T/m}}{\lambda} (5.31)
\]

\[
\omega' = \frac{\omega}{\lambda} (5.32)
\]

From now on all prime superscripts will be dropped.

(b) The Dispersion Relation

In eq. (5.13) the value of \( \alpha_i \), \( \kappa_i \), \( \psi_j \) and \( \rho_j \) given in eqs. (5.16) - (5.20), (5.29), (5.15), (5.30) are substituted; the result, multiplied by \( i \) is

\[
(\omega + i - k \psi_3) h = -i \left\{ \frac{1}{2} \chi_{33} (\psi_3^2 - \frac{v_3^2}{3}) + \frac{2}{3} \zeta_3 \psi_3 \left( \frac{v_3^2}{3} \right) \right\}
\]

\[
- \left[ \psi + \psi_3 \psi_3 + \frac{1}{2} (v^2 - 3) \zeta + \frac{3}{4} \chi_{33} (v^2 - \frac{v_3^2}{3}) \right]
\]

\[
+ \frac{1}{2} \zeta_3 \psi_3 \left( \frac{v_3^2}{3} \right) \right] \}
\]

In eq. (5.33), \( \psi, \psi_3, \zeta, \chi_{33} \) and \( \zeta_3 \) will be successively eliminated leaving a relation between \( \psi \) and \( \kappa \). First \( \chi_{33} \) and \( \zeta_3 \) are reexpressed in terms of \( \psi, \psi_3, \) and \( \zeta \). Multiplying eq.(5.33) by \( \omega(\psi) \psi_3 \), integrating the result over \( \psi \) and making use of eqs. (5.19), (5.18) and (5.16) one obtains
\begin{equation}
\omega u_3 = k \int \omega h \nu^2 d\nu
\end{equation}

\begin{align*}
&= k \left( h_{33} + \frac{1}{2} \int \omega h \nu^2 d\nu \right) \\
&= k \left( h_{33} + \nu + \tau \right)
\end{align*}

solving for $h_{33}$

\begin{equation}
h_{33} = \frac{\omega}{k} u_3 - \nu - \tau
\end{equation}

Eq. (5.33) is multiplied by $\omega(\nu)\nu^2$, the result integrated over $\nu$ yields an equation for $S_3$

\begin{equation}
S_3 = 3(\nu + \tau) \frac{\omega}{k} - 5u_3
\end{equation}

Eq. (5.33) is multiplied by $\omega(\nu)$; the result is integrated over $\nu$; one gets the continuity equation

\begin{equation}
\omega \nu = ku_3
\end{equation}

The RHS of eq. (5.35) - (5.37) are substituted into eq. (5.33); the result is

\begin{equation}
(\omega + i - k \nu_3) \lambda = i \left\{ \frac{1}{4} \left( \frac{\omega}{k} \nu - \nu - \tau \right)(\nu_3^2 - \nu^2) + \frac{5}{18} \frac{\omega}{k} (3\tau - 2\nu) \right\} + \nu_3 \left( \frac{\nu_3^2 - 1}{\nu_3} \right) + \nu + \nu \frac{\omega}{k} \nu_3 + \frac{1}{2} \lambda (\nu_3^2 - 3) \tau \right\}
\end{equation}
Eq. (5.38) is multiplied by \( \frac{w(v)}{(\omega + i - k v_3)} \); the result is integrated over \( v \); one finds

\[
(5.39) \quad v = \frac{i}{\sqrt{\pi}} \int_{-\infty}^{\infty} \frac{e^{-v_3^2/\omega}}{\omega + i - k v_3} \left\{ \frac{i}{6} \left( \frac{\omega}{k^2} v - v - \tau \right) (v_3^{2} - i) \right\} \\
+ \frac{i}{18} \frac{\omega}{k} (3 \tau - 2 v) (v_3^2 - 3 v_3) + v + \frac{\omega}{k} v_3 + \frac{i}{2} (v_3^{2} - i) \tau \right\}
\]

To eliminate \( \tau \) we evaluate the integral \( \int w k v \, dv \); first the integral \( \int w k (v_3^2 + v_3) \, dv \) is evaluated; multiplying eq. (5.38) by \( \frac{w(v)}{\omega + i - k v_3} \) and integrating the result over \( v \) we obtain, making use of (5.39)

\[
(5.40) \quad \int w k (v_3^2 + v_3) \, dv = 2 v + \frac{i}{\sqrt{\pi}} \int_{-\infty}^{\infty} \frac{e^{-v_3^2/\omega}}{\omega + i - k v_3} \left\{ -\frac{1}{3} \left( \frac{\omega}{k^2} v - v - \tau \right) + \frac{2}{1} \frac{\omega}{k} (3 \tau - 2 v) v_3 + 2 \tau \right\}
\]

From eq. (5.34)

\[
(5.41) \quad \int w k v_3 \, dv = \frac{\omega}{k} u_3 = \frac{\omega}{k^2} v
\]

Adding (5.40) and (5.41)
\begin{align*}
(5.42) \quad \int \omega \kappa v^2 dv &= 2 \nu + \frac{\omega^2}{k^2} \nu + \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \frac{e^{-v_3^2/2}}{\omega + i - k\nu_3} dv_3 \left\{ - \frac{1}{3} \left( \frac{\omega^2}{k^2} \nu - \nu - \tau \right) + \frac{2}{3} \frac{\omega}{k} (3\nu - 2\nu) \nu_3 + 2\tau \right\} \\
&= 3 (\tau + \nu)
\end{align*}

Solving for \( \tau \)

\begin{align*}
(5.43) \quad \tau &= -1 + \frac{1}{3} \frac{\omega^2}{k^2} + \frac{i}{3} \left( 1 - \frac{\omega^2}{k^2} \right) A - \frac{1}{3} i \frac{\omega}{k} B \frac{3 - \frac{7}{3} i A - \frac{2}{3} i \frac{\omega}{k} B}{3 - \frac{7}{3} i A - \frac{2}{3} i \frac{\omega}{k} B} \nu
\end{align*}

where

\begin{align*}
(5.44) \quad A &= \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \frac{e^{-v_3^2/2}}{\omega + i - k\nu_3} dv_3 \\
B &= \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \frac{e^{-v_3^2/2}}{\omega + i - k\nu_3} dv_3
\end{align*}

Replacing in (5.39) the value of \( \tau \) just obtained we get the dispersion relation

\begin{align*}
(5.45) \quad 1 &= i \left\{ \frac{1}{6} \left( \frac{\omega^2}{k^2} - 1 \right) (1 - A) - \frac{1}{6} \frac{\omega}{k} (D - 3B) + A + \frac{\omega}{k} B + \left[ \frac{1}{3} (1 - A) \\
&+ \frac{1}{6} \frac{\omega}{k} (D - 3B) \right] \right\} \left\{ -1 + \frac{1}{3} \frac{\omega^2}{k^2} + \frac{i}{3} \left( 1 - \frac{\omega^2}{k^2} \right) A - \frac{1}{3} i \frac{\omega}{k} B \frac{3 - \frac{7}{3} i A - \frac{2}{3} i \frac{\omega}{k} B}{3 - \frac{7}{3} i A - \frac{2}{3} i \frac{\omega}{k} B} \right\}
\end{align*}

where

\begin{align*}
(5.46) \quad C &= \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \frac{e^{-v_3^2/2}}{\omega + i - k\nu_3} dv_3 \\
D &= \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \frac{e^{-v_3^2/2}}{\omega + i - k\nu_3} dv_3
\end{align*}

This is the dispersion relation from which one can extract numerically the curves labelled \( S^*(n, 5) \) in figures 2 and 3.
(c) The Propagation Constant \( k \) At Low Frequencies

From the dispersion relation, eq. (5.45), which is of the form 
\( \varepsilon(\omega, k) = 0 \) we calculate the propagation constant \( k \) in the low frequency limit. To this purpose, \( \varepsilon(\omega, k) \) is expanded in powers of \( \omega \). The first step is to obtain a series expansion of the integrals \( A, B, C \) and \( D \) for small values of \( \omega \).

We note that in the limit \( \omega \to 0 \), \( \frac{\omega}{k} \to \infty = \sqrt{5k\omega/3m} \); therefore, for the dimensionless values of \( \omega \) and \( k \) defined in (5.31) and (5.32), limit 
\( \frac{\omega}{k} \to 0 \) 
\( \omega \to 0 \) 
\( \frac{\omega}{k} = \sqrt{5/3} \) so that when \( \omega \) is small, \( k \) is also small and of the same order of magnitude; the integral \( A \) can be expanded as follows:

\[
A \equiv \frac{i}{\sqrt{2\pi}} \int_{-\infty}^{\infty} e^{-\frac{\omega^2}{2}/2} \frac{d\omega}{\omega + i - k\nu_3}
\]

\[
= \frac{i}{\sqrt{2\pi}} \int_{-\infty}^{\infty} e^{-\frac{\omega^2}{2}} \frac{d\omega}{1 + \left( \frac{\omega}{\nu_3} \right)^2 (1 - \nu_3^2)}
\]

\[
= \frac{i}{\sqrt{2\pi}} \int_{-\infty}^{\infty} e^{-\frac{\omega^2}{2}} \left\{ 1 - \frac{\omega}{\xi} (1 - \nu_3^2) + \left( \frac{\omega}{\xi} \right)^2 (1 - \nu_3^2)^2 - \left( \frac{\omega}{\xi} \right)^3 (1 - \nu_3^2)^3 + \ldots \right\} d\omega
\]

where

\[ \xi = \frac{k}{\omega} \]

carrying out the integration up to the 6th power in \( \omega \) one finds

\[
A = \frac{i}{\xi} \left\{ 1 - \nu_3^2 (1 + 2\nu_3^2 - \nu_3^4) + \nu_3^2 (1 + 3\nu_3^2 + \nu_3^4) - \nu_3^4 (1 + 6\nu_3^2 + 3\nu_3^4) \right. \\
- \nu_3^6 (1 + 10\nu_3^2 + 15\nu_3^4) + \nu_3^4 (1 + 15\nu_3^2 + 45\nu_3^4 + 15\nu_3^6) \right\}
\]
where
\[ r \equiv w/\iota \]

In a similar manner we find

\begin{align*}
(5.49) \quad B & = \frac{1}{i} \left\{ \chi x - 2\chi^2 x + \chi^3 (3x + 3x^3) - \chi^4 (4x + 12x^3) \\
& \quad + \chi^5 (5x + 30x^3 + 15x^5) - \chi^6 (6x + 60x^3 + 90x^5) \right\} \\
(5.50) \quad C & = \frac{1}{i} \left\{ 1 - \chi + \chi^2 (1 + 3x^2) - \chi^3 (1 + 9x^2) + \chi^4 (1 + 18x^2) \\
& \quad + 15x^4 - \chi^5 (1 + 30x^2 + 75x^4) + \chi^6 (1 + 45x^2 + 225x^4 + 105x^6) \right\} \\
(5.51) \quad D & = \frac{1}{i} \left\{ 3\chi x - 6\chi^2 x + \chi^3 (9x + 15x^3) - \chi^4 (12x + 60x^3) \\
& \quad + \chi^5 (15x + 150x^3 + 105x^5) - \chi^6 (18x + 300x^3 + 630x^5) \right\}
\end{align*}

Substituting these values of \(A, B, C\) and \(D\) into (5.45) and after tedious but straightforward simplification and rearrangement, one finds

\begin{align*}
(5.52) \quad \chi^3 \left[ (20x^2 - 12) + \chi (45 - 6x^2 - 45x^4) + \chi^2 (-126 - 210x^2 \\
& \quad + 292x^4) + \chi^3 (336 + 1048x^2 - 439x^4 - 495x^6) \right] = 0
\end{align*}

The expression in the square bracket is of the form

\begin{align*}
(5.53) \quad E(x) = \mathcal{E}_0(x) + \mathcal{E}_1(x) + \mathcal{E}_2(x) + \mathcal{E}_3(x) = 0
\end{align*}
where

\[ E_0(x) = 20x^2 - 12 \quad , \quad E_1(x) = 45 - 6x^2 - 45x^4 \]

\[ E_2(x) = -126 - 210x^2 + 292x^4 \quad , \quad E_3(x) = 336 + 1048x^2 - 789x^4 - 495x^6 \]

A solution \( x \) of \( E(x) \) must be of the form

\[(5.54) \quad x = x_0 + \eta x_1 + \eta^2 x_2 + \eta^3 x_3 \]

substituting this value of \( x \) into (5.53) and expanding in Taylor series

\[(5.55) \quad E(x) = E_0(x_0 + \cdots + \eta^3 x_3) + \cdots + \eta^3 E_2(x_0 + \cdots + \eta^3 x_3) \]

\[= E_0(x_0) + \cdots + \frac{\eta}{3!} (\eta x_1 + \eta^2 x_2 + \eta^3 x_3)^3 E''_0(x_0) + \eta \{ E_1(x_0) \]  

\[+ \cdots + \frac{\eta^3}{3!} (\eta x_1 + \eta^2 x_2 + \eta^3 x_3)^3 E''_1(x_0) \} + \cdots + \eta^3 \{ E_3(x_0) + \cdots \} \]

\[= E_0(x_0) + \eta \{ x_1 E_0(x_0) + E_1(x_0) \} + \eta^2 \{ x_2 E_0(x_0) + \frac{1}{2} x_1^3 E''_0(x_0) \]

\[+ x_1 E_1(x_0) + E_2(x_0) \} + \eta^3 \{ x_2 E_0(x_0) + x_1 x_3 E_0''(x_0) + \frac{1}{6} x_1^3 E''_0(x_0) \]

\[+ x_2 E_1(x_0) + \frac{1}{2} x_1^2 E''_1(x_0) + x_1 E_2(x_0) + E_3(x_0) \} = 0 \]

For \( E(x) = 0 \), each coefficient of \( \eta^n (n = 0, \ldots, 3) \) must vanish separately, thus
(5.56) \[ E_0(x_0) = 0 \]

(5.57) \[ x_1 E_0'(x_0) + E_1(x_0) = 0 \]

(5.58) \[ x_2 E_0''(x_0) + \frac{1}{2} x_1^2 E_0'''(x_0) + x_1 E_1'(x_0) + E_2(x_0) = 0 \]

(5.59) \[ x_3 E_0'(x_0) + x_1 x_1 E_0''(x_0) + \frac{1}{4} x_2^2 E_0'''(x_0) + x_2 E_1'(x_0) + \frac{1}{2} x_1^2 E_1''(x_0) + x_1 E_2'(x_0) + E_3(x_0) = 0 \]

Substituting in (5.56) the value of \( E_0 \) given in (5.53), we solve for \( x_0 \); with \( x_0 \) known, we proceed to (5.57) and solve for \( x_1 \), and so on; in this manner we find

\[
x_0 = \sqrt{3/5}
\]

\[
x_1 = -\frac{63}{100} \sqrt{5/3}
\]

(5.60) \[
x_2 = \frac{1161}{800} \sqrt{5/3}
\]

\[
x_3 = -\frac{177}{40} \sqrt{5/3}
\]

therefore

(5.61) \[
x = \frac{\omega'}{k'} = \sqrt{3/5} \left( 1 + i \frac{\omega'}{\lambda} \frac{2i}{x_0} - \omega'^2 \frac{1161}{800} - i \omega'^3 \frac{59}{8} \right)
\]

and in terms of the real \( \omega \) and \( k \)

(5.62) \[
k = \frac{\omega}{\omega_0} \left( 1 + i \frac{\omega}{\lambda} \frac{2i}{x_0} - \left(\frac{\omega}{\lambda}\right)^2 \frac{1161}{800} - i \left(\frac{\omega}{\lambda}\right)^3 \frac{59}{8} \right)
\]
\( \omega/\lambda \) is reexpressed in terms of \( \varphi^2 \) defined by Greenspan. From (5.28) and (5.23)

\[
(5.63) \quad \lambda = q_n B_i \frac{d}{dr} \frac{1}{r^2} = q_n \frac{8}{15 \pi^4} I(0) \left( \frac{2 V_0}{m} \right)^\frac{1}{2} \Gamma \left( \frac{7}{2} \right) \tag{for a Maxwell gas}
\]

hence

\[
(5.64) \quad \frac{\omega}{\lambda} = \frac{\omega}{q_n \frac{8}{15 \pi^4} I(0) \left( \frac{2 V_0}{m} \right)^\frac{1}{2} \Gamma \left( \frac{7}{2} \right)}
\]

On the other hand (Greenspan, 1965) \(^30\)

\[
(5.65) \quad \varphi^2 = \frac{C_o^2 \rho}{\gamma_o \omega \mu}
\]

\( \left( C_o^2 = \frac{5 K T_o}{3 m} \right) \quad \rho = m n \quad \gamma_o = \frac{5}{3} \) \( (\mu = \text{coefficient of viscosity}) \)

For a Maxwell gas the exact value of \( \mu \) is (Chapman and Cowling, 1961)

\[
(5.66) \quad \mu = \frac{5 \left( K T_o / m \right)^{\frac{1}{2}} \left( 2 K T_o / V_0 \right)^{\frac{1}{2}}}{8 \Gamma \left( \frac{7}{2} \right) \left( 4 I(0) / \pi \right)}
\]

so that

\[
(5.67) \quad \varphi^2 = \frac{16 n \Gamma \left( \frac{7}{2} \right) I(0) \left( \frac{2 V_0}{m \pi} \right)^{\frac{1}{2}}}{5 \omega^2}
\]
from (5.64) and (5.67) we find

\[
\frac{\omega}{\lambda} = \frac{2}{3 \tau_g}
\]

Furthermore Greenspan's definition of the propagation constant (1965) is

\[
k_g = \frac{\kappa + i \gamma}{(\omega/c_0)} \quad (\kappa \text{ is the absorption coefficient and } \gamma = \omega/c)
\]

while in terms of \(\kappa\) and \(\gamma\) our \(k\) is

\[
k = \gamma + i \kappa
\]

so that

\[
k_g = \frac{i k^*}{(\omega/c_0)} \quad (\ast \text{ denotes complex conjugation})
\]

In (6.71), replacing \(k\) by the RHS of (5.62) and \(\omega/c\) by \(2/3 \tau_g\), we find, for a Maxwell gas,

\[
k_g = i + \frac{7}{10 \tau_g} - i \frac{43}{4 \delta \tau_g^2} - \frac{59}{2 \tau_g}
\]

\(\lambda\) for a gas of hard spheres is, taking into account eq. (5.27),

\[
\lambda = 9 n_o B^{(a)}
\]

\[
= \frac{34}{5} n_o a^3 \sqrt{K T_o \pi/\mathfrak{m}}
\]

whence

\[
\frac{\omega}{\lambda} = \frac{\omega}{2y n_o a^2 \sqrt{K T_o \mathfrak{m}/\mathfrak{m}}}
\]
The fourth order approximation of the coefficient of viscosity of a gas of hard spheres is (Chapman and Cowling, 1961)

\[(5.75) \quad \mu_4 = 1.016 \frac{5 \sqrt{KTm}}{16 \pi^{1/2} \sigma^2}\]

Substituting into (5.65) we find

\[(5.76) \quad \frac{\nu_4}{\sigma_4} = \frac{16 n \sqrt{KTm}}{5(1.016) \omega \pi^{1/2} \sigma^2}\]

From (5.74) and (5.76) the following relation results

\[(5.77) \quad \frac{\omega}{\lambda} = \frac{2}{(1.016) \frac{2}{3} \nu_4}\]

so that for a hard sphere gas the propagation constant is

\[(5.78) \quad k_4 = \frac{i}{c} + \frac{3}{10(1.016)^2 \nu_4} - \frac{i}{40(1.032)^2 \nu_4^2} - \frac{177}{21(1.048)^2 \nu_4^3}\]

(d) Discussion

We note that for both the hard sphere and Maxwell gases the coefficients of \( \frac{\nu_4}{\sigma_4} \), \( n = 0, 1, 2, 3 \) in the expansion of \( k_4 \) in powers of \( \frac{1}{\sigma_4} \) are independent of temperature. For a hard sphere gas, the coefficients of \( \frac{1}{\sigma_4} \), \( \frac{1}{\sigma^2_4} \), \( \frac{1}{\sigma^3_4} \) are 1.6%, 3.2% and 4.8% smaller than the corresponding coefficients for a Maxwell gas; since
these models are the limits of the soft and hard atoms one may deduce that velocity and absorption of sound are almost independent of the nature of the intermolecular potential, however it was found (Sirovich and Thurber, 1965b) that in the moderate and high frequency ranges the hard sphere results agree slightly better with experiment.

The various expansions of $\frac{k}{c}$ for a Maxwell gas up to 3rd order in $\frac{1}{n_q}$ are

Navier-Stokes

$$(5.79) \quad k_q = i + \frac{7}{10 n_q} - i \frac{141}{200 n_q^2} - i \frac{1559}{2000 n_q^3}$$

Burnett

$$(5.80) \quad k_q = i + \frac{7}{10 n_q} - i \frac{43}{40 n_q^2} - i \frac{1203}{2000 n_q^3}$$

Super-Burnett

$$(5.81) \quad k_q = i + \frac{7}{10 n_q} - i \frac{43}{40 n_q^2} - \frac{7 \cdot 102563}{2 \cdot 5^6 n_q^3}$$

13-Moments

$$(5.82) \quad k_q = i + \frac{7}{10 n_q} - i \frac{43}{40 n_q^2} - i \frac{527}{400 n_q^3}$$

Foch-Uhlenbeck

$$(5.83) \quad k_q = i + \frac{7}{10 n_q} - i \frac{43}{40 n_q^2} - \frac{1031}{400 n_q^3}$$
The first term in the expansion is the constant speed; the second term is the classical attenuation; the third term is the dispersion in the speed. All $k_q'$ agree up to $1/n_q$; all $k_q''$, except the N-S value agree up to $1/n_q$; all coefficients of $1/n_q^3$ are different. They are 0.779, 2.101, 2.872, 1.318, 2.578 and 2.185 respectively.

The Navier-Stokes equations which are a result of the first order Chapman - Enskog method of expansion in powers of a parameter proportion to $1/n_q$ are therefore valid only up to first order in $1/n_q$ so that the coefficients of $1/n_q^2$ and $1/n_q^3$ in the Navier-Stokes expansion of $k_q$ cannot be trusted.

In figures 4 and 5 are plotted the quantities $(T_e' - \xi_0)/T_e'$ and $(1 - \xi_0/c)$ vs $\xi^2$ for the different theoretical models and the corresponding experimental values of Greenspan for Neon.

Recalling that

$$k_q = \frac{\mu + i \xi}{\mu} = \frac{\mu \xi}{\xi} + i \xi$$

and

$$n_q = \frac{3}{5 \eta}$$
we see that \((1-c/c)\) and \(\frac{1}{6}v' - \frac{\alpha c_t}{\omega} / \frac{1}{3} v'\) are proportional to the third term of \(k_g\) and the fourth term of \(k_{c_w}\) multiplied by \(c_{w}\) respectively; thus all values of \((1-c/c)\) except the Navier-Stokes value are equal and all values of \(\frac{1}{6}v' - \frac{\alpha c_t}{\omega} / \frac{1}{3} v'\) are different.

The Navier-Stokes and 13-Moments values of \((1-c/c)\) in figure 4 are certainly too small. The slope of the B line seems slightly smaller than the slope of the experimental curve at the origin since the B line lies below the 2nd and 3rd experimental points from the origin.

As expected, the Burnett value of \((1-c/c)\) in figure 5 agrees well with experiment while the Navier-Stokes result is too small.

In conclusion, we note that in the expansion of \(k_g\) in powers of \(1/\tau_g\) the coefficient of \(\tau_g^2\) is the same for all models. The coefficient of \(\tau_g^3\) is sensitive to the method of approximation and is different for each model. Comparison with experimental data for Neon does not reveal which coefficient of \(\tau_g^3\) is the most reliable; however, it can be fairly safely deduced that the experimental value lies somewhere between 2.101 and 2.872 and, as far as agreement with experiment is concerned, any of the four coefficients of \(\tau_g^3\) of B, SB, ST and FU is within the right ball park.
Figure 4. Comparison between theory and experiment of the dispersion in the speed of sound at low frequencies. SB = Super Burnett; FU = Foch-Uhlenbeck; ST = Sirovich-Thurber; B = Burnett; 13M = 13-Moments; dots are experimental values for Neon.

Figure 5. Comparison between theory and experiment of the non-Kirchoffian frequency dependence of the absorption of sound at low frequencies.
6. **METAStABLE STATES**

The existence of superheated liquid and supercooled vapor states is well known (see for instance Landau and Lifshitz, 1965); they correspond to the sections on the \( \mu - \upsilon \) curve with a positive slope below and above the parallel to the \( \upsilon \)-axis which divides this curve into two parts of equal areas. Van Kampen (1964) showed that the densities \( n \) of these states are the homogeneous solutions of eq.(4.11a) which correspond to local minima of the free energy; a more general treatment of this topic was later given by Lebowitz and Penrose (1966). The correspondence of these states to local minima of the free energy implies that they are thermodynamically stable i.e. they are stable against small perturbations which vary so slowly that they can be considered as a succession of equilibrium states.

One cannot find out from equilibrium statistical mechanics theories whether these states are stable against non quasi-static perturbations; for such an investigation a kinetic theory approach is more appropriate; deSobrino (1967) was able to show, using certain approximations for the RHS of the linearized kinetic equation (6.19), that superheated liquid and supercooled vapor states are stable against sufficiently small perturbations. In this section, the problem of determining the stability of these states is reconsidered making fewer and more accurate approximations.

From a mathematical standpoint, the problem of determining the stability of a state is closely related to the problem of sound propagation; it requires deriving the dispersion relation
for the Van der Waals gas described in section 2 and studying the properties of the roots of this equation. The main problem is again to approximate the linearized collision integral, \( J(k) \), for such a gas. \( J(k) \) can be split into two parts. (appendix A).

\[
(5.1) \quad E(\omega, k, v(k), \eta) = 0
\]

where \( L(k) \) is the familiar linearized collision integral of a dilute gas and \( K(k) \), a non local term. In deSobrino's paper \( L(k) \) is approximated by the Krook model which is a special case of the GJS model with \( \eta = 3 \); \( K(k) \) by \( K \left( \sum_{i=1}^{2} a_i \cdot \eta_i \right) \) and \( \eta \) by \( (1 - n^2)^{-1} \).

The Krook model does not yield correct results for sound propagation (Sirovich and Thurber, 1965b) and though it might be suitable for a qualitative analysis such as the study of stability, a certain uneasiness about the adequacy of this model persists.

In this thesis the GJS model of the previous section (\( \eta = 5 \)), is used to approximate \( L(k) \); \( K(k) \) is approximated by \( K \left( \sum_{i=1}^{5} a_i \cdot \eta_i \right) \); furthermore, except for the requirement that it be a monotonically increasing function of density, which is physically plausible, no assumption is made on the functional form.

(a) The GJS Model For a Gas of Hard Spheres with a Long Range Attractive Potential

In this section the kinetic equation of a gas of hard spheres with an attractive tail, eq. (2.10), is linearized and a GJS model of this linearized equation is derived for a plane wave perturbation.
On the LHS of the kinetic equation

\[ \frac{\partial f}{\partial t} = \frac{\partial f}{\partial x} + \frac{\partial f}{\partial \xi} - \frac{1}{m} \frac{\partial^2 f}{\partial \xi^2} \int d^3r' V((r-r')/\xi) n(r', t) \]

one writes

\[ f = f_0 (1 + \xi) \]

\[ \xi = h(k) e^{i(k \cdot \xi - \omega t)} \]

\[ n = n_0 (1 + \nu) \]

\[ \nu = \nu(k) e^{i(k \cdot \xi - \omega t)} \]

and obtains, to first order in \( h \) and \( \nu \),

\[ \frac{\partial f_0}{\partial t} = i f_0 \left\{ (-\omega + \frac{\xi}{\xi} k) h + \frac{m_0 \nu(k)}{k^2} \xi \cdot k \nu \right\} \]

where

\[ \nu(k) = \int V(r) e^{-i k \cdot r} d^3r \]

The collision integral for a gas of hard spheres

\[ J(4) = \iint \left\{ \eta(4 + \xi \sigma \xi) \frac{f_0(4 + \xi \sigma \xi)}{f_0(4 + \xi \sigma \xi)} - \eta(4 - \xi \sigma \xi) f_0(4 - \xi \sigma \xi) \right\} \]

where

\[ \sigma = \frac{\xi}{\xi} \]

is linearized and expanded in Taylor series up to first order; the result is

\[ J(4) = f_0 \left\{ \eta(4 \xi \sigma \xi) + \xi(4 \sigma \xi) \right\} \]
where

\[(6.12) \quad \mathcal{L}(\eta) = \sum_{n} \int_{0}^{1} \left[ \frac{1}{2} \frac{d}{d\eta} \right] \frac{1}{\eta} \eta^2 \rho_{\eta} \eta^{\prime} d\eta^{\prime}
\]

\[(6.13) \quad \kappa(k_{\eta}) = \sum_{n} \int_{0}^{1} \left\{ \eta \eta^\prime \left( \frac{d}{d\eta} \right) \left( \eta \eta^{\prime} \right) \right\} \frac{1}{\eta} \eta^2 \rho_{\eta} \eta^{\prime} d\eta^{\prime}
\]

\[(6.14) \quad \lambda_{\eta} = \frac{5}{z} q_{1} q_{2}
\]

It is shown in appendix A that \(\kappa(k_{\eta})\) can be approximated by \(\kappa(k_{\eta})\).

For a plane wave the RHS of (6.12) and (6.13) become

\[(6.15) \quad \mathcal{L}(\eta) = \lambda \kappa(k_{\eta}) = -\lambda \left\{ \frac{1}{3} \frac{d}{d\eta} \left( \eta^2 - \frac{1}{3} \right) + \frac{2}{3} \frac{d}{d\eta} \left( \eta^2 - \frac{1}{3} \right) - \eta^3 \right\} + \frac{1}{2} \left( \eta^2 - 2 \right) + \frac{2}{3} \frac{d}{d\eta} \left( \eta^2 - \frac{1}{3} \right) + \frac{d}{d\eta} \left( \frac{1}{3} \right)
\]

\[(6.16) \quad \kappa(k_{\eta}) = \frac{i K n_{e} b \eta}{\sqrt{\pi}} \left\{ - \left( \eta_{o} \frac{b_{1}}{b} + \frac{2}{3} \eta^2 \right) \left( \eta_{o} \frac{b_{2}}{b} + \frac{2}{3} \eta^2 \right) \right\}
\]

where

\[(6.17) \quad \eta^2 = \frac{3}{\sqrt{K T_{e} / m}}
\]

\[(6.18) \quad \frac{d\eta}{d(n_{e} b)}
\]

the dimensionless collision frequency \(\lambda\) is defined in (5.5); the dimensionless collision integral \(\kappa(k_{\eta})\) is defined in (5.6); its value, the RHS of (6.15), has already been derived in section 5. The evaluation of \(\kappa(k_{\eta})\) is carried out in appendix A.

In the linearized kinetic equation

\[(6.19) \quad \frac{d\rho_{\eta}}{d\tau} = \dot{\rho}_{\eta} \left\{ \eta \mathcal{L}(\eta) + \kappa(k_{\eta}) \right\}
\]
replacing $\frac{p_{\xi}}{\xi}$ by the RHS of (6.8), $\xi(\xi)$ and $k(k)$ by the RHS of (6.15) and (6.16) and expressing the result in terms of the dimensionless variables

$$k' = \frac{k \sqrt{k T / m}}{\lambda \eta}$$

$$\omega' = \frac{\omega}{\lambda \eta}$$

and $\zeta$ defined in (6.17), one finds, after multiplication by $i$

$$\left(\omega + i - \nu_3 k\right)k_3 = \frac{\nu_0 V(k \lambda \eta / \sqrt{k T / m})}{k T} \nu_3 k v + i \left\{ \frac{1}{2} \frac{\nu_3}{\nu_3^2} \nu_3 \nu v + \frac{2}{3} \frac{\nu_3}{\nu_3^2} \nu_3 \nu v \left( \frac{\nu_3^2}{3} - \frac{2}{3} \right) \right\} - k n e \lambda \eta \left\{ - \left( \frac{b n o}{n} + 2 \right) \nu_3 v + \left( \frac{1}{2} - \frac{3}{16} \nu_3^2 \right) \nu_3 \nu v + \left( 1 - \frac{3}{2} \nu_3^2 - \frac{1}{2} \nu_3^2 \right) u_3 - \frac{3}{2} \left( \nu_3^2 + \frac{3}{2} \nu_3^2 \right) \nu_3 v_3 \right. \right.$

$$\left. - \left( \frac{4}{3} \nu_3^2 - 2 \nu_3 \nu v + 3 \nu_3^2 + 12 \nu_3^2 \nu_3 \frac{S_3^2}{350} \right) \right\}$$

The prime superscript on $\omega'$ and $k'$ have been dropped. Eq. (6.22) is the GJS model for a gas of hard spheres with an attractive potential and for a plane wave perturbation.

(b) The Dispersion Relation

As in section 5, we proceed to eliminate successively $\nu_3, S_3, u_3, v$ and $v$ from eq. (6.22). We multiply (6.22) by $w(\sigma)\sigma$ integrate the result and taking into account eqs. (5.16) - (5.20) solve for $\nu_3$

$$\nu_3 = \frac{w^2}{k T} - \frac{5}{2} - 2 b n \eta - b n^2 \frac{\nu_3}{\cdot} - c(1 - 2 n \eta)}{1 + \frac{2}{5} b n \eta}$$
where

\[(6.24) \quad \xi = \frac{\eta \sqrt{1 + \frac{k \lambda \eta}{\sqrt{k \tau_0 \tau}}}}{k \tau_0}\]

To find \(S_3\), we multiply (6.22) by \(w(v)v^2\) and integrate the result; we obtain

\[(6.25) \quad S_3 = \frac{\omega \left( \frac{3\tau - 2v(1 + b \eta)}{1 + \frac{3}{5} b \eta} \right)}{1 + \frac{3}{5} b \eta}\]

Multiplying (6.22) by \(w(v)\) and integrating one finds the continuity equation

\[(6.26) \quad \omega v - ku_3 = 0\]

In (6.22), replacing \(p_{33}, S_3\) and \(u_3\) by their values in (6.23), (6.25) and (6.26) we obtain

\[(6.27) \quad (\omega + i - k v_3) \eta = \frac{-\tau(1 + b \eta) + \tau(1 + \frac{3}{5} b \eta + b^2 \eta^2 - \frac{w^3}{k})}{1 + \frac{3}{5} b \eta} \left\{ \frac{\xi}{4} (\xi^3 - \xi^2) \right\}
\]

\[+ \frac{2}{250} k b \eta \left\{ - \frac{2}{15} \xi^3 - 2 \xi^2 + \frac{3}{5} \xi + \frac{6}{5} \xi^2 \right\} + \frac{\omega}{k} \left( \frac{3\tau - 2v(1 + b \eta)}{1 + \frac{3}{5} b \eta} \right) \left\{ \frac{\xi}{18} \xi^3 \left( \frac{\xi^3 - 1}{5} \right) + \right\}
\]

\[+ \frac{k b \eta}{250} \left\{ - \frac{2}{15} \xi^3 - 2 \xi^2 + 3 \xi^4 + 12 \xi^2 \xi^2 \right\} \right\}
\]

\[+ \tau \{ \frac{i}{2} (\xi^2 - 3) - k b \eta \xi^2 (\frac{1}{5} - \frac{3}{5} \eta) \} \}
\]

(6.27) is multiplied by \(\frac{w(v)}{\omega + i - k v_3}\) and the result integrated over \(v\).
To eliminate $\tau$ we must evaluate the integral $\int w(u) u^2 \, du$. First
we multiply (6.27) by $\frac{w(u)(u_1^2 + u_2^2)}{w + i - k \tau}$ and integrate the result.
Making use of (6.28, we find

\begin{equation}
\frac{1}{2 \pi} \int_{-\infty}^{\infty} \frac{e^{-\frac{\pi^2}{4u^2}} \, du_3}{w + i - k \tau} \left\{ \frac{T}{1 + \frac{2}{5} b \eta} + \nu \left( 1 + \frac{5}{2} + 2 b \eta + b \eta n \gamma' - \frac{u_3^2}{k} \right) \right\}
\end{equation}

The integral $\int w(u) u^2 \, du$ has already been evaluated when $\rho_{33}$ was reexpressed in terms of $\nu$ and $\tau$ (eq. (6.23)); it is

\begin{equation}
\int w(u) u^2 \, du = \frac{T}{1 + \frac{2}{5} b \eta} + \nu + \tau
\end{equation}

Adding (6.29) and (6.30) we find
And from (5.16) and (5.18) we also have

\[(6.32) \quad \int w_h \nu^2 \, dw = 3(\tau + \nu)\]

Equating the RHS of (6.31) and (6.32) and solving for \( \tau \)

\[(6.33) \quad \tau = \nu \left\{ \frac{1 + \frac{\xi}{3} + 2b_{\nu} + b_{\nu}^2 \eta - \frac{\nu^2}{3}}{1 + \frac{2}{3} b_{\eta}} \left( \frac{2}{3} B + \frac{12}{350} k_{\eta} \eta (A + 6 \xi) + \frac{4}{5} b_{\eta} \eta A \right) \right\} + \frac{2 \nu}{1 + \frac{2}{3} b_{\eta}} \left( \frac{2}{3} B + \frac{12}{350} k_{\eta} \eta (A + 6 \xi) - \frac{3 \nu}{1 + \frac{2}{3} b_{\eta}} \left( \frac{2}{3} B + \frac{12}{350} k_{\eta} \eta (A + 6 \xi) \right) - 2iA - \frac{6}{5} k_{\eta} \eta B \right\} \]
Substituting this value of $\tau$ into (6.28) we obtain the dispersion relation

$$\tag{6.34} 1 = - \left( \frac{1 + \xi + 2 \beta \eta + \beta^2 \eta^2 - \frac{\omega^2}{K^2}}{1 + \frac{3}{2} \beta \eta} \right) \left\{ \frac{i}{8} (c - a) + \frac{3}{23} \beta \eta \left( - \frac{16}{15} B + \frac{8}{5} D \right) \right\} + kB \left( \xi + \frac{2 \beta \eta + \beta^2 \xi^2 + \frac{i \omega}{K^2}}{1 + \frac{3}{2} \beta \eta} \right) \left\{ \frac{i}{18} (a - b) + \beta \eta \left( - \frac{8}{15} B + \frac{1}{5} D \right) \right\} + \frac{3 \omega}{K^2} \left( \frac{i}{18} (a - b) + \beta \eta \left( - \frac{8}{15} B + \frac{1}{5} D \right) \right)

where

$$A, B, C, D \text{ are defined in (5.44) and (5.46)}$$

$$\tag{6.35} \mathcal{F} = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} e^{-\frac{\omega^2}{2}} d\omega$$

and

$$\tag{6.36} \mathcal{G} = \frac{\tau}{\sqrt{\xi}}$$

In the limit as $\beta \eta \to 0$, $\xi \to 0$ and $\eta \to 1$, equations (6.33) and (6.34) reduce to equations (5.43) and (5.45) of section 5 which are respectively the equation for $\mathcal{F}$ and the dispersion relation for a dilute gas.
(c) **Stability Criterion**

To study the stability of uniform density states we consider the behaviour of the perturbation \( \phi_0 e^{i(h \frac{z}{\tau} - \omega t)} \) in time. The space dependence of \( \phi_0 \) is kept fixed.

The dispersion relation, eq. (6.34) is of the form

\[
\mathcal{E}(\omega, k, \nu(k), \gamma) = 0
\]

\( k, \nu(k) \) and \( \gamma \) are parameters and \( \omega \) is variable and complex. The values of \( \omega(k, \nu(k), \gamma) \) for which \( \mathcal{E} = 0 \) are the frequencies of oscillation of the fluid. A zero of \( \mathcal{E} \) in the upper half plane \( S_+ \) corresponds to an exponential growth indicating that the unperturbed state is unstable. A zero of \( \mathcal{E} \) on the real axis or on the lower half plane \( S_- \) corresponds to a stationary or damped perturbation.

The problem is to determine whether \( \mathcal{E} \) has zeros on the \( S_+ \) plane. One has the following theorem (see for example Wylie, 1960):

If \( f(z) \) is analytic within and on a closed curve \( C \) and if \( f(z) \) has no zeros on \( C \) then the number of zeros of \( f(z) \) within \( C \) is

\[
N = \frac{1}{2\pi i} \oint_C \frac{f'(z)}{f(z)} \, dz
\]

(6.37)

The RHS of this equation is just the net number of times \( f(z) \) encloses the origin counterclockwise on a complex \( z \)-plane as \( z \) moves along \( C \) once.

To find the number of zeros of \( \mathcal{E} \) on \( S_+ \), we first show that \( \mathcal{E} \) is analytic on \( S_+ \), (this is done in appendix B) then take for contour \( C \) the segment of the real axis between \( -R \) and \( R \) and the semicircle on \( S_+ \) with radius \( R \) and centered at the origin. In the
limit as \( R \to \infty \), \( \mathcal{C} \) encloses \( S_+ \). Next we plot \( \mathcal{E}(\omega) \) on the complex \( \mathbb{E} \)-plane as the complex variable \( \omega \) moves along \( \mathcal{C} \); this plot will show the number of times \( \mathcal{E}(\omega) \) encloses the origin counterclockwise. It will be shown that in the limit as \( R \to \infty \), \( \mathcal{E}(\omega) \) remains constant on the semicircle and it is sufficient to plot \( \mathcal{E}(\omega) \) as \( \omega \) increases from \( -\infty \) to \( \infty \) on the real axis. In fact we need only find the zeros of the imaginary part of \( \mathcal{E}(\omega) \), the corresponding values of the real part of \( \mathcal{E}(\omega) \) and the direction in which \( \mathcal{E}(\omega) \) crosses the real axis at these points.

As it stands, the function \( \mathcal{E}(\omega, k, \nu(k), \eta) \) defined in (6.34), does not readily lend itself to analysis. We now derive approximations for this function for various frequencies.

We have mentioned in the beginning of this subsection that the dimensionless wave number \( k' \) is kept fixed; we will now estimate the order of magnitude of \( k \) for which

\[
\frac{\nu V(k)}{kT} \nu V(k)^{-k'} V
\]

the term in the linearized kinetic equation (6.22), due the attractive potential, is non negligible compared to the collision integral.

The Fourier transform of \( V(r) \)

\[
V(k) = \int V(r) e^{-i \frac{kr}{k}} dr
\]

can be rewritten as

\[
V(k) = \frac{u \pi}{k} \int_0^\infty r V(r) \sin kr dr
\]

and since \( V(r) \) has a finite range \( d \)

\[
V(k) = \frac{u \pi}{k} \int_0^d r V(r) \sin kr dr
\]
We assume that for \( \alpha r < d \), there exist an \( M \) and an \( m \) such that

\[
-M < r V(r) < -m
\]

then we have the following inequality

\[
\frac{4 \pi M}{k^2} (\cos kd - 1) < V(k) < \frac{4 \pi m}{k^2} (\cos kd - 1)
\]

(i) When \( kd \ll 1 \) then \( l = \frac{1}{k} > d \) and \( \cos kd \) can be expanded in powers of \( kd \); the above inequality becomes

\[
-2\pi M d^2 < V(k) < -2\pi m d^2
\]

For a slowly varying potential, \( M \) is not much larger than \( m \) and \( M \) and \( m \) are of the order of \( r V_o \) where \( \alpha r < d \) and \( V_o \) is the strength of the potential; it follows that \( \frac{r V(k)}{k^2} \sim O\left(\frac{V_o}{k^2} \frac{r d^2}{d^3}\right) \); \( \Delta \) is the interparticle distance. In order for the so-called metastable states to exist, the temperature \( \tau \) must satisfy the condition \( \frac{\omega}{b \kappa T} > \frac{2\sqrt{\pi}}{\lambda} \), where \( \omega = -\int V(r)dr \) and \( b = \frac{3}{2} \pi \sigma^3 \); but \( -\int V(r)dr \sim V_o d^3 \) therefore \( \frac{r V(k)}{k^2} \sim O\left(\frac{V_o}{d^3} \frac{r d^2}{d^3}\right) \). The term, in the linearized kinetic equation, due to the attractive potential is \( \frac{r V(k)}{k^2} k_0 v_0 \); the dimensionless wave number \( k' \) is the ratio of the mean free path \( \alpha \) to the perturbation wavelength \( \lambda \); \( k' = \frac{a}{\xi} \); \( v_3 = \frac{5}{3} \frac{\pi^2}{\sqrt{\kappa T f m}} \); for a near equilibrium state the velocity distribution is almost Gaussian so that \( \omega_3 \sim 1 \). Therefore \( \frac{r V(k)}{k^2} k_0 v_3 \sim \frac{a}{\xi} V_o \left(\frac{r}{d} \right) \frac{d^2}{d^3} \)

\[
\left(\frac{\sigma}{\Delta c}\right)^3 \sim O\left(\frac{1}{3}\right) \text{ so that, for a dense gas, } \left(\frac{\sigma}{\Delta c}\right)^3 \sim O\left(1\right)
\]

The mean free path \( \alpha \) is of the order of \( \frac{1}{\omega_\Delta} = \left(\frac{\Delta}{\rho}\right)^2 \Delta \); then

\[
\frac{\alpha}{\Delta} \sim O\left(\frac{\Delta}{\rho}\right)^2 \sim O\left(1\right)
\]

the mean free path, for a dense gas, is of the order of the interparticle distance. In section 2 we have
assumed that $d \gg \Delta$; therefore $d \gg a$. Also, since $a < r < d$ and $l \gg d$, then $l \gg r$; therefore

$$\frac{n V(k)}{k T} v_3 k' v \sim O \left( \frac{s}{d} \right)^3 \frac{r}{d} \frac{a}{d} \frac{v}{v} \ll v$$

The rate of change of $\lambda$ due to collisions, $(\partial \lambda / \partial t)_e$, is, in dimensionless variables, of the order of $h \sim v$; therefore, for wavelengths $l \gg d \gg a$, the term in the linearized kinetic equation due to the attractive potential is negligible compared to the collision term.

(ii) When $kd \gg 1$ then $l \ll \frac{1}{k} \sim d$; our inequality becomes

$$- \frac{\eta M}{k^2} < V(k) < - \frac{\eta m}{k^2}$$

and

$$V(k) \sim O \left( \frac{r V_v}{k^2} \right) = V_v r k^2$$

$$\frac{n V(k)}{k T} v_3 k' v \sim O \left( \frac{1}{\Delta^3} \frac{V_v}{k T} r k^3 \right) \sim O \left( \frac{1}{\Delta^3} \left( \frac{s}{d} \right)^3 \frac{r}{d} \frac{\varepsilon}{k} \right) = \left( \frac{s}{\Delta} \right)^3 \frac{r}{d} \frac{\varepsilon}{k} \frac{v}{v}$$

In this case the contribution to the linearized kinetic equation due to the potential term is much larger than in (i) where $k \gg a$; while in (ii) $l \gg a$... If we choose $r$ small enough this term will become non negligible compared to the collision term.

(iii) When $kd < 1$ then $l \ll \frac{1}{k} \ll d$. For $l \sim a$ we have

$$\frac{n V(k)}{k T} v_3 k' v \sim O \left( \left( \frac{s}{d} \right)^3 \frac{r}{d} \frac{a}{d} \frac{v}{v} \right) \sim O \left( \left( \frac{s}{d} \right)^3 \frac{r}{d} \frac{a}{d} \frac{v}{v} \right) \ll v$$
The potential term is much smaller than its value in (ii) since it is proportional to \( \frac{a^3}{d} \) while in (ii) it is proportional to \( \frac{a}{d} \).

(iv) When \( kd \gg 1 \) and \( l \ll a \ll d \), then

\[
\frac{\nu V(k)}{kT} \frac{\nu_3}{K^3} \nu \sim 0 \left( \left( \frac{\pi}{\Delta} \right)^3 \left( \frac{\rho}{d} \right)^2 \frac{a}{d} \frac{\nu}{\nu} \right) \left( \frac{\pi}{\Delta} \right)^3 \frac{\rho}{d} \frac{a}{d} \frac{\nu}{\nu} ;
\]

\[
\frac{\nu V(k)}{kT} \frac{\nu_3}{K^3} \nu \text{ is smaller than its value in (iii).}
\]

In conclusion, we see that the values of wavelength \( \ell \) for which \( \frac{\nu V(k)}{kT} \frac{\nu_3}{K^3} \nu \) is largest are those of the order of the range of the potential: \( \ell \sim d \gg a \) so that \( k' \approx \frac{a}{\ell} \ll 1 \). For these values of \( \ell \), when the temperature is sufficiently small, the contribution due to the attractive potential is non negligible compared to the collision term. For wavelengths too large or too small (\( \ell > d \) and \( \ell \ll a \)), \( \frac{\nu V(k)}{kT} \frac{\nu_3}{K^3} \nu \) is negligible. We shall choose \( k' \) such that

\[
(6.34) \quad k' \sim 0 \left( \frac{a}{d} \right) \ll 1
\]

In the above discussion on the magnitude of the wave number we have used the original notation where \( k \) is the real wave number with dimension \( L^{-1} \) and \( k' \) is the dimensionless wave number defined in (6.20).

We return now to the problem of approximating the function \( E(\omega, k'; \nu(k'), m) \) and for the remaining part of this chapter, will be dealing only with the dimensionless wave number \( k' \); the prime superscript on \( k' \) is again dropped.

As \( \omega \) increases from \(-\infty\) to \( \infty \) on the real axis, the inequality

\[
(6.39) \quad |\omega| \gg k
\]
is always satisfied except for values of $\omega$ in the vicinity of the origin. This is a consequence of condition (6.38). When (6.39) holds, the integral $A$ can be expanded as follows

$$A = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \frac{e^{-\frac{\omega^2}{2}}}{\omega + i - k \nu_3} d\nu_3 = \frac{1}{\omega + i} \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \frac{e^{-\frac{\nu_3^2}{2}}}{1 - \frac{k \nu_3}{\omega + i}} d\nu_3 $$

$$= \frac{1}{\omega + i} \int_{-\infty}^{\infty} e^{-\frac{\nu_3^2}{2}} \left( 1 + \frac{k \nu_3}{\omega + i} + \left( \frac{k \nu_3}{\omega + i} \right)^2 + \left( \frac{k \nu_3}{\omega + i} \right)^3 + \ldots \right) d\nu_3 $$

$$= \frac{1}{\omega + i} \left\{ 1 + \left( \frac{k}{\omega + i} \right)^2 + 3 \left( \frac{k}{\omega + i} \right)^4 + 15 \left( \frac{k}{\omega + i} \right)^6 + \ldots \right\} $$

Similarly

$$B = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \frac{\nu_3 e^{-\frac{\nu_3^2}{2}}}{\omega + i - k \nu_3} d\nu_3 = \frac{1}{\omega + i} \left\{ \frac{k}{\omega + i} + 3 \left( \frac{k}{\omega + i} \right)^3 + 15 \left( \frac{k}{\omega + i} \right)^5 + \ldots \right\} $$

$$C = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \frac{\nu_3^2 e^{-\frac{\nu_3^2}{2}}}{\omega + i - k \nu_3} d\nu_3 = \frac{1}{\omega + i} \left\{ 1 + 3 \left( \frac{k}{\omega + i} \right)^2 + 15 \left( \frac{k}{\omega + i} \right)^4 + 105 \left( \frac{k}{\omega + i} \right)^6 + \ldots \right\} $$

$$D = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \frac{\nu_3^3 e^{-\frac{\nu_3^2}{2}}}{\omega + i - k \nu_3} d\nu_3 = \frac{1}{\omega + i} \left\{ 3 \frac{k}{\omega + i} + 15 \left( \frac{k}{\omega + i} \right)^3 + 105 \left( \frac{k}{\omega + i} \right)^5 + \ldots \right\} $$

$$F = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \frac{\nu_3^4 e^{-\frac{\nu_3^2}{2}}}{\omega + i - k \nu_3} d\nu_3 = \frac{1}{\omega + i} \left\{ 3 + 15 \left( \frac{k}{\omega + i} \right)^2 + 105 \left( \frac{k}{\omega + i} \right)^4 + 495 \left( \frac{k}{\omega + i} \right)^6 + \ldots \right\} $$

Substituting these values of $A, B, C, D$ and $F$ into (6.34), expanding in powers of $k$ retaining only the zeroth order in $k$ we find

$$E \sim E_0 = Re \ E_0 + i \ Im \ E_0$$
where

\[
R \text{e } E_0 = \left\{ \begin{array}{c}
\omega^4 \left[ \frac{9 + 61e + 146e^2 + 119e^3}{9 + 61e + 146e^2 + 119e^3} \right]
\frac{15 + 120e + 323e^2 + 287e^3}{9 + 61e + 146e^2 + 119e^3} \omega^2 - 
\frac{20 + 176 + 66e^2 + 140e^3}{9 + 61e + 146e^2 + 119e^3} \omega
\end{array} \right\} \left\{ (\omega^2 + 1)^3 (1 + 2e) \right\}
\]

\[
q + 86.5e + 327e^2 + 576e^3 + 406e^4 \left[ \left( \frac{1}{3} + \frac{5.33e + 10e^2}{3 + 14.4e + 20e^2} \right)^2 + 
\frac{3 + 18.4e + 30.3e^2}{3 + 14.4e + 20e^2} \right] \right\}
\]

(6.47) \quad \text{Im } E_0 = - \left\{ \omega^3 \left[ \frac{26 + 189e + 475e^2 + 403e^3}{26 + 189e + 475e^2 + 403e^3} \right] \omega^2 - 
\frac{86}{26} \left[ \frac{1 + 10e + 31e^2 + 30e^3}{26 + 189e + 475e^2 + 403e^3} \right] \right\} \left\{ \text{denominator of } R \text{e } E_0 \right\}

and

(6.48) \quad \epsilon = \frac{1}{3} \text{bnn}

For a function \( E(\omega, k) \) of the form

\[
E(\omega, k) = E_0(\omega) + k E_1(\omega) + k^2 E_2(\omega) + \ldots
\]

We can show, using Newton's well known method of successive approximation (this method is given in most books of Mathematical Functions; see, for instance, Abramowitz and Stegun, 1965), that the zeros of \( E \) are of the form

\[
\omega = \omega_0 + k \omega_1 + k^2 \omega_2 + \ldots
\]
The zeroth order approximation of $E$, $E_0$, contains to zeroth order in $k$, all the zeros of $E$ so that retaining more terms in the expansion of $E$ does not yield more zeros but only more accurate values of the zeros of $E$. Unless we want to determine these zeros accurately, it is sufficient, in a qualitative analysis such as the study of stability, to keep the first term, $E_0$, of the expansion of $E$. Since it was assumed that $k \ll 1$, $E_0$ and $\omega$ are very good approximations of $E$ and $\omega$.

$\text{Im} E_0$ has a zero at $\omega = \infty$. Furthermore

$$
(6.51) \quad \lim_{\omega \to \infty} \text{Im} E_0(\omega, \epsilon) = \lim_{\omega \to \infty} \left( \frac{36 + 189 \epsilon + 475 \epsilon^2 + 403 \epsilon^3}{\omega(1 + \epsilon)(9 + 86.5 \epsilon + 327 \epsilon^2 + 576 \epsilon^3 + 400 \epsilon^4)} \right)
$$

so that as $\omega$ increases from $-\infty$, $E(\omega, \epsilon)$ crosses the real axis upward at $R e E_0(\omega, \epsilon)$ which is

$$
(6.52) \quad \lim_{|\omega| \to \infty} R e E_0 = \frac{9 + 61 \epsilon + 146 \epsilon^2 + 119 \epsilon^3}{(1426)(9 + 86.5 \epsilon + 327 \epsilon^2 + 576 \epsilon^3 + 400 \epsilon^4)}
$$

$\text{Im} E_0(\omega, \epsilon)$ has also a triple zero at the origin. This triple zero will be examined later using an approximation of $E(\omega, k)$ valid for values of $|\omega| \ll 1$. (Recall that $E$ given in (6.45) - (6.47) is valid only for $|\omega| \gg k$ and cannot be trusted for $\omega$ near the origin).

The other zeros of $\text{Im} E_0(\omega, \epsilon)$ are those of the expression
\[ f(\omega, \epsilon) = \omega^6 + \frac{86}{26 + 189 \epsilon + 475 \epsilon^2 + 403 \epsilon^3} \omega^4 - \frac{29 + 216 + 91 \epsilon^2 + 91 \epsilon^3}{26 + 189 \epsilon + 475 \epsilon^2 + 403 \epsilon^3} \omega^2 - \frac{16 (1 + 10 \epsilon + 31 \epsilon^2 + 30 \epsilon^3)}{26 + 189 \epsilon + 475 \epsilon^2 + 403 \epsilon^3} \]

which is of the form

\[ f(y, \epsilon) = y^4 + p(\epsilon) y^2 + q(\epsilon) y + \lambda(\epsilon) \]

where

\[ y = \omega^2 \]

and

\[ p > 0 \quad q < 0 \quad \lambda < 0 \]

We see that \( f(-\infty, \epsilon) \to -\infty \) and \( f(\infty, \epsilon) = \infty \) so that \( f(y, \epsilon) \) crosses the real axis at least once. The derivative of \( f(y, \epsilon) \) with respect to \( y \)

\[ \frac{\partial f(y, \epsilon)}{\partial y} = 3 y^2 + 2 p(\epsilon) y + q(\epsilon) \]

has, for all values of \( \epsilon \), a positive and a negative root.

\[ y = \frac{-2p + \sqrt{4p^2 - 12q}}{6} > 0 \]

\[ y' = \frac{-2p - \sqrt{4p^2 - 12q}}{6} < 0 \]
This implies that $f(y, \epsilon)$ has a local maximum at a negative value of $y_1'$ and a local minimum at a positive value of $y_1'$. Finally $f(y_1', \epsilon) = \delta(\epsilon) < 0$. From all these informations, one deduces that $f(y, \epsilon)$ must have one of the three following forms:

![Figure 6. Plot of f(y) vs. y.](image)

Whether $f(y_1', \epsilon)$ has two complex conjugate roots, a double root or two unequal real roots is irrelevant since these roots are either complex or negative and hence unphysical (recall that $y_1' = \omega^2$; $\omega$ real). On the other hand, $f(y, \epsilon)$ always has one and only one real, positive root, $y_1(\epsilon)$. This root is physically meaningful.

At this point we introduce explicitly the assumption that the pair correlation function at contact $\eta(b_\eta)$ is a monotonically increasing function of the density $n$; so that $\epsilon$, defined in (6.48), is a monotonically increasing function of $n$.

$\epsilon_\delta(\omega, \epsilon)$ does not depend on the density $n$ explicitly but through $\epsilon$. Because of the above assumption, increasing $\epsilon$ implies increasing $n$. 

We now return to the discussion of the double root \( \pm \sqrt{y_1(\varepsilon)} = \pm \omega_1(\varepsilon) \) of \( \text{Im} E_0 \). For a dilute gas, \( \varepsilon = 0 \),

\[
(5.53) \quad f(y, 0) = y^3 + \frac{16}{9(26)} y^2 - \frac{20}{9(26)} y - \frac{16}{27(26)}
\]

has a positive real root at

\[
y_{1}(0) = 0.294
\]

to which corresponds

\[
\pm \omega_{1}(0) = \pm 0.542
\]

We wish to show that the root \( y_{1}(\varepsilon) \) of \( f(y, \varepsilon) \) is a monotonically increasing function of \( \varepsilon \). It can be shown (Appendix C) that the functions \( n(\varepsilon) \), \( q(\varepsilon) \) and \( h(\varepsilon) \) defined in (6.53) are monotonically decreasing functions of \( \varepsilon \):

\[
h'(\varepsilon) < 0 \quad ; \quad q'(\varepsilon) < 0 \quad ; \quad h'(\varepsilon) < 0
\]

where

\[
h' = \frac{dh}{d\varepsilon} \quad \text{etc}...\]

Now

\[
\frac{dy_1}{d\varepsilon} = \frac{\partial f(y, \varepsilon)/2\varepsilon}{(\partial f/\partial y)y_1}
\]

since

\[
f(y, \varepsilon) = y^3 + h(\varepsilon)y^2 + q(\varepsilon)y + h(\varepsilon)
\]

we have

\[
\frac{dy_1}{d\varepsilon} = \frac{n'(\varepsilon)y_1^2 + q'(\varepsilon)y_1 + h'(\varepsilon)}{(\partial f/\partial y)y_1}
\]
From figure 6 it is found that \( y_1(\varepsilon) > 0 \) and \( \frac{dy_1}{d\varepsilon} > 0 \) hence \( \frac{dy_1}{d\varepsilon} > 0 \).

Therefore \( y_1(\varepsilon) \) and \( \omega_1(\varepsilon) \) are the lower bounds of \( y_1(\varepsilon) \) and \( \omega_1(\varepsilon) \).

\[
\begin{align*}
y_1(\varepsilon) &> y_1(\varepsilon) = 0.294 \\
\omega_1(\varepsilon) &> \omega_1(\varepsilon) = 0.542
\end{align*}
\]

Let us take for example \( bn = 1 \), a very high density. If we take for \( \eta \) the Pade approximant

\[
\eta = \frac{1 + 0.0635 nb + 0.017 \eta b^2}{1 - 0.56 nb + 0.08 \eta b^2}
\]

Then to \( nb = 1 \) corresponds

\[
\varepsilon = \frac{1}{5} bn \eta = 0.416
\]

and

\[
f(y, 0.416) = y^3 + 0.25 y^2 - 0.168 y - 0.035
\]

has a positive real root at

\[
y_1(0.416) = 0.407
\]

whence

\[
\pm \omega_1(0.416) = \pm 0.639
\]

In recapitulation, we have shown that, in addition to the roots at infinity and at the origin, \( I_{\omega} E_0(\omega, \varepsilon) \) has always a double root
\( \pm \omega_1(\varepsilon) \) whose absolute value is an increasing function of \( \varepsilon \) hence \( \eta \) and for densities \( \eta \) between \( 0 \) and \( 1 \), bounded by
\[
0.542 \leq \omega_1(\varepsilon) \leq 0.639
\]

We determine the direction in which \( \Xi \) crosses the real axis on the complex \( \Xi \)-plane at \( R \Xi E(\pm \omega_1, \varepsilon) \). The imaginary part of \( \Xi \) is of the form
\[
(6.57) \quad \text{Im} \Xi_0(\omega, \varepsilon) = -\frac{N(\varepsilon) \omega^2 \hat{d}(y, \varepsilon)}{D(y, \varepsilon)}
\]
where
\[
N(\varepsilon) > 0 \\
D(y, \varepsilon) > 0
\]

Recalling that \( u_0 = \omega^2 \) and that \( \frac{\partial^2 \phi}{\partial y^2} > 0 \) (figure 6), we find that the derivative of \( \text{Im} \Xi_0 \) with respect to \( \omega \) at \( \pm \omega_1 \) is negative:
\[
\left( \frac{\partial (\text{Im} \Xi_0)}{\partial \omega} \right)_{\pm \omega_1} = -\frac{2N(\varepsilon)}{D(y, \varepsilon)} \omega_1 \left( \frac{\partial^2 \phi(y, \varepsilon)}{\partial y^2} \right)_{y_1} < 0
\]
thus as \( \omega \) increases from \( -\omega_1 - \varepsilon \) to \( -\omega_1 + \varepsilon \), \( \text{Im} \Xi_0(\omega, \varepsilon) \) decreases from a positive value to zero at \( -\omega_1 \) to a negative value at \( -\omega_1 + \varepsilon \); \( \Xi(\omega, \varepsilon) \) crosses the real axis downward at \( R \Xi E(-\omega_1, \varepsilon) \). Similarly \( \Xi(\omega, \varepsilon) \) crosses the real axis downward at the same point as \( \omega \) increases from \( \omega_1 - \varepsilon \) to \( \omega_1 + \varepsilon \)
\[
( R \Xi E(\omega_1, \varepsilon) = R \Xi E(-\omega_1, \varepsilon) = R \Xi E(y, \varepsilon) )
\]

Next we evaluate \( R \Xi E_0(\pm \omega_1, \varepsilon) \). \( R \Xi E_0(\omega, \varepsilon) \), defined in
(6.46) is of the form

\[
\mathcal{Re} E_0 = \left\{ \omega^6 + \frac{h_1(\varepsilon)}{\omega^4 + q_1(\varepsilon) \omega^2 + \lambda_1(\varepsilon)} \right\} \left\{ (\omega^2 + 1)^3 (1 + 2\varepsilon)(9 + 86.5\varepsilon + 3276\varepsilon^2 + 576\varepsilon^3 + 400\varepsilon^4) \left[ (\omega^2 - \lambda_2(\varepsilon))^2 + \eta^2(\varepsilon) \right] \right\}
\]

\[|h_1(\varepsilon)|, |q_1(\varepsilon)|, |\lambda_1(\varepsilon)|, |\lambda_2(\varepsilon)| \text{ written out explicitly in (6.46)}\] are increasing functions of \(\varepsilon\). As \(\varepsilon\) and \(\omega(\varepsilon)\) increase from 0 to 0.416 and 0.542 to 0.639 respectively the expression in the square bracket in the numerator becomes less negative while the expression in the square bracket in the denominator is positive and increases. Compared to the rate of change of these quantities, the rate of decrease of \(\frac{q_1(\varepsilon)}{\omega^2 - \lambda_2(\varepsilon)^2 + \eta^2(\varepsilon)}\) is greater. Therefore \(\mathcal{Re} E_0(\omega, \varepsilon)\) increases and is bounded by

\[(6.59) \quad \mathcal{Re} E_0(\pm 0.042, 0) = -0.121 \leq \mathcal{Re} E_0(\pm \omega, \varepsilon) \leq -0.047 = \mathcal{Re} E_0(\pm 0.047, 0.416)\]

We now investigate the zeros of \(\mathcal{Im} E\) at the origin. In the case where both \(|\omega|\) and \(k\) are small, the integrals A, B, C and D have already been evaluated (eq. (5.48) - (5.51)); their expansions up to fourth order in \(k\) and in terms of \(\varepsilon\)

\[(6.60) \quad \mathcal{Re} E_0(\pm 0.047, 0.416)\]

\[Z = \frac{\omega}{k} = \frac{1}{\mathcal{Im} E}_0 \]

can readily be deduced from (5.48) - (5.51). They are
We can find \( F \) in a similar way

\[
F = -3i + 3k_3 + 3ik^2(5 + z^2) - 3k^3(15z + z^3) - 3k^4(35 + 30z^2 + z^4). 
\]

The RHS of \((6.61) - (6.65)\) are substituted into \((6.34)\) which becomes after tedious but straightforward calculations

\[
E(k, \beta, \varepsilon) = k^3 \left[ i \beta \left\{ \frac{\varepsilon}{3} \left( \frac{\varepsilon}{1 + 3\varepsilon} \right) \frac{1}{(1 + 3\varepsilon)(1 + 5\varepsilon)} \right\} + \frac{k}{(1 + 3\varepsilon)(1 + 5\varepsilon)^2} \left\{ \left( 1 + 5 + 10\varepsilon + b^2\eta^{-1} \right) \right\} (5 + \frac{716}{7} \varepsilon + \frac{2280}{7} \varepsilon^3 + \frac{44397}{7} \varepsilon^4 + 4860 \varepsilon^5) \right] - \frac{2}{7} \left[ \left( 1 + 5 + 10\varepsilon + b^2\eta^{-1} \right) \right] \]

\[
\left( 5 + \frac{762}{15} \varepsilon + \frac{4143}{15} \varepsilon^2 + \frac{4676}{5} \varepsilon^3 + 1506 \varepsilon^4 + 630 \varepsilon^5 \right) + \frac{29}{9} \varepsilon + \frac{25332}{315} \varepsilon^2 + \frac{571908}{315} \varepsilon^3 + \frac{1478145}{315} \varepsilon^4 + \frac{775630}{31} \varepsilon^5 \right] - \frac{7}{3} \left[ 5 + \frac{2509}{30} \varepsilon \right] \]

\[
\left( \frac{8}{9} \left( \frac{1 + 5\varepsilon}{1 + 3\varepsilon} \right) + \frac{k}{(1 + 3\varepsilon)(1 + 5\varepsilon)^2} \left\{ \left( 1 + 5 + 10\varepsilon + b^2\eta^{-1} \right) \right\} (5 + \frac{716}{7} \varepsilon + \frac{2280}{7} \varepsilon^3 + \frac{44397}{7} \varepsilon^4 + 4860 \varepsilon^5) \right] - \frac{2}{7} \left[ \left( 1 + 5 + 10\varepsilon + b^2\eta^{-1} \right) \right] \]

\[
\left( 5 + \frac{762}{15} \varepsilon + \frac{4143}{15} \varepsilon^2 + \frac{4676}{5} \varepsilon^3 + 1506 \varepsilon^4 + 630 \varepsilon^5 \right) + \frac{29}{9} \varepsilon + \frac{25332}{315} \varepsilon^2 + \frac{571908}{315} \varepsilon^3 + \frac{1478145}{315} \varepsilon^4 + \frac{775630}{31} \varepsilon^5 \right] - \frac{7}{3} \left[ 5 + \frac{2509}{30} \varepsilon \right] \]
In the dilute gas limit as $b_{\infty} \to 0$ and $\xi \to 0$ (recalling that $\xi = \frac{1}{\infty}$) the RHS of (6.66) reduces to the first two terms of the LHS of (5.52) which is the dispersion relation of a rarefied gas at low frequencies.

From (6.66) we see that $\text{Im} \, E(k, \omega, \epsilon)$ has a zero at $\frac{\pi}{2} = 0$.

$E(k, \omega, \epsilon)$ crosses the real axis downward at

$$
Re \, E(k, \omega, \epsilon)_{\text{sign}} = \frac{k^4}{(1+2\epsilon)(1+3\epsilon)^2} \left( 5 + \frac{716}{7} \epsilon + \frac{576}{7} \epsilon^2 + \frac{22800}{7} \epsilon^3 + \frac{44797}{7} \epsilon^4 + 4860 \epsilon^5 \right)
$$

$Re \, E(k, \omega, \epsilon)$ has the sign of the expression $(1+\xi + 10\epsilon + b^2 \eta'^2)$.  

$\text{Im} \, E$ has a double zero at

$$
\frac{2}{3} \omega = 1 + \xi + 10 \epsilon + b^2 \eta'^2 + \frac{2}{3} (1+5\epsilon)^2
$$

There are three possibilities

(a) For sufficiently large negative values of $\xi$ 

$$
1 + \xi + 10 \epsilon + b^2 \eta'^2 + \frac{2}{3} (1+5\epsilon)^2 < 0
$$

and the zeros $\pm \frac{2}{3} \omega$ of $\text{Im} \, E$ are imaginary. It follows from (6.69) that 

$$
Re \, E(k, \omega, \epsilon) < 0
$$

(b) For $-\frac{2}{3} (1+5\epsilon)^2 < 1 + \xi + 10 \epsilon + b^2 \eta'^2 < 0$

the zeros of $\text{Im} \, E$ are real and it can readily be seen from (6.66) that

$$
Re \, E(k, \omega, \epsilon) < 0 < Re \, E(k, 0, \epsilon) < 0
$$
(c) For \( 1 + 5 + 10 \varepsilon + b^n \varepsilon' > 0 \)

the coefficients of all powers of \((1+5+10 \varepsilon + b^n \varepsilon')\) are negative hence

\[
\Re E(k, \pm 3 \varepsilon, \varepsilon) < 0 < \Re E(k, 0, \varepsilon)
\]

From (6.66) it can be seen that

\[
\left( \frac{\partial \Im E(k,3 \varepsilon, \varepsilon)}{\partial \varepsilon} \right)_{3 \varepsilon} > 0
\]

\[
\left( \frac{\partial \Im E(k,3 \varepsilon, \varepsilon)}{\partial \varepsilon} \right)_{3 \varepsilon} > 0
\]

so that when the zeros \( \pm 3 \varepsilon \) of \( \Im E \) are real, \( E \) crosses the real axis upward both times at \( \Re E(k, \pm 3 \varepsilon, \varepsilon) \).

To the three cases discussed above correspond the following hodographs

\[
\text{Figure 7.a. Plot of } E(w,k) \text{ for } 1 + 5 + 10 \varepsilon + b^n \varepsilon' \left(-\frac{7}{3}(1+\varepsilon)\right). \text{ Unstable situation.}
\]
(d) Discussion

Let us consider the quantity \( 1 + \xi + 10 \varepsilon + b^2 \eta^2 \). For

\[
V(r) = - \left( d^4 W / 4 \pi r \right) e^{-dr},
\]

\( \xi(k) \) is of the form \( \xi(k) = \xi(0) + O(k^2) \).

Since \( k \ll 1 \), one can in general perform a Taylor series expansion

of \( \xi(k) \) about \( k = 0 \) and keep only the first term, \( \xi(0) \), so that

\[
1 + \xi(k) + 10 \varepsilon + b^2 \eta^2 < 1 + \frac{\nu \xi(0)}{kT} + 2 b \eta \eta + b^2 \eta^2.
\]
But the equation of state of a gas of hard spheres with an attractive tail is

\[ \rho = n \kappa T \left( 1 + b n \eta \right) + \frac{1}{2} n^2 \gamma (\epsilon) \]

from which one finds that

\[ \frac{1}{kT} \left( \frac{\partial \ln \rho}{\partial n} \right)_T = 1 + \frac{1}{2} b n \eta + b n^2 \eta + \frac{n \gamma (\epsilon)}{kT} \]

therefore, to zeroth order in \( \eta \), \( 1 + \dot{\varepsilon} (\epsilon) + 10 \epsilon + b n^2 \eta \) is just 

\[ \frac{1}{kT} \left( \frac{\partial \ln \rho}{\partial n} \right)_T \]

times the compressibility of this gas. If we take \( \eta = (1 - b n)^{-1} \),

\[ 1 + \dot{\varepsilon} (\epsilon) + 10 \epsilon + b n^2 \eta \]

reduces to \( \varepsilon (\epsilon) + n^2 \) which is proportional to the compressibility of the Van der Waals gas as was pointed out by deSobrino.

Figures (7.a) and (7.b) show that when the compressibility is negative, the gas is in an unstable state; figure (7.c) shows that the states traditionally regarded as metastable are stable against sufficiently small perturbations.

Qualitatively, figures (7.a), (7.b) and (7.c) are identical to the corresponding figures of deSobrino. This is as we expect since in the approximations of \( L(\eta) \) and \( K(\eta) \) the difference lies in the accuracy but not in the method of approximation. Furthermore this agreement of our findings with deSobrino’s was already strongly hinted at by the calculations of Sirovich and Thurber on sound propagation as it was found that the Krook model, though not quantitatively correct, has the same qualitative properties as the higher-moment models.
Finally, two remarks on the validity of the approximations made in this section:

On the study of sound propagation, the agreement with experiment at high frequencies which Sirovich and Thurber obtained, indicates that the GJS model seems most suitable to the study of stability of metastable states which requires evaluating the linearized kinetic equation at frequencies ranging from $-\infty$ to $\infty$.

Some doubt was raised as to the validity of approximating $K(\lambda)$ by $K(\lambda_0)$ at high frequencies. We have argued that (appendix A) the non zero terms in the expansion of $\lambda(\lambda)$ are much larger than the corresponding terms of $K(\lambda)$ so that the latter may be neglected.

In conclusion, we have investigated the stability of metastable states using a more accurate approximation of the Enskog collision integral and a more general pair correlation function $\eta$ and confirmed deSobrino's results.
CHAPTER 4. CONCLUSION

7. CONCLUSION

By not restricting ourselves to a specific form of the pair correlation function at contact $n_{ij}$, we have shown that the results obtained by deSobrino for the traditional Van der Waals gas are valid for a more general gas of hard spheres with an attractive long range potential.

Using the method of Sirovich and Thurber we find that, to first order, the dispersion of sound at low frequencies is the same as that obtained by previous calculations (except for the Navier-Stokes value which is incorrect); the absorption of sound, up to 3rd order in $\omega$, is slightly less than the Burnett value and slightly greater than the Wang Chang - Uhlenbeck value; all three are in fairly good agreement with the experimental result of Greenspan.

Qualitatively, the results shown in figures 7.a, 7.b, 7.c, concerning the stability of uniform density stationary states are identical to those of deSobrino; here again the conclusion is valid for any Van der Waals gas. This consistency with previous results along with careful checks indicate that calculations are free of errors and that the approximations used are adequate. We have shown that all uniform density states are stable against small perturbations; these include those states at temperatures $T<T_c$ and for which the compressibility $\left(\frac{\partial n}{\partial N}\right)_T = kT(1+\xi(\omega)+\omega \epsilon + \omega^2 n_{ij})$ is positive and small. On the other hand it was shown numerically by Strickfaden and deSobrino (1970) that these same states are unstable against suffi-
ciently large perturbations therefore these states are metastable.

In this thesis we have assumed the following dependence of \( \eta \) on \( r \) and \( t \)

\[ \eta = \Phi(\eta(r,t), t, \sigma) \]

In analogy to equilibrium theory where \( \eta \) is a function of separation, density and temperature, we may assume that \( \eta \) is also a function of local temperature (we use here Chapman and Cowling's definition of local temperature).

\[ (7.1) \quad \eta = \Phi(\eta(r,t), T(r,t), \sigma) \]

this may be more realistic and the calculations do not seem much more complicated. Dymond and Alder (1966) implicitly took into account the dependence of \( \eta \) on temperature through \( \sigma(T) \); they obtained values for the transport coefficients for rare gases at \( T > T_c \) and \( n > n_c \) which agree to within 10% with experiment.

A more difficult problem is that of using a velocity dependent frequency \( \lambda(\xi) \) model to approximate \( \mathcal{L}(\xi) \). Except for the Maxwell gas, the spectrum of the \( \mathcal{L} \)-operator of a gas with a finite range has a continuous part (Grad, 1963) so that the method of expanding \( \mathcal{L}(\xi) \) in eigenfunctions of \( \mathcal{L}_{\text{Maxwell}} \) may not be a very faithful reproduction of the spectrum of the \( \mathcal{L} \)-operator of a Van der Waals gas.*

For a cut off potential, \( \mathcal{L}(\xi) \) takes the form

\[ (7.2) \quad \mathcal{L}(\xi) = \mathcal{M}(\xi) - \lambda(\xi) I \]

*
where $M$ has a complete discrete spectrum

$$M \psi_i = \lambda(\xi) \lambda_i \psi_i$$  \hspace{1cm} (7.3)$$

so that

$$M(k) = \lambda(\xi) \sum_{i=1}^{N} \lambda_i \psi_i \left( \lambda(\xi) \psi_i, h \right)$$  \hspace{1cm} (7.4)$$

($f,g$) is the inner product in an $L^2$ space. Noting that the first five eigenfunctions are just the summational invariants with eigenvalue $\lambda_i = 1$, $i = 1, \ldots, 5$, Cercignani (1966) introduced the following model

$$\overline{L}(k) = \lambda(\xi) \left\{ \sum_{i=1}^{5} \psi_i \left( \lambda(\xi) \psi_i, h \right) - h \right\}$$  \hspace{1cm} (7.5)$$

which, when $\lambda$ is velocity independent, becomes the BGK model. The next step would be to use the approximation on the RHS of (7.5) to investigate the problems studied in this thesis.

*However Grad (1963) showed that for a hard potential ($V = \frac{V_c}{T^{\frac{1}{2}}} + s\sigma^s$) with an angular cut off the Cross and Jackson approximation may be used.*
APPENDIX A

In this appendix we shall present the calculations leading to an approximation of the linearized Enskog collision integral.

The Enskog collision integral

\[ I_L = \int \left\{ \eta(r + \frac{1}{2} \sigma \Omega) \xi(r + \frac{1}{2} \sigma \Omega) - \eta(r - \frac{1}{2} \sigma \Omega) \xi(r - \frac{1}{2} \sigma \Omega) \right\} \sigma^2 \xi \Omega \, d\Omega \, d\xi \]

is linearized by writing

\[ I_L = I_L(1 + \kappa) \]

The result is, to first order in \( \kappa \),

\[ I_L(\kappa) = I_L(0) + \kappa' \]

where

\[ \kappa' = \int \left\{ \eta(r + \frac{1}{2} \sigma \Omega) - \eta(r - \frac{1}{2} \sigma \Omega) \right\} \sigma^2 \xi \Omega \, d\Omega \, d\xi \]

and

\[ I_L'(\kappa) = \int \left\{ \eta(r + \frac{1}{2} \sigma \Omega) \left( \bar{v}(r) + \bar{v}'(r + \sigma \Omega) \right) - \eta(r - \frac{1}{2} \sigma \Omega) \left( \bar{v}(r) + \bar{v}'(r - \sigma \Omega) \right) \right\} \sigma^2 \xi \Omega \, d\Omega \, d\xi \]

The integral \( \kappa' \) is independent of \( \kappa \). \( \kappa \) is expanded in terms of the eigenfunctions \( \Psi_i \) of the dimensionless linearized collision operator of a Maxwell gas \( I_M \)

\[ \kappa = \kappa_0 + \kappa_1 \]
where
\[(A.4a)\quad \lambda_0 = \sum_{i=1}^{N} a_i \Psi_i\]
and
\[(A.4b)\quad \lambda_1 = \sum_{i=N+1}^{\infty} a_i \Psi_i\]

Substituting into (A.3) we get
\[(A.5)\quad \mathcal{L}e(\lambda) = \int_0 (\lambda' + \mathcal{L}'(\lambda_0) + \mathcal{L}'(\lambda_1))\]

Let us consider in detail the integral
\[(A.6)\quad \mathcal{L}'(\lambda_1) = \int \left\{ \eta_1(r + \xi \sigma_2) \left( \frac{\partial}{\partial r} + \frac{\partial}{\partial \xi \sigma_2} \right) - \eta_1(r - \xi \sigma_2) \right\} \]
\[\left( \lambda_1(r) + \lambda'_1(r - \xi \sigma_2) \right) \int_0 \sigma^2 \omega d\omega d\xi'\]
expanding in Taylor series, keeping first derivatives and first order in perturbation
\[(A.7)\quad \mathcal{L}'(\lambda_1) = \eta \mathcal{L}(\lambda_1) + \eta \mathcal{K}'(\lambda_1)\]

where
\[(A.7a)\quad \mathcal{L}(\lambda_1) = \int \left\{ \lambda_1(r) \right\} \int_0 \sigma^2 \omega d\omega d\xi'\]
and
\[(A.7b)\quad \mathcal{K}'(\lambda_1) = \int \sigma^2 \omega \cdot \nabla \left( \lambda_1 + \lambda'_1 \right) \int_0 \sigma^2 \omega d\omega d\xi'\]

\(\mathcal{L}\) is the linearized Boltzmann collision operator defined in section 5. For a plane wave perturbation.
Substituting into (A.7) we note that since the first three eigenfunctions \( \psi_1, \psi_2 \) and \( \psi_3 \) are summational invariant,

\[
A_i \mathcal{L}(\psi_i) = A_i \int \left( \psi_i' + \psi_i - \psi_i - \psi_i \right) \phi_0^t \delta^2 \cdot \xi \; d\xi \; d\xi' = 0 \quad (i=1,2,3)
\]

while

\[
A_i \mathcal{L}(\psi_i) = A_i \int \left( \psi_i' - \psi_i - \psi_i \right) \phi_0^t \delta^2 \cdot \xi \; d\xi \; d\xi' = 0.
\]

However, for \( i > 3 \) \( \mathcal{L}(\psi_i) \neq 0 \) and \( \mathcal{L}(\psi_i) \neq 0 \); furthermore, the coefficient of \( (\psi_i' - \psi_i) \phi_0^t \delta^2 \cdot \xi \) in the integral in (A.9) is one while the coefficient of the same quantity in the integral in (A.10) is of the order of \( \sigma/(1/k)^{\alpha} \) so that unless \( |(\psi_i)| \sim \left( \frac{\sigma}{k} \right)^{\alpha} \) (which is not the case for \( \psi_q \) and \( \psi_r \) defined in (5.15) and, we hope, in general) we can assume that for \( i = 1 \sum_{i=1}^{\infty} A_i \psi_i \) \((N > 3)\)

\[
|\mathcal{L}(\psi_i)| \quad \text{is much larger than} \quad |K''(\psi_i)| \quad \text{and therefore}
\]

\[
A_i \mathcal{L}(\psi_i) = \eta \mathcal{L}(\psi_i) + \eta K''(\psi_i) \sim \eta \mathcal{L}(\psi_i)
\]

Eq. (A.5) becomes

\[
A_i \mathcal{L}(\psi_i) = \phi_0 \left( K' + \mathcal{L}'(\psi_i) + \mathcal{L}'(\psi_i) \right)
\]

\[
\simeq \phi_0 \left( K' + \eta \mathcal{L}(\psi_i) + \eta K''(\psi_i) + \eta \mathcal{L}(\psi_i) \right)
\]

\[
\simeq \phi_0 \left( K' + \eta K''(\psi_i) + \eta \mathcal{L}(\psi_i) \right)
\]

\[
= \phi_0 \left( K(\psi_i) + \eta \mathcal{L}(\psi_i) \right)
\]
Expanding $K^i$, defined in (A.3), in Taylor series to first order in $\sigma$ and substituting the result into the definition of $K$ in (A.12) we obtain for $K(h_0)$

$$(A.13) \quad K(h_0) = \int \frac{d\xi}{2\pi} \{ \sigma \cdot \eta \eta - \eta \sigma \cdot \eta \xi (k_0 + h_0) \} \sigma \cdot \eta d\xi d\eta$$

Substituting into (A.13) the values

$$h_0 = h_0(\xi) e^{i(k_0 \xi - \omega t)}$$

$$\eta(\xi) = \eta(b \eta(\xi))$$

$$\eta(r) = n_0(1 + \nu(r))$$

$$\nu(r) = \nu e^{i(k_0 r - \omega t)}$$

$$q = \frac{\xi}{\sqrt{K_{00}m}}$$

we get

$$(A.15) \quad K = \frac{2b}{\pi} i n_0 \sqrt{k_{00}m} \int d^3r d^3\eta \frac{(3k_0^2 \xi_0 \eta_0 + k_0 \cdot \xi_0 + \frac{b_0 \eta_0 \xi_0}{\eta}) \rho \eta (r')}{\eta}$$

where

$$b = \frac{2}{3} \pi \sigma^3$$

$$\eta' = \frac{\partial \eta}{\partial (b n_0)}$$

$$\xi' = \frac{\xi}{\sqrt{K_{00}m}}$$

$$\omega'(\xi) = \frac{1}{(2\pi)^{3/2}} \xi e^{-\xi^2/2}$$

An approximation of the linearized Boltzmann collision integral $\mathcal{L}(h)$ in eq. (A.12) has already been given in section 5 in connection with the study of sound propagation. We now turn to the evaluation of the integral $K(h_0)$ on the RHS of (A.14); to be consistent with the 5-Moments approximation of $\mathcal{L}(h)$ we take $h_0 = \sum_{i=1}^{5} a_i \xi_i \cdot \eta_i$. 
The integrand of (A.14) is made up of three terms, one involving $\lambda_0$, a second $\lambda_0'$ and the third $\nu$. The first integration can be evaluated readily. Integration over $Q$ yields $\frac{\xi \eta \lambda}{2} \nu \lambda$, so

$$\frac{3b}{2\pi} i \eta n_0 \sqrt{k_{m1m}} \int_{0}^{\pi} \sin d\theta' d\phi' \Omega_\mu \Omega_\nu k_v k_0 \lambda' \nu (\nu') =$$

$$-i k \eta n_0 \sqrt{k_{m1m}} (\nu_3 - \nu \nu_3')$$

The $z$-axis has been chosen along the $\lambda$ vector. In a similar way the third integral is evaluated, the result is

$$\frac{3b}{2\pi} i \eta n_0 \sqrt{k_{m1m}} \int_{0}^{\pi} \sin d\theta' d\phi' \Omega_\mu \Omega_\nu k_v k_0 \lambda' \nu (\nu') = -i k \eta n_0 \sqrt{k_{m1m}} \nu \lambda'$$

The 5-Moments approximation of $\lambda'$ is

$$\lambda'_0 = \nu + \frac{\nu^2}{2} (\nu'^2 - 3) + \frac{\nu}{2} \lambda' + \frac{1}{2} \sum_{ij} \Omega'_i \Omega'_j - \frac{1}{2} \sum_{ij} \eta'^i \eta'^j (1 - \nu'^2)$$

In the 2nd integral, replacing $\lambda'_0$ by the RHS of (A.17) we find

$$\frac{3b}{2\pi} i \eta n_0 \sqrt{k_{m1m}} \int_{0}^{\pi} \sin d\theta' d\phi' \Omega_\mu \Omega_\nu k_v k_0 \{ \nu + \frac{\nu^2}{2} (\nu'^2 - 3) + \nu' \lambda' + \frac{1}{2} \sum_{ij} \Omega'_i \Omega'_j - \frac{1}{2} \sum_{ij} \eta'^i \eta'^j (1 - \nu'^2) \} \nu (\nu')$$

This integral is the sum of five integrals, the first one involving $\nu$, the 2nd one involving $\tau$ etc. $\tilde{\nu}'$ is rewritten in terms of $\nu'$; we have
These values are substituted into the expression (A.17a); the first three integrals of (A.17a) involving \( \nu, \zeta \) and \( \omega \) can be evaluated readily; as an example the integral involving \( \omega \) is evaluated. The third integral is

\[
\Gamma_{3} = \frac{3}{2\pi} \eta_{\mu} \nu_{\mu} \Omega_{\mu} \Omega_{\nu} \{ \nu_{\nu}' - \Omega_{\nu} \eta_{\nu} \} \nu_{\nu}' \nu_{\nu}''
\]

Integration over \( \Omega \) is first carried out. We take as \( \zeta \)-direction the direction of \( \Omega \); then \( d\omega = \sin \theta d\theta d\phi \); \( \Omega \cdot q = q \cos \theta \); it can easily be shown that

\[
\int d\Omega \Omega_{\mu} \Omega_{\nu} = \frac{2}{3} \pi \delta_{\mu \nu}
\]

\[
\int d\Omega \Omega_{\mu} q_{\mu} \Omega_{\nu} q_{\nu} \Omega_{\rho} \Omega_{\sigma} = \frac{2\pi}{15} q_{\nu} q_{\mu} \delta_{\mu \sigma} + \frac{4\pi}{15} q_{\mu} q_{\nu} q_{\rho}
\]

\[
\int d\Omega (\Omega \cdot q)^{2} \Omega_{i} = \frac{2\pi}{3} q_{i}^{2} q_{i}
\]
After integration over $\omega$, (A.22) becomes

\[
(A.26) \quad \frac{3b}{2\pi} \varepsilon_\eta \pi \sqrt{\sqrt{\pi} \alpha^m} \int \! du \left\{ \frac{2\pi}{3} \delta_{\mu\nu} q_{\mu} q_{\nu} \kappa \nu u^\prime u - \frac{2\pi}{15} q^2 \delta_{\nu \sigma} q_{\nu} u u^\prime \right\} w^\prime
\]

now we take the $z$-axis parallel to $\mathbf{k}$; carrying out the integration we get

\[
(A.27) \quad I_3 = -i \kappa \eta b n \sqrt{\sqrt{\pi} \alpha^m} \nu (\mathbf{r}^2 + 2 \mathbf{r}^2) \frac{1}{5}
\]

In a similar manner, we evaluate $I_1$ and $I_2$ the results are

\[
(A.28) \quad I_1 = \frac{3b}{2\pi} \varepsilon_\eta \pi \sqrt{\sqrt{\pi} \alpha^m} \int \! du' du \Omega \cdot \mathbf{b} \nu \mathbf{r}^\prime \left( \frac{1}{15} \mathbf{r}^2 \right) w^\prime
\]

\[
(A.29) \quad I_2 = \frac{3b}{2\pi} \varepsilon_\eta \pi \sqrt{\sqrt{\pi} \alpha^m} \int \! du'' du \Omega \cdot \mathbf{b} \nu \mathbf{r}'' \frac{1}{15} \left( \mathbf{r}^2 \mathbf{r}'' \right) w^\prime
\]

\[
= i \kappa \eta b n \sqrt{\sqrt{\pi} \alpha^m} \left( \frac{1}{15} \mathbf{r}^2 \mathbf{r}'' \right) \nu
\]

$I_4$, the integral in (A.17a) involving $\mathbf{p}_{ij}$, is written out explicitly using eq. (A.9)

\[
(A.30) \quad I_4 = \frac{3b}{2\pi} \varepsilon_\eta \pi \sqrt{\sqrt{\pi} \alpha^m} \int \! du'' du \mathbf{b} \cdot \mathbf{r}'' \frac{1}{15} \mathbf{p}_{ij} \nu \mathbf{r}_{ij}^\prime - \nu_{ij}^\prime \mathbf{r}_{ij} \left( \mathbf{r}^2 \right) + \mathbf{r}_{ij} \left( \mathbf{r}^2 \right)^{ij} w^\prime
\]

The first integral of (A.30) can be evaluated readily; the second and third integrals are identical and are also easily evaluated with the
help of eqs. (A.23) - (A.25). The results are

\[(A.31) \quad T_{11} = \frac{3b}{2\pi} \iota \eta_{12} \sqrt{\eta_{12}} \mu \left\{ \int \mu \mu \delta_{12} \delta_{12} \frac{1}{2} \eta_{12} \mu \mu \eta_{12} \right\} \]

\[(A.32) \quad T_{12} = T_{13} = - \frac{3b}{2\pi} \iota \eta_{12} \sqrt{\eta_{12}} \mu \left\{ \int \mu \mu \delta_{12} \delta_{12} \frac{1}{2} \eta_{12} \mu \mu \eta_{12} \right\} \]

\[- (\omega \cdot J) \eta_{12} = \frac{2}{5} \iota \eta_{12} \sqrt{\eta_{12}} \mu \mu \eta_{12} \]

The fourth integral must be evaluated with some care

\[(A.33) \quad T_{44} = \frac{3b}{2\pi} \iota \eta_{12} \sqrt{\eta_{12}} \mu \left\{ \int \mu \mu \delta_{12} \delta_{12} \frac{1}{2} \eta_{12} \mu \mu \eta_{12} \right\} \]

In the coordinate system in which the z-axis is parallel to \( \Omega \) which we shall now call the \( \Omega \)-system, the \( \Omega \)-unit vector is

\[(A.34) \quad \Omega = \hat{e}_\varphi \cos \varphi + \hat{e}_\theta \sin \varphi + \hat{e}_z \cos \varphi \]

The 3rd rank tensor \( \Omega \times \Omega \times \Omega \) has ten distinct elements

\[\Omega_3 = \sin^2 \theta \cos^2 \varphi \]; \( \Omega_2 \Omega_2 \Omega_2 = \sin^2 \theta \cos^2 \theta \cos^2 \varphi \); \( \Omega_1 \Omega_2 \Omega_2 = \sin^2 \theta \cos^2 \theta \sin \varphi \]

\[\Omega_2 = \sin^2 \theta \sin^2 \varphi \]; \( \Omega_1 \Omega_2 \Omega_2 = \sin^2 \theta \cos \theta \sin^2 \varphi \); \( \Omega_2 \Omega_2 \Omega_2 = \sin^2 \theta \cos \theta \cos^2 \varphi \)

\[\Omega_3 = \cos^2 \theta \]; \( \Omega_1 \Omega_2 \Omega_2 = \sin^2 \theta \cos \theta \cos \varphi \); \( \Omega_2 \Omega_2 \Omega_3 = \sin^2 \theta \cos \theta \sin \varphi \)

Of these, only three give non zero contribution after integration over \( \varphi \) from zero to \( 2\pi \); they are \( \Omega_2 \), \( \Omega_3 \Omega_2 \), and \( \Omega_2 \Omega_3 \); also \( \eta_{ij} \) is a symmetric tensor (see definition of \( \eta_{ij} \), eq. (5.19)).
Taking into account these informations, eq. (A.33) becomes

$$I_{44} = \frac{2b}{2\pi} i \eta \omega_0 \sqrt{\kappa \tau_{10} m} \left[ \int d\omega \frac{1}{\Omega^2} \left( \frac{\omega^2}{\xi} \right)^{\frac{3}{2}} \left( \frac{2}{5} \frac{V_3}{V} \right) c \right] \left[ k_3 + \frac{2}{5} \frac{V_3}{V} \right] \left( 2 k_3 + k_3 \right) \omega'^{\prime}$$

First, the integration over $\omega'$ is carried out; the result is

$$I_{44} = \frac{3b}{2\pi} i \eta \omega_0 \sqrt{\kappa \tau_{10} m} \left[ \int d\omega \frac{1}{\Omega^2} \left( \frac{\omega^2}{\xi} \right)^{\frac{3}{2}} \left( \frac{2}{5} \frac{V_3}{V} \right) c \right] \left( 2 k_3 + k_3 \right) \omega'^{\prime}$$

Before integration over $\omega'$ is carried out, $k_3 \gamma_3$ and $k_3 \gamma_3$ must be rewritten in the coordinate system in which the $z$-axis is parallel to $k$, which we call the $k$-system.

Thus in the $k$-system

$$k_3 = \hat{k} : k = \frac{9}{5} k$$

in the $k$-system

$$\frac{9}{5} = \hat{k} : k = \frac{9}{5} k$$

in the $k$-coordinate system

$$\gamma_3 = (\hat{k} : \hat{k}) \hat{\kappa} = \hat{k} : \hat{k} = \frac{9 \cdot 9}{9^2}$$
in the $k$-coordinate system

\[(\text{A.40}) \quad \frac{q^2}{q^4} = \frac{1}{q^2} \left( \frac{q^4}{q^2} + \frac{q^4}{q^2} + \frac{q^4}{q^2} \right) \]

\[= \frac{1}{q^2} \left( -\frac{1}{2} \frac{q^4}{q^2} + \frac{3}{2} \frac{q^4}{q^2} \right) \]

Therefore the quantity which, in the $\frac{q^2}{q^4}$ system, is $k_3 \cdot k_2$ is $\frac{q^2}{q^4}(-\frac{1}{2} \frac{q^4}{q^2} + \frac{3}{2} \frac{q^4}{q^2})/q^4$ in the $k$ system.

Similarly

\[(\text{A.41}) \quad k_i k_j = (\hat{k} \cdot \hat{k}) \cdot \hat{k} = k \cdot \hat{k} \cdot \hat{k} \]

in the $k$-coordinate system

\[(\text{A.42}) \quad k \cdot \hat{k} = \frac{\frac{3}{2}}{3} \frac{\hat{k} \cdot \hat{k}}{k} \]

The RHS of (A.38), (A.40) and (A.42) are substituted into eq. (A.36); integration over $\Omega'$ is carried out; the result is

\[(\text{A.43}) \quad \mathcal{I}_{44} = -\frac{3}{2} \frac{i}{2} \eta \eta \left( \text{A.40} \right) \frac{1}{2} \frac{q^4}{q^2} \left( \frac{2}{5} + \frac{2}{5} \frac{q^4}{q^2} + \frac{4}{5} \frac{q^4}{q^2} \right) \]

The integral of (A.7a) which contains the factor $S_i$, \n
\[(\text{A.44}) \quad \mathcal{I}_5 = \frac{3}{2} \frac{i}{2} \eta \eta \left( \text{A.40} \right) \int \frac{d\Omega'}{\Omega'} \int \frac{d\Omega}{\Omega} \left[ \frac{1}{2} \frac{q^4}{q^2} \right] \frac{1}{2} \frac{q^4}{q^2} \]

is the sum of two integrals: the first one, $\mathcal{I}_{51}$, involving $S_i \left( \frac{42}{5} - \frac{1}{2} \right) \Omega'$ and the second one, $\mathcal{I}_{52}$, involving $S_i \left( \frac{42}{5} \right) \Omega'$. Substituting for $\Omega'$ the RHS of (A.18), making use of (A.13) and (A.14), we obtain for $\mathcal{I}_{51}$
The integral \( I_{\tau L} \) is written out explicitly

\[
I_{\tau L} = \frac{3b}{2\pi} i \eta n_0 \sqrt{\kappa t_{1/m}} \int \frac{d\omega'_d d\omega}{\Omega - \Omega' - b + \frac{1}{2} s'} \nu_1' \nu_2' \nu_1 \nu_2 \Theta \left( \nu_1^2 + \nu_2^2 \right)
\]

The first four integrals of \( I_{\tau L} \) can be readily evaluated with the help of eqs. (A.23) - (A.25): They are

\[
I_{\tau L} = \frac{3b}{2\pi} i \eta n_0 \sqrt{\kappa t_{1/m}} \int \frac{d\omega'_d d\omega}{\Omega - \Omega' - b + \frac{1}{2} s'} \nu_1' \nu_2' \nu_1 \nu_2 \Theta \left( \frac{1}{2} \nu_1^2 \nu_2^2 \right)
\]

\[
= \frac{3}{50} i k \eta b n_0 \sqrt{\kappa t_{1/m}} S_3 (5 + \nu_1^2 + 2 \nu_2^2)
\]

\[
I_{\tau L} = \frac{3b}{2\pi} i \eta n_0 \sqrt{\kappa t_{1/m}} \int \frac{d\omega'_d d\omega}{\Omega - \Omega' - b + \frac{1}{2} s'} \nu_1' \nu_2' \nu_1 \nu_2 \Theta \left( \frac{1}{2} \nu_1^2 \nu_2^2 \right)
\]

\[
= \frac{-1}{85} i k \eta b n_0 \sqrt{\kappa t_{1/m}} S_3 (15 + \nu_1^2 + 2 \nu_2^2)
\]

\[
I_{\tau L} = \frac{3b}{2\pi} i \eta n_0 \sqrt{\kappa t_{1/m}} \int \frac{d\omega'_d d\omega}{\Omega - \Omega' - b + \frac{1}{2} s'} \nu_1' \nu_2' \nu_1 \nu_2 \Theta \left( \frac{1}{2} \nu_1^2 \nu_2^2 \right)
\]

\[
= \frac{-1}{50} i k \eta b n_0 \sqrt{\kappa t_{1/m}} S_3 (25 + 3 \nu_1^2 + 6 \nu_2^2)
\]
\( \mathcal{I}_{52e} \) and \( \mathcal{I}_{52f} \) are more involved and will be evaluated in more detail; let us first consider \( \mathcal{I}_{52e} \)

\[
(\text{A.51}) \quad \mathcal{I}_{52e} = -\frac{3b}{2\pi} jn \sqrt{k_{16}m} \int_{0}^{\infty} d\omega' d\omega \left( \omega' - \omega \right)^{4} \mathcal{L}_{2 \omega \omega'} \mathcal{L}_{1 \omega \omega'} \mathcal{L}_{2 \omega' \omega'} \mathcal{L}_{1 \omega' \omega'} \omega'
\]

Replacing, in (A.51), \( \omega \) by the RHS of (A.34) and integrating the result over \( \omega \), we find

\[
(\text{A.52}) \quad \mathcal{I}_{52e} = -\frac{3b}{2\pi} i n \sqrt{k_{16}m} \int_{0}^{\infty} d\omega' \left( \frac{2\pi q}{3} \right)^{4} \left( k_{2} S_{3} + k_{1} S_{1} + k_{3} S_{2} \right) \omega'
\]

\( k_{3} S_{3} \) and \( k_{2} S_{2} \) are reexpressed in the \( k \)-coordinate system

\[
\begin{align*}
S_{3} &= \hat{S} \cdot \hat{k} = \frac{S_{3} \cdot q}{q} \\
S_{2} &= \hat{k} \cdot \hat{S}_{2} = \frac{k \cdot q}{q}
\end{align*}
\]

in the \( k \)-coordinate system

\[
(\text{A.53}) \quad \left( S \cdot \frac{q}{q} \right) \left( k \cdot \frac{q}{q} \right) = \frac{q}{q} S_{3} k
\]

\[
(\text{A.54}) \quad k \cdot S_{2} = k S_{3}
\]

Substitution of the RHS of (A.53) and (A.54) into (A.52) and integration over \( \omega' \) yields

\[
(\text{A.55}) \quad \mathcal{I}_{52e} = -\frac{1}{350} ikn \sqrt{k_{16}m} S_{3} \left( 105 + 42 \nu^{2} + 3 \nu^{4} + 84 \nu_{2}^{2} + 12 \nu_{3}^{2} \nu^{2} \right)
\]

Next, we evaluate \( \mathcal{I}_{52f} \)

\[
(\text{A.56}) \quad \mathcal{I}_{52f} = \frac{3b}{2\pi} i n \sqrt{k_{16}m} \int_{0}^{\infty} d\omega' d\omega \left( \omega' - \omega \right)^{2} \mathcal{L}_{2 \omega \omega'} \mathcal{L}_{1 \omega \omega'} \mathcal{L}_{2 \omega' \omega'} \mathcal{L}_{1 \omega' \omega'} \omega'
\]
The integration over $\mathcal{Q}$ is first carried out following the same method used in evaluating the integral $\mathcal{I}_{\nu'}$, (A.33).

\[(A.57) \quad I_{S2,F} = \frac{\beta b}{2\pi} \Psi (k_{12}m) \int_0^1 \frac{dz}{2} \left( 2 \mathcal{I}_2 (\frac{1}{3}) + \mathcal{I}_3 \right) + \mathcal{I}_4 \nu' k_3' \]

Before integrating over $\nu'$, the quantities in parentheses are rewritten in the $k'$-coordinate system

\[k_3 s_2 \nu' s_2 = k, \frac{9}{9} s_2 \nu' \frac{9}{9} = \frac{1}{9} q_3 \nu' q_3 k s_3 \]

\[k_3 s_3 \nu' \frac{9}{9} = k, \frac{9}{9} \nu' \frac{9}{9} = k_3 s_3 \nu' \frac{9}{9} \]

Substitution into (A.57) and integration over $\nu'$ yields

\[(A.59) \quad I_{S2,F} = \frac{1}{175} i k b n \sqrt{k_{12}m} \frac{1}{2} (10.5 + 32 \nu^2 + 21 \nu^2) \]

$K$ is obtained by adding the RHS of (A.15), (A.16), (A.27), (A.28), (A.29), (A.32), (A.43), (A.45), (A.47) - (A.50), (A.55) and (A.59)

\[(A.60) \quad K = i k y \nu b \sqrt{k_{12}m} \left\{ - \left( \frac{b n \nu}{\eta} \right) + (1 - \frac{3}{10} \nu^2) \nu_3 \nu + \right. \]

\[+ \left. \left( 1 - \frac{2}{5} \nu^2 - \frac{1}{5} \nu^2 \right) \nu_3 - \frac{2}{2} \left( - \frac{27}{15} + \frac{2}{5} \nu^2 + \frac{1}{5} \nu^2 \right) \nu_3 \nu_3 - \mathcal{S}_3 \left( - \frac{2}{2} \nu^2 - \frac{21}{10} \nu^2 + \frac{3}{2} \nu^2 + \frac{1}{2} \nu^2 \right) \right\} \]
The RHS of (A.60) is the linearized value of the \( K \)-integral for a plane wave. The sum of the first three terms on the RHS of (A.60) is equal to \( K(\xi^{(s)}) \) where \( \xi^{(s)} \) is the local Maxwellian; \( K(\xi^{(s)}) \) is the approximation of \( K(\xi) \) used by deSobrino.
APPENDIX B

We will now show that the function $E(\omega, k, \nu(k), \eta)$ in the dispersion relation $E = 0$, (eq.(6.34)), is regular on the upper half plane $S_+$. $E$ is an expression involving the integrals $A, B, C, D$ and $F$ which can be rewritten in the form

\[(B.1) \quad I = -i \frac{\sqrt{2\pi}}{k} \frac{1}{2\pi i} \int_{-\infty}^{\infty} \frac{\xi(x)}{x - \xi} \, dx\]

where

$$\xi = \frac{w+i}{k}$$

depending on whether $I$ stands for $A, B, C, D$ or $F$. (It can be easily shown that $B, C, D$ and $F$ are simply related to $A$). The RHS of (B.1) is a Cauchy integral defined and regular on the $S_+$ plane; (see for instance R. Balescu, 1963). If follows that the poles of $E$, if any, must come from the zeros of the denominator of $Q$ defined in (6.33) and (6.36) and the problem of proving the analyticity of $E$ on $S_+$ reduces to showing that the denominator of $Q$,

\[(B.2) \quad \xi = 2 + \frac{1 + b
\eta}{1 + \frac{2}{5} b
\eta} \left( -\frac{i}{2} A + \frac{\xi}{5} k b \eta B + i \right) - \frac{3 \frac{\nu}{2}}{1 + \frac{3}{5} b \eta} \left( \frac{2}{3} i B + \frac{12}{50} k b \eta (A + 6 C) - 2 i A - \frac{6}{5} k b \eta B \right)\]

has no zeros on $S_+$. Of course $\xi$ is a sum of $A$'s and $B$'s and therefore is regular on $S_+$ so that

$$\frac{1}{2\pi i} \int_{S} \frac{\xi'(\omega)}{\xi(\omega)} \, d\omega = N$$
is the number of zeros of $\mathcal{S}$ inside $\mathcal{G}$. An analysis similar to the one carried out in section 6 is given here; the function $\mathcal{S}$ is plotted on a complex $\mathcal{S}$-plane as $\omega$ increases from $-\infty$ to $\infty$ on the real axis of the complex $\omega$-plane.

For values of $\omega$ such that $|\omega| > k$, the integrals $A$ and $B$ can be expanded in powers of $k/(\omega + \epsilon)$ (eqs. (6.40) and (6.41)) and the results substituted into (B.2). To zeroth power in $k$, $\mathcal{S}$ is equal to

\begin{equation}
\mathcal{S} = \frac{1}{(\omega \mathcal{U})^2 (1 + 5 \epsilon + 6 \epsilon^2)} \left\{ \left( \frac{2}{5} \left( 5 + 24 \epsilon + 33 \epsilon^2 \right) \omega^2 - \frac{2}{5} \left( 1 + 8 \epsilon + 15 \epsilon^2 \right) \right) \omega^2 + \frac{2}{5} \left( 15 + 9 \epsilon + 14 \epsilon^2 \right) \omega^2 + \omega \left( \frac{3}{2} \frac{12 \epsilon + 4 \epsilon^2}{15} \right) \omega^2 + \omega \right\}
\end{equation}

The imaginary part of $\mathcal{S}$, $\operatorname{Im}\mathcal{S}$, has a zero at $\omega = \pm \infty$ and $\mathcal{S}(\pm \infty, \epsilon)$ crosses the real axis upward at

\begin{equation}
\operatorname{Re}\mathcal{S}(\pm \infty, \epsilon) = \frac{3}{5} \frac{\left( 5 + 24 \epsilon + 33 \epsilon^2 \right)}{1 + 5 \epsilon + 6 \epsilon^2} > 0
\end{equation}

From (B.3) it is apparent that $\operatorname{Im}\mathcal{S}$ also has a zero at the origin.

For $\omega$ near the origin, the expansions (6.61) and (6.62) for $A$ and $B$ are substituted into (B.2) the result is, to first order in $\omega$,

\begin{equation}
\mathcal{S} = \frac{2}{3} \frac{1 + 5 \epsilon}{1 + 2 \epsilon} \left\{ 1 - i \omega \left( \frac{1}{2} + \frac{(1 + 2 \epsilon)(2 + \frac{1}{5} \epsilon)}{(1 + 5 \epsilon)(1 + 3 \epsilon)} \right) \right\}
\end{equation}

$\operatorname{Im}\mathcal{S}(0, \epsilon) = 0$ and $\mathcal{S}$ crosses the real axis downward at $\operatorname{Re}\mathcal{S}(0, \epsilon) = \frac{2}{3} \frac{(1 + 5 \epsilon)}{(1 + 2 \epsilon)}$.

The hodograph of $\mathcal{S}$, figure 3, does not enclose the origin hence $\mathcal{S}$ has no zero on $S_+$ which is what we set out to prove.
Figure 8. Plot of $\mathcal{L}(\omega, \varepsilon)$ showing analyticity of $E(w,k)$ on $S_+$. 
APPENDIX C

The expressions \( h(\epsilon) \), \( |q(\epsilon)| \) and \( |p(\epsilon)| \) defined in (6.53) are of the form

\[
S(\epsilon) = \frac{p(\epsilon)}{q(\epsilon)}
\]

where

\[
p(\epsilon) = a_0 + a_1 \epsilon + a_2 \epsilon^2 + a_3 \epsilon^3 \quad ; \quad q(\epsilon) = b_0 + b_1 \epsilon + b_2 \epsilon^2 + b_3 \epsilon^3
\]

then

\[
p'(\epsilon) = a_1 + 2a_2 \epsilon + 3a_3 \epsilon^2 \quad ; \quad q'(\epsilon) = b_1 + 2b_2 \epsilon + 3b_3 \epsilon^2
\]

We wish to determine the sign of \( S'(\epsilon) \) which is the sign of \( p'(\epsilon)q(\epsilon) - q'(\epsilon)p(\epsilon) \). The coefficients of \( p'q - q'p \) are

\[
\begin{align*}
  n = 0 & \quad (a_1 b_0 - a_0 b_1) \\
  n = 1 & \quad 2(a_2 b_0 - a_0 b_2) \\
  n = 2 & \quad (a_2 b_1 - a_1 b_2) + 3(a_3 b_0 - a_0 b_3) \\
  n = 3 & \quad 2(a_3 b_1 - a_1 b_3) \\
  n = 4 & \quad (a_3 b_2 - a_2 b_3)
\end{align*}
\]

A sufficient condition for \( S'(\epsilon) > 0 \) (\( S'(\epsilon) < 0 \)) is that

\( a_m b_n - a_n b_m > 0 \) (\( a_m b_n - a_n b_m < 0 \)) for \( m > n \) because then all the coefficients are positive (negative); if \( a_m > 0 \) and \( b_n > 0 \) for all \( m \)'s then the condition is equivalent to

\[
(c.1) \quad \frac{a_m}{b_m} > \frac{a_n}{b_n} \quad \text{for} \ m > n
\]
(c.2) \( \left( \frac{a_m}{b_m} < \frac{a_n}{b_n} \right) \) for \( m > n \)

(This is readily generalizeable to the case where \( P \) and \( Q \) are polynomials of degree \( N \)).

The coefficients \( a_n \) and \( b_n \) of \( p(\epsilon) \) satisfy (C.2) and those of \( |q(\epsilon)| \) and \( |\delta(\epsilon)| \) satisfy (C.1); therefore
\[
|p'(\epsilon)| < 0, \quad |q'(\epsilon)| < 0 \quad \text{and} \quad |\delta'(\epsilon)| < 0.
\]
BIBLIOGRAPHY


