INELASTIC LIGHT SCATTERING FROM THERMAL FLUCTUATIONS IN GASES

by

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Abstract

We have studied the Brillouin spectrum of light scattered by the dilute monatomic one component gases xenon and helium and by the xenon-helium binary gas mixture.

In a one component monatomic gas the scattered light spectrum for a scattering process with momentum transfer, $\mathbf{K}$, and energy transfer, $\omega$, is proportional to the power spectrum, $S(\mathbf{K}, \omega)$, of fluctuations in the density of the gas. In a dilute monatomic gas this spectrum should be obtainable from the Boltzmann equation. In 1959 Gross and Jackson proposed a method of solution of the Boltzmann equation (the kinetic model procedure) whereby one could calculate the space-time dependence of phenomena of arbitrary frequency, $\omega$, and wavelength, $\lambda$, i.e. both in the kinetic regime where $\lambda$ is small compared to the molecular mean free path, and in the hydrodynamic regime where there are many collisions over the length $\lambda$. Recently, Sugawara, Yip, and Sirovich have applied the kinetic model procedure to the calculation of the density fluctuation spectrum of the Maxwell molecule and hard sphere gases.

We have measured the density fluctuation spectrum, $S(\mathbf{K}, \omega)$, in xenon gas at $T = 22^\circ C$, $K = 2 \times 10^{-4} \text{ cm}^{-1}$, through the kinetic-hydrodynamic transition. We find the spectra calculated via the kinetic model procedure for both Maxwell molecules and hard spheres to be in excellent agreement with the measured spectra. This result shows the kinetic model procedure to be an accurate method of solution of the Boltzmann equation and is evidence of the insensitivity of time dependent phenomena in a dilute system to the exact form of the intermolecular potential.

We have studied non-hydrodynamic behavior in the helium-xenon binary gas mixture with xenon dilute. Because of the large molecular mass ratio and scattering cross section ratio of xenon to helium, the light scattered by the xenon may be separated from the total scattered light spectrum. We have studied the spectrum of the light scattered by the xenon as a function of helium pressure. At low helium pressure xenon atoms are in free flight over the length $2\pi/K$, and the resulting scattered light spectrum is Gaussian. At high helium pressure the xenon atoms diffuse over the length $2\pi/K$ and the spectrum is Lorentzian. The study of the Gaussian to Lorentzian evolution of the scattered light spectrum shows that the Fokker-Planck model is appropriate to approximate
the xenon-helium collision.

From the splitting and width of the Brillouin components of the scattered light spectrum, we have made a preliminary study of the sound velocity and attenuation in the helium-xenon binary gas mixture. These measurements indicate the presence of a relaxation of the sound attenuation at frequencies \( \omega \) in the vicinity of \( \omega_u \), the reciprocal of the time required for the equilibration of the velocity difference between the two species of the mixture to occur. Recently Goldman and Sirovich have formulated a theory which accounts for the finite equilibration time of the velocity and temperature difference between the species in a binary gas mixture. Partial agreement is obtained between the velocities and attenuation calculated from the Goldman-Sirovich theory and the measurements.

Thesis Supervisor: George B. Benedek
Title: Professor of Physics
There is music wherever there is harmony, order, or proportion; and thus far we may maintain the music of the Spheres: for those well ordered motions and regular paces, though they give no sound to the ear yet to the understanding they strike a note most full of harmony.

Sir Thomas Browne
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CHAPTER I: INTRODUCTION

A. Background

1. Historical Note

The dilute monatomic gas, because of its relative simplicity, has always been of considerable physical interest, and the investigations of its properties have proven to be of central importance in the development of thermodynamics, statistical mechanics, and the atomic theory of matter. The beginnings of the modern theory of dilute gases can be traced to 1658 when Gassendi re-established the atomic view of matter by presenting an atomic theory, based on small, hard-moving atoms, that explained qualitatively the existence of the three states of matter. Bernoulli was the first to quantify the kinetic theory when in 1738 he derived the inverse relationship of pressure and volume, explaining the experimental results of Boyle. Kinetic theory made its greatest advances in the hands of Maxwell and Boltzmann whose work resulted in the Boltzmann transport equation, describing statistically the temporal development of the state of a gas in terms of a single particle distribution function and the properties of binary molecular collisions. Since then, wide ranging experimental and theoretical work has made the dilute monatomic gas the most thoroughly understood of all macroscopic physical systems, but it is only recently that some of the most important and useful advances in kinetic theory have been made: e.g., the demonstration, directly from the Boltzmann equation, of the existence of collective excitations (sound) in a gas; and the continuing efforts to obtain solutions of and accurate approximations of the Boltzmann equation.

During the past few years many problems in non-equilibrium statistical mechanics have been addressed, among them the study of time dependent fluctuation phenomena in dilute gases. The initial motivation for the work in gases arose from the study of molecular dynamics in liquids using inelastic neutron scattering. Van Hove demonstrated in
1954 that the energy-angle cross section for the scattering of monochromatic neutrons was related to the time dependence of atomic motions in a condensed system through the density-density correlation function, \( G(r, t) \). The calculation of \( G(r, t) \) on a molecular level for a liquid was not possible (and still is not). It was natural, then, to turn to the dilute gas where, although neutron scattering experiments were not feasible for technical reasons, atomic motions could be understood in terms of binary collisions and the Boltzmann equation, and detailed calculations could be made on a molecular level in the hope of shedding light the more complicated situation in a liquid. Such was the motivation for the first study of density correlations in a dilute gas and their relation to neutron scattering. \(^9\)

In 1966, however, Nelkin and Yip\(^{10}\) suggested that inelastic light scattering (Brillouin scattering) would be applicable to the study of \( G(r, t) \) for a dilute gas and would allow one to determine the validity of the Boltzmann equation and solutions thereof in describing rapidly varying phenomena in a dilute gas. They showed further that a Brillouin scattering experiment could probe in the hydrodynamic regime, i.e. disturbances of a wave vector small compared to the inverse mean free path \( 1/l \) and of a frequency \( \omega \) small compared to the inverse time between collisions \( 1/\tau_c \), as well as in the kinetic regime, i.e. disturbances such that \( K > 1/l, \omega > 1/\tau_c \). Previous tests of kinetic theory of rapidly varying phenomena in the hydrodynamic to kinetic transition had been limited to forced sound propagation experiments. The first application of Brillouin scattering to the testing of kinetic theory was in 1965 by May, Rawson and Welsh\(^{11}\) and in 1966 by Greytak and Benedek.\(^{12}\) The latter authors demonstrated clearly that the spectrum of light scattered by a dilute gas could serve as a test of various theoretical solutions of the Boltzmann equation. The experiments to be described represent the most extensive application of Brillouin scattering to the study of dilute one component gases to date and the extension of the technique to the study of a binary gas mixture.
2. Brillouin Scattering

When a macroscopic system is in thermodynamic equilibrium, small amplitude fluctuations in the thermodynamic parameters which characterize the system still occur. In a transparent fluid these fluctuations will produce a space and time dependent index of refraction and thereby cause the scattering of light. We shall restrict our discussion throughout to fluids composed of isotropic, spherically symmetric, polarizable molecules and neglect processes which involve energy exchange with internal atomic or molecular states. Under these assumptions the index of refraction depends strongly only on the particle number density and the scattering is a probe of density fluctuations.

The conservation of momentum for the light scattering process requires that the scattering of light with an incident wave vector $\mathbf{k}_0$ through an angle $\theta$ to a final wave vector $\mathbf{k}_s$, couples only to the spatially periodic fluctuation of wave vector $\mathbf{k} = \mathbf{k}_s - \mathbf{k}_0$. The frequency distribution of light scattered into the direction $\mathbf{k}_s$ will then be determined by the time dependence of the fluctuation of wave vector $\mathbf{k}$. The magnitude of $\mathbf{k}$ is given in terms of $k_0$ and the scattering angle $\theta$ by $K = 2k_0 \sin \theta / 2$. The spatial period, $\Lambda = 2\pi/K$, of the sampled fluctuation is the length over which the scattering process samples the system. For the scattering of 6328 Å light one finds $\Lambda \approx 3100$ Å so that microscopic density fluctuations can be probed.

The inelastic scattering of light was first considered by Brillouin \(^{13}\) and independently by Mandel'shtam \(^{14}\) who showed that propagating density fluctuations (thermal sound waves) would produce in the spectrum of the scattered light two sharp lines (Brillouin lines) split symmetrically about the incident frequency an amount $\Delta \omega = \pm K c_0$ rad/sec where $c_0$ is the sound speed in the medium. The splitting $K c_0$ is the frequency of a sound wave having a wave vector $K$. The split lines may be viewed as arising from either the modulation of the incident light by the time dependence ($e^{\pm iK c_0 t}$) of the propagating fluctuations or as a Doppler shift of the incident light by a periodic density disturbance moving along $\mathbf{K}$ at a velocity of $\pm c_0$. Subsequent work showed that the width of the shifted lines is related to the acoustic attenuation \(^{15}\) and that there is, in addition,
an unshifted component (thermal line) arising from heat diffusion whose width is determined by the thermal diffusivity. (16), (14)

The Brillouin and thermal lines were first observed in the scattered light spectrum by E. Gross (17) in 1930. However, because of the small frequency shifts and scattering cross sections involved, the study of the density fluctuations by inelastic light scattering was of limited use as a research tool until 1964 (18), (19) when the laser, an ideal source for such experiments, due to its intensity, monochromaticity and collimation, was employed, making possible accurate determinations of spectra. (20)

3. The Spectrum of Light Scattered by Dilute Gases

The dynamical behavior of small deviations from equilibrium in a simple fluid is completely described by the two point correlation functions of the system. These correlation functions are ensemble averaged products of densities of conserved quantities taken at two different space-time points. Of the two point correlation functions the density-density correlation function \( G(\vec{r}, t) \), is the most important because it contains nearly all of the dynamical information about the system and because it is measurable both by light and neutron scattering. We define \( G(\vec{r}, t) \) as

\[
G(\vec{r}, t) \equiv \langle n(\vec{r}, t) n(0, 0) \rangle / n_0
\]

where \( n(\vec{r}, t) \) is the particle number density at \( (\vec{r}, t) \), \( n_0 \) is the average number density and \( \langle \rangle \) denotes ensemble averaging. For a classical system the correlation function \( G(\vec{r}, t) \) is the density of particles at \( (\vec{r}, t) \) given that some particle was at \( (0, 0) \). The relation of the energy angle cross section for the scattering of monochromatic neutrons to \( G(\vec{r}, t) \) was first discussed by van Hove. (8)

The extension of the work of van Hove to light scattering was done by Komarov and Fisher (21) who showed that for a monatomic fluid the power spectrum of the scattered field \( S(\vec{K}, \omega) \), with light of wave vector \( \vec{K}_o \) and frequency \( \omega_o \) incident, is proportional to the density fluctuation power spectrum \( S_n(\vec{K}, \omega) \); i.e. to the space-time Fourier
transform of the density-density correlation function

$$S(\mathbf{k}, \omega) \propto S_0(\mathbf{\vec{r}}, \omega) = \int d^3r \int dt \exp \{i(\mathbf{k} \cdot \mathbf{r} - \omega t)\} G(\mathbf{r}, t).$$

Here $\mathbf{\vec{k}} = \mathbf{k} - \mathbf{k}_0$ and $\omega$ is the shift in frequency from $\omega_0$. The scattered light spectrum $S(\mathbf{k}, \omega)$ then can serve to test various theoretical forms of $G(\mathbf{r}, t)$, or, if the proper form is known, can serve to measure the parameters of the system which determine $G(\mathbf{r}, t)$.

The calculation of $G(\mathbf{r}, t)$ from the properties of the fluid can be approached from either a macroscopic or microscopic point of view. The macroscopic approach is applicable to a system which remains in local thermodynamic equilibrium. The state of such a system can be described by a set of space-time dependent thermodynamic variables and their equations of motion (hydrodynamic equations). The thermodynamic quantities which characterize the system undergo small amplitude spontaneous fluctuations about their equilibrium values, the space-time behavior of which determines the correlation functions of the system. The correlation functions may be calculated by assuming that the time dependence of a spontaneous fluctuation is given by the hydrodynamic equations, and then creating a "spontaneous" fluctuation by an appropriate external influence or initial preparation of the system. Following the former course, Kadanoff and Martin have determined the external influence which produces a disturbance in a fluid such that the fluid remains in local thermodynamic equilibrium. From the response of the fluid to such an external influence, they have calculated the correlation functions, including $G(\mathbf{r}, t)$, for a simple fluid described by the Navier-Stokes equations of hydrodynamics. Mountain, calculating the response of the same system to the appropriate initial condition has obtained similar results for $G(\mathbf{r}, t)$.

Selwyn has formulated a generalized hydrodynamic theory for a simple fluid wherein the correlation functions for conserved quantities can be approximately calculated from the Liouville equation using linear response theory. Selwyn then uses the calculated correlation functions to derive the hydrodynamic equations which govern the space-time behavior of the conserved variables. He has applied his theory to the calculation of $G(\mathbf{r}, t)$ for a dilute gas of Maxwell molecules. He has obtained
for this system, in a rigorous way, the lowest order corrections to the Navier-Stokes equations which can be attributed to non-hydrodynamic behavior.

The resulting "hydrodynamic" spectrum $S(K, \omega)$ in a simple fluid displays distinct features which can be identified with the dominant collective modes of motion of the system. The spectrum is well approximated by three Lorentzian lines: a line at the incident frequency of half-width at half height (HWHH) $\Gamma_C = D_T K^2$, arising from non-propagating entropy fluctuations at constant pressure and two lines of HWHH $\Gamma_B = \alpha c_0$ shifted with respect to the incident frequency by $\Delta \omega = \pm K c_0$, arising from propagating pressure fluctuations at constant entropy. Here $D_T$ is the thermal diffusivity, $c_0$ the adiabatic sound velocity at the frequency $\Delta \omega$ and $\alpha$ the sound attenuation coefficient at the frequency $\Delta \omega$. The prominent features (splittings, widths) of the hydrodynamic spectrum thus involve many of the interesting thermodynamic derivatives and transport coefficients of the fluid.

The validity of the hydrodynamic equations rests on the existence of local thermodynamic equilibrium which in turn is enforced by interparticle collisions. The hydrodynamic equations are applicable to the description of a fluid, then, only in the long wavelength low frequency limit ($\ell \ll 1/K, \omega \ll 1/\tau_C$) in which a particle undergoes many collisions over the characteristic length and time which the fluctuations are probed. In a dilute gas, however, we can easily study conditions for which $\ell > 1/K$ and $\omega > 1/\tau_C$, so that a more general approach to the calculation of $S(\vec{K}, \omega)$ is required. Such is the microscopic approach which attempts to obtain $G(\vec{r}, t)$ and $S(\vec{K}, \omega)$ directly from molecular properties via statistical mechanics. This approach has found its greatest success in the case of the dilute gas. The microscopic basis for the description of a dilute gas is the Boltzmann equation

$$ \left( \partial_t + \vec{v} \cdot \nabla \right) f(\vec{r}, \vec{v}, t) = \left( \partial_t / \partial t \right)_{\text{coll}} $$

which, with appropriate boundary conditions, determines the temporal evolution of the $\mu$ space particle density $f(\vec{r}, \vec{v}, t)$. The means of calculating $S(\vec{K}, \omega)$ for a dilute gas have been provided by Van Leeuwen and Yip.
who showed, starting from the Liouville equation, that $G(\mathbf{r}, t)$ is the velocity integral of $f(\mathbf{r}, \mathbf{v}, t)$,

$$G(\mathbf{r}, t) = \int d^3\mathbf{v} f(\mathbf{r}, \mathbf{v}, t),$$  \hspace{1cm} (1.2)

the solution of the linearized Boltzmann equation, subject to the initial condition

$$f(\mathbf{r}, \mathbf{v}, t) = f_0(\mathbf{v}) [n_0 + \delta(\mathbf{r})]$$  \hspace{1cm} (1.3)

where $f_0(\mathbf{v})$ is the equilibrium Maxwellian distribution. The density-density correlation function $G(\mathbf{r}, t)$ then is the system response to the initial placement of an additional thermalized particle at $(0, 0)$. The linearized Boltzmann equation is appropriate for such calculations because the deviations from equilibrium being considered are small.

The solution of the Boltzmann equation for $S(\mathbf{K}, \omega)$ has itself been approached in several ways. In the low frequency long wavelength limit the hydrodynamic equations for a gas may be obtained directly from the Boltzmann equation through the Chapman-Enskog procedure. With the hydrodynamic equations in hand, the methods applicable to the macroscopic description are available to calculate $S(\mathbf{K}, \omega)$. The Chapman-Enskog procedure requires that the only time dependence of $f(\mathbf{r}, \mathbf{v}, t)$ be through the moments of $f(\mathbf{r}, \mathbf{v}, t)$ which correspond to the local density, $n(\mathbf{r}, t)$, temperature, $T(\mathbf{r}, t)$, and velocity $\mathbf{u}(\mathbf{r}, t)$. With this requirement the Boltzmann equation may be solved subject to the condition that deviations from local thermodynamic equilibrium are small. The solution is carried out by a perturbation expansion of $f(\mathbf{r}, \mathbf{v}, t)$ in the parameter $K_\ell$ about the local equilibrium distribution and yields hydrodynamic equations in $n$, $T$, and $\mathbf{u}$ which determine the space-time behavior of these quantities and, therefore, the behavior of $f(\mathbf{r}, \mathbf{v}, t)$. The precise set of hydrodynamic equations obtained depends on the order of approximation employed, higher order being required further into the kinetic regime. In the zero order approximation, local thermodynamic equilibrium is enforced and there is no dissipative transverse momentum flux or heat flux. The conservation of particle number, momentum and energy in a collision leads to the Euler conservation equations for a nonviscous fluid. In the first order approximation deviations from local equilibrium are permitt-
ed and one obtains momentum flux and heat flux terms which are propor-
tional to first order spatial derivatives of $\vec{u}$ and $T$, the proportionality
constants being transport coefficients, the viscosity and thermal conduct-
itivity respectively. The Navier-Stokes equation for momentum transport
and the Fourier heat conduction equation for energy transport are, there-
fore, obtained in this order. Higher order approximations involve, in
addition, momentum and heat transport proportional to higher order
spatial derivatives and additional transport coefficients. The calcula-
tion of $S(K,\omega)$ using the second order (Burnett) hydrodynamic equations
has been carried out by Nelkin and Ranganathan\cite{28} and by Foch.\cite{29}
The comparison of measurements of the dispersion relations for sound
propagation\cite{30} with those of the Chapman-Enskog procedure shows that
the Navier-Stokes approximation is valid for $K < 0.17$ and that the Burnett
approximation is useful somewhat further into the kinetic regime, being
valid for $K < 1.7$. Extension of the Chapman-Enskog procedure to higher
orders, however, does not yield further improvement.

A number of solutions of the Boltzmann equation valid at
arbitrary frequency and wavelengths have been attempted. Yip and
Ranganathan\cite{31} have calculated $S(K,\omega)$ using the Fokker-Planck approxi-
mation. This approach replaces the collision operator in the Boltzmann
equation with a differential operator obtained from assuming that the
particle trajectories are smooth (i.e., that the particles experience only
soft collisions). The evolution of $f(\vec{r},\vec{v},t)$ then is a continuous Markoff
process.\cite{32} The results for $S(K,\omega)$ in the Fokker-Planck approximation
show qualitatively the expected behavior but do not give the proper hydro-
dynamic limit. The Eucken ratio $E = \kappa / \eta C_v$ for this model is $E = 10/9$,
considerably different for the value of $E = 5/2$ for a monatomic gas,
obtained from calculation of transport coefficients and verified experi-
mentally. Thus if the Fokker-Planck spectra are adjusted to yield the proper
central line width $\Gamma_C$ the resulting Brillouin width $\Gamma_B$ will be incorrect.
Subsequently, Ranganathan and Yip\cite{33} calculated $S(K,\omega)$ from the linear-
ized Boltzmann equation for Maxwell molecules using the polynomial ex-
pansion of Wang Chang and Uhlenbeck (WCU). With this technique the
distribution function $f(\vec{r},\vec{v},t)$ is expanded in a complete orthonormal
infinite set of functions of $\vec{v}$ which are eigenfunctions of the collision
operator, (34) One then obtains from the Boltzmann equation an infinite set of linear differential equations which may be solved by replacing the eigenvalues of the collision operator with zero beyond a cutoff point. When the resulting spectra cease to change as the cutoff point is extended to keep more eigenvalues intact one has an exact solution of the Boltzmann equation for $S(K, \omega)$. In the hydrodynamic limit only low order velocity moments of the distribution are required and convergence is rapid. The further into the kinetic limit that one goes, however, the more necessary the higher velocity moments become to the description of $f(\mathbf{r}, \mathbf{v}, t)$ so that the WCU method does not converge well in the kinetic limit.

The most satisfactory calculations to date of $S(K, \omega)$ for a dilute gas have been recently done by Sugawara, Yip, and Sirovich, (35) using the kinetic model hierarchy proposed by Gross and Jackson. (36) The kinetic model approximation is similar to that of the WCU method in that the distribution function is expanded in orthonormal polynomial functions of $\mathbf{v}$, but a better approximation is made to the eigenvalues $\lambda_1$ of the collision operator. With this method the $\lambda_i$ beyond a certain order (say M) are set to a constant value, in this case, $\lambda_M$. This procedure preserves all moments of the distribution function at least approximately, allowing convergence in both the kinetic and hydrodynamic regimes. Spectra have been calculated for successive orders of approximation and are found to cease to change when sufficient orders are included, (35) One has then an exact solution of the Boltzmann equation for $S(K, \omega)$ for all values of the wavelength to mean free path ratio. The method has been applied to both Maxwell and hard sphere molecules to evaluate the effect of intermolecular potential on $S(K, \omega)$. The spectra for these two choices of potential are nearly identical, differing at most by only a few percent. The light scattering experiment then serves to test the method of solution of the Boltzmann equation rather than the particular intermolecular potential employed. Sirovich and Thurber (37) have applied the kinetic model to the sound propagation problem and have attained the best agreement with experiment to date. The lowest order kinetic model approximation is the familiar Bhathagar-Gross-Krook model (38) from which Yip and
Nelkin have calculated $S(\vec{K}, \omega)$.\(^{(39)}\) Ranganathan and Yip have also considered other low order kinetic models.\(^{(36)}\)

The evolution of the scattered light spectrum $S(\vec{K}, \omega)$, calculated from the kinetic model for Maxwell molecules as one proceeds from the kinetic to the hydrodynamic regime is shown in fig. (1.1). In the figure the parameter $x$ is the frequency shift $\omega$, scaled by

$$\Delta \omega = K \nu_m = K \sqrt{\frac{2k_B T}{m}},$$

the 1/e halfwidth of the Gaussian spectrum in the kinetic limit, i.e. $x = \omega/\Delta \omega$. The spectra are all normalized to unit area in $x$ and symmetric about $x = 0$, although we have plotted only the portion for positive $x$. The parameter $y$ determines the wavelength to mean free path ratio, i.e., $y \approx 1/K \xi$. With this definition as $y$ increases we approach the hydrodynamic regime and as $y$ decreases we approach the kinetic regime.

In the hydrodynamic limit we see the development of the distinct lines in $S(x, y)$ which arise from the collective hydrodynamic modes. At $x = 0$ the entropy fluctuation peak is found. The pressure fluctuation peaks are shifted in $\omega$ by $\pm K c_0$. In a dilute gas in the hydrodynamic regime we have

$$K c_0 = \sqrt{\frac{5 k_B T}{3 m}} = \sqrt{\frac{5}{6}} \Delta \omega$$

so that the pressure fluctuation peaks are located at $|x| = \sqrt{\frac{5}{6}}$. The collective mode linewidth (damping) varies inversely with $y$. For large values of $y$ the widths are small compared to $K c_0$ and the modes are well defined. As $y$ decreases, however, the mode damping increases until they eventually disappear.

The ultimate kinetic spectrum ($y \rightarrow 0$) is a Gaussian of 1/e halfwidth $K \nu_m (x = 1)$. In this limit the particles undergo few collisions over the length $1/K$ and the spectrum may be calculated on the basis that the scattered light is Doppler shifted by molecules that move along straight lines with the Gaussian equilibrium velocity distribution. Since the equilibrium velocity distribution falls to 1/e at $\nu_m$, and since a molecule that moves along $\vec{K}$ with velocity $\nu$ Doppler shifts light by a frequency
Figure 1.1: Exact solution of the Boltzmann equation for the scattered light spectrum, $S(x, y)$, for a dilute gas of Maxwell Molecules.
\[ \omega = K_\nu \] we find the Gaussian spectral distribution which falls to \(1/e\) at
\[ \omega = K_\nu \] For xenon gas at room temperature and scattering angle
\[ \theta = 10.6^\circ \] we find \(K_\nu \approx 56\) MHz. Under the same conditions one has
\[ y \approx 0.2 \] at a pressure \(p = 20 \text{ mmHg}\) and \(y \approx 6\) at \(p = 600 \text{ mmHg}\).

4. Motivation for this Work

In the hydrodynamic regime \((\ell \ll 1/K)\), there is much experimental evidence to indicate the correctness of the Boltzmann equation for describing phenomena involving small amplitude deviations from equilibrium. This comes from the excellent agreement between the measured transport coefficients and those calculated from the Boltzmann equation and from the confirmation of the hydrodynamic predictions in sound propagation experiments. In the transition \((\ell < 1/K)\) and the kinetic \((\ell > 1/K)\) regimes, however, experimental tests of the Boltzmann equation have been limited to forced sound propagation experiments. Such experiments have been of significance in testing solutions of the Boltzmann equation applied to rapidly varying phenomena. We might, however, consider Brillouin scattering as a complementary method of studying such phenomena for a number of reasons. Forced sound propagation experiments measure directly the dispersion relation for the acoustic mode. This dispersion relation determines to a large extent the shape and location of the Brillouin lines in the density fluctuation spectrum and this in the scattered light spectrum. The Brillouin scattering and forced sound propagation experiments are, therefore, closely related.

A problem arises in the interpretation of forced sound propagation experiments because the Boltzmann equation cannot be solved for the exact experimental boundary conditions. The solution of the sound propagation problem can be carried out if one confines the gas to an infinite half-space bounded by an oscillating wall. One then obtains dispersion relations for the resulting plane wave propagating pressure variation, the characteristics of which depend only on the properties of the gas. The experimental geometry, however, consists of two parallel quartz plates spaced by a distance \(d\), one being the source (oscillating wall) and the other being the receiver, which measures the pressure (mean normal stress) a distance \(d\) from the source. The difficulty arises in that for
measurements in the kinetic regime one must have \( t \sim d \) to obtain sufficient received signal, thus one is confined to measuring the sound field within a mean free path of the source. In this limit the measured pressure may not be simply that arising from the sound field but may depend on geometry and other modes of propagation.

Recently, Sirovich and Thurber have found good agreement between the kinetic model calculation of acoustic dispersion relations and forced sound propagation data.\(^{(37)}\) This agreement indicates that the above effects are probably small but make the residual difference between experiment and theory difficult to interpret. In this regard the light scattering technique offers several advantages over forced sound propagation in that: i) the boundary condition on the Boltzmann equation appropriate to the calculation of the scattered light spectrum is clearly understood and can be dealt with exactly; ii) the optical probe interacts only very weakly with the system under study and the nature of this interaction does not change from the kinetic to the hydrodynamic regime. The light scattering technique has the additional important advantage of yielding information on the entropy fluctuation (thermal diffusion) mode.

The kinetic model calculation has been carried out for the density fluctuation spectrum\(^{(35)}\) and for the acoustic dispersion relation\(^{(37)}\) for both hard sphere and Maxwell molecules. These calculations show that the acoustic dispersion relation may be somewhat more sensitive to the intermolecular potential than is the density fluctuation spectrum, especially in the kinetic limit. If this is the case the forced sound experiments would seem more appropriate to the study of the effect of the molecular interaction in time dependent phenomena and the light scattering experiments, because of the insensitivity of the spectrum to the intermolecular potential, would seem more appropriate to the study of methods of solution of the Boltzmann equation. In any case, at the present time, the light scattering experiment offers enough concrete advantages to be pursued.
5. Previous Measurements of Brillouin Spectra in Dilute Gases

Previous measurements of the Brillouin spectra of gases have been made by May, Rawson, and Welsh\textsuperscript{(11)} who observed the extreme kinetic limit of argon and hydrogen and obtained the expected Gaussian line shape.

Greytak and Benedek\textsuperscript{(12)} have measured the spectrum of light scattered by xenon for two values of \( y \approx 1/Kt \): in the hydrodynamic regime they find agreement within experimental error with the spectrum calculated from the hydrodynamic equations. In the transition regime, their data has been compared to the spectrum calculated from the kinetic model approximation\textsuperscript{(44)} and reasonable agreement is attained. They have also measured spectra in the polyatomic gases CO\textsubscript{2} and CH\textsubscript{4}.\textsuperscript{(45)}

May and Rawson\textsuperscript{(46)} have obtained Brillouin spectra from hydrogen gas and found good agreement with the hydrodynamic theory for \( y \approx 1/Kt > 17 \) but observed deviations from hydrodynamic behavior for \( y \approx 4 \), which must be attributable at least in part to the onset of the transition regime. The spectra from polyatomic gases are modified by the energy exchange of translational modes of motion with internal molecular vibrational and rotational states and these deviations from monatomic gas spectra can be used to probe such energy exchange. However, comparison of experiment to theory for polyatomic gases outside of the hydrodynamic regime is complicated by the fact that the theory is not as thoroughly developed as that for the monatomic gas, spectra having been calculated for a low order kinetic model\textsuperscript{(45)} only.

6. Summary

In summary, inelastic light scattering can provide a straight-forward test of solutions of the linearized Boltzmann equation for a dilute monatomic gas from the kinetic to the hydrodynamic limits. The scattered light spectrum \( S(K, \omega) \) has been calculated from the linearized Boltzmann equation via a convergent approximation procedure that yields exact results, and thus is available for testing. We now turn to the work of this thesis.
B. This Work

1. General Description

We have measured the frequency spectrum of monochromatic (6328 Å) light scattered at an angle of 10.6° (K = 2 × 10^4 cm^-1) by the dilute monatomic pure gases xenon and helium, and by the xenon-helium monatomic gas mixture. All measurements were carried out at room temperature. The light source for these experiments was a frequency stabilized single frequency He-Ne laser which produced 15mw of optical power. Scattered light, at angles near 10.6°, was collected using a conical lens, frequency analyzed with spherical Fabry-Perot interferometers and detected by an ITT FW 130 photomultiplier and a photon counting system.

2. Experiments in Monatomic Gases

Experiments on the pure xenon were carried out at sixteen sample pressures ranging from 10 mm Hg. to 500 mm Hg. A marked change is observed in the shape of the measured spectra as the pressure is changed, since at the lowest pressures one has y ~ 0.1 and kinetic behavior while at highest pressure one has y ~ 5.5, well into the hydrodynamic regime. Spectra were measured in helium gas in the vicinity of y = 4. Theoretical spectra from the kinetic model and hydrodynamic calculation were numerically convolved with the observed instrumental profile and compared to the experimental spectra. We find the exact solution of the Boltzmann equation from the kinetic model calculation to be in very good agreement with the data throughout the kinetic-hydrodynamic transition. The present measurements, however, do not allow clear choice of Maxwell molecule or hard sphere molecule as being more appropriate to xenon under the above conditions. The exact hydrodynamic calculation of Mountain and the hydrodynamic calculation of Kadanoff and Martin are found applicable for y > 6. The Burnett approximation is found adequate for the description of the sound propagation modes further into the kinetic regime, for y > 3, but provides the thermal diffusion mode well only for y > 6.
The best agreement of a hydrodynamic calculation with the exact solution of the Boltzmann equation is provided by Selwyn's generalized hydrodynamic theory applied to the Maxwell gas. His spectra are in excellent agreement with the spectra of the exact solution for \( y > 3 \). None of the hydrodynamic theories was found to be particularly accurate in providing \( S(x, y) \) for \( y < 3 \).

3. Experiments in a Binary Mixture of Monatomic Gases

We have studied the spectrum of light scattered by a dilute monatomic gas mixture. We do not approach the mixture problem here in a general way, although we do obtain some generally applicable results. Rather we exploit the peculiar properties of the helium-xenon mixture to study one kind of kinetic behavior in this mixture. The motivation for this study was the possibility of determining the applicability of various approximate models for the xenon-helium collision.

We show that the spectrum \( S(\vec{k}, \omega) \) of the light scattered by a dilute binary gas mixture may be expressed as follows:

\[
S(\vec{k}, \omega) \propto n_i \alpha_i \alpha_5 S_\nu(\vec{k}, \omega) + \alpha_\nu S_\nu(\vec{k}, \omega) + n_i S_\nu(\vec{k}, \omega) + n_2 \alpha_2 S_{22}(\vec{k}, \omega).
\]  

Here \( S_{ij}(\vec{k}, \omega) \) is the space-time Fourier transform of \( G_{ij}(\vec{r}, t) \), where \( G_{ij}(\vec{r}, t) \) is the density of particles of kind \( i \) at \( (\vec{r}, t) \) given a particle of kind \( j \) at \( (0, 0) \), \( n_i \) is the average number density of component \( i \), and \( \alpha_i \) is proportional to the light scattering cross section for component \( i \).

The spectral density \( S_{ij}(\vec{k}, \omega) \), in analogy to \( S(\vec{k}, \omega) \) for the one component gas, is determined by the space-time evolution of the \( \mu \) space distribution \( f_{ij}(\vec{r}, \vec{v}, t) \) for species \( i \) subject to the placement of a thermalized particle of species \( j \) at \( (0, 0) \). The temporal evolution of the state of a binary gas mixture is determined by the coupled kinetic equations for the \( f_{ij}(\vec{r}, \vec{v}, t) \). These equations are

\[
(\partial_t + \vec{v} \cdot \vec{\nabla}) f_i(\vec{r}, \vec{v}, t) = (\partial f_i/\partial t)_i^{\text{coll}} + (\partial f_i/\partial \vec{v})_i^{\text{coll}}, \quad i = 1, 2.
\]
In the case of the mixture the evolution of \( f_i(\vec{r}, \vec{v}, t) \) is determined by both \( i - i \) collisions and \( i - j \) collisions. The equations couple because \( \frac{\partial f_i}{\partial t} \) depends on \( f_j(\vec{r}, \vec{v}, t) \). The calculation of \( S_{ij}(\vec{k}, \omega) \) follows from these kinetic equations for the mixture in the same way that \( S(\vec{k}, \omega) \) was obtained for the Boltzmann equation for the one component gas, but is more involved and has not been carried out for arbitrary frequencies and wavelengths. We have obtained the total spectrum \( S(\vec{k}, \omega) \) for a binary gas mixture in the hydrodynamic limit, applying the results of Mountain and Deutch \(^4^7\) who calculated \( S(\vec{k}, \omega) \) for a general hydrodynamic binary fluid system. From \( S(\vec{k}, \omega) \) we have obtained the spectra \( S_{ij}(\vec{k}, \omega) \) in the hydrodynamic limit.

The hydrodynamic limit of the scattered light spectrum in a binary gas mixture is the sum of contributions arising from density and concentration fluctuations:

\[
S(\vec{k}, \omega) = r_d A(\vec{k}, \omega) + r_c B(\vec{k}, \omega).
\]

(1.6)

Here \( A(\vec{k}, \omega) \) is the density fluctuation spectrum and has the same three component form as \( S_n(\vec{k}, \omega) \) for a one component gas. The transport coefficients and thermodynamic derivatives which determine the linewidths and Brillouin splitting are those of the mixture. The concentration fluctuation spectrum \( B(\vec{k}, \omega) \) has the form

\[
B(\vec{k}, \omega) = \frac{2Dk^2}{\omega^2 + (Dk^2)^2},
\]

(1.7)

a Lorentzian line at the incident frequency of HWHH \( \Gamma_D = DK^2 \), where \( D \) is the mutual diffusion coefficient of the mixture. The spectra \( A(\vec{k}, \omega) \) and \( B(\vec{k}, \omega) \) are normalized to have the same integral over all \( \omega \). The coefficient \( r_d \) then is the fraction of the scattered optical power which is contained in the density fluctuation spectrum and \( r_c \) is the fraction in the concentration fluctuation spectrum \( (r_d + r_c = 1) \). The ratio \( r_d \) is determined only by the light scattering cross sections \( A_i^2 \) and number densities \( n_i \) of the two species.

Further consideration of the gas mixtures concerns only the helium-xenon mixture. This system was chosen because of the large mass ratio of a xenon atom to a helium atom \( (m_x / m_h = 32.6) \) and the
large light scattering cross section ratio of xenon to helium \( \frac{a^2_x}{a^2_h} = 378 \). We may describe the experiment which was performed as follows. Pure xenon was introduced into the cell at a pressure (\( \sim 17 \text{ mmHg} \)) such that the spectrum \( S_{xx}(\vec{K}, \omega) \) was nearly Gaussian (\( y \sim 0.2 \) in fig. (1.1)). Helium gas was then added and the spectrum of the mixture observed as the helium pressure \( p_h \) was increased and xenon pressure held constant. The spectral density \( S_{xx}(\vec{K}, \omega) \) could be extracted from the scattered light spectrum and was measured as a function of helium pressure.

At zero helium pressure the xenon atoms are in nearly free flight over the length \( 1/K(l_x > 1/K) \). As the helium pressure is increased, however, they experience more and more numerous collisions with helium atoms over the length \( 1/K \). In the limit of high helium pressure (\( \sim 3000 \text{ mm Hg} \)) the xenon mean free path \( l_x \) will become small compared to \( 1/K (l_x \ll 1/K) \) and the xenon atoms will execute a random walk over this distance. This is the diffusion limit. The transition of the motion of the xenon atoms from free flight to random walk will have associated with it a marked change in the spectral shape of \( S_{xx}(\vec{K}, \omega) \). A distinct narrowing of \( S_{xx}(\vec{K}, \omega) \) is observed as the helium pressure is increased, with the shape approaching that of \( B(\vec{K}, \omega) \), i.e. a Lorentzian line of HWHH \( \Gamma_D = DK^2 \) where \( D \) is the mutual diffusion coefficient of the mixture and \( K \) is the magnitude of the scattering vector. In the limit of high helium pressure, the xenon atoms are dilute and are independent diffusing scatterers over the length \( 1/K \). Since the diffusion coefficient depends inversely on the pressure we have \( D \sim 1/p_h \) and the spectrum \( S_{xx}(\vec{K}, \omega) \) narrows with increased helium pressure. The form of \( S_{xx}(\vec{K}, \omega) \) when \( l_x \ll 1/K \), i.e. a Lorentzian of HWHH \( \Gamma_D = DK^2 \), indicates that the space-time behavior of \( G_{xx}(\vec{r}, t) \) is being determined by a diffusion equation in this limit.

The narrowing of \( S_{xx}(\vec{K}, \omega) \) as the xenon mean free path decreases is a manifestation of "collision narrowing". This phenomenon influences, in the way just described for \( S_{xx}(\vec{K}, \omega) \), the shape of some Doppler broadened spectral lines in gases: namely those for which pressure broadening (de-excitation by collision) is not important. Collision narrowing was first discussed by Dicke(50) who obtained the Lorentzian line shape in the
diffusion limit. Since then several authors have expanded on Dicke's work and generalized the line shape calculation to include the simultaneous effects of collision narrowing and pressure broadening.\(^{(51),(52),(53)}\)

Measurements of the combined collision narrowing and pressure broadening of several Raman lines in gaseous hydrogen have recently been reported by Murray and Javan\(^{(54)}\) and by Cooper, May, Hara and Knapp.\(^{(55)}\) Collision narrowing was first observed by Wittke and Dicke\(^{(56)}\) for a microwave transition in atomic hydrogen and by Rank and Wiggins\(^{(57)}\) in infrared absorption spectra.

The purpose of the experiments in the helium-xenon mixture was to study the evolution of \(S_{xx}(\vec{K},\omega)\) from the kinetic limit to the diffusion limit. The large mass ratio and concentration ratio of helium to xenon simplifies the calculation and measurement of \(S_{xx}(\vec{K},\omega)\) through this kinetic-diffusion transition. In the limit of high helium pressure the mean free paths for xenon and helium are small compared to \(1/K\) and \(S_{xx}(\vec{K},\omega)\) is obtainable from the hydrodynamic calculation. Because of the large xenon to helium cross section ratio the concentration fluctuation spectrum \(r_{cB}(\vec{K},\omega)\) is nearly identical with \(S_{xx}(\vec{K},\omega)\) so that \(S_{xx}(\vec{K},\omega)\) can be determined by subtracting the density fluctuation spectrum \(A(\vec{K},\omega)\) from the total spectrum. The large mass ratio \((m_x/m_h \sim 32)\) renders the density fluctuation spectrum broad compared to the concentration fluctuation spectrum which simplifies this subtraction. This method could be used to extract \(S_{xx}(\vec{K},\omega)\) from the total spectrum at all helium pressures.

The calculation of \(S_{xx}(\vec{K},\omega)\) is based on the kinetic equation for \(f_x(\vec{r},\vec{v},t)\) which, from eq. (1.5), contains collision operators for both xenon-xenon and xenon-helium collisions. The coupled equations are not required to calculate \(f_x(\vec{r},\vec{v},t)\), however, because, when xenon is dilute, fluctuations in the helium density do not significantly influence \(S_{xx}(\vec{K},\omega)\) and the helium may be taken to be in equilibrium. The operator \((\delta f_x/\delta t)_{\text{coll}}\) for xenon-helium collisions can then be approximated under this assumption. The kinetic equation for \(f_x(\vec{r},\vec{v},t)\) was solved by approximating the collision operator for xenon-xenon collisions by the kinetic model used for the one component gas. The Fokker-Planck
model (30) was used to approximate the xenon-helium collision operator. This model would seem appropriate to the xenon in a helium-xenon collision since it assumes the particle trajectories to be smooth. The xenons, because of their large mass relative to helium, undergo only a small momentum change in a collision with a helium and thus have relatively smooth trajectories.

Measurements of \( S_{xx}(\vec{R}, \omega) \) throughout the kinetic-diffusion transition show that the Fokker-Planck model is appropriate to the calculation of \( S_{xx}(\vec{R}, \omega) \) under the conditions described.

We have also made a preliminary investigation of the velocity and attenuation of sound in the helium-xenon binary mixture. In a binary gas mixture sound attenuation arises from thermal conductivity and viscosity as in the case of a pure gas but also arises from diffusion if the two components differ in molecular mass. This occurs because gradients in the component densities in a gas mixture drive the particle flux (diffusion) currents of each species, i.e., density gradients produce non-zero average particle velocities \( \vec{u}_i \) for each component \( i \). A gradient in the overall pressure in a mixture of disparate masses, as would be produced in a sound wave, sets up a relative particle flux in the mixture, that is a non-zero relative velocity \( \vec{u}_i - \vec{u}_j \). The relative velocity \( \vec{u}_i - \vec{u}_j \) is reduced in a dissipative way by intercomponent collisions and this dissipation contributes to the acoustic attenuation.

At low frequencies the contribution to the attenuation due to diffusion can be calculated from the hydrodynamic and diffusion equations for the mixture. (58), (59) The correctness of these calculations at low frequencies has been verified by experiment. (60), (61) The range over which the hydrodynamic calculation is applicable is limited on the high frequency end by the finite time required for the relaxation of the velocity difference \( \Delta \vec{u} = \vec{u}_i - \vec{u}_j \). If at \( t = 0 \), in a spatially uniform mixture, some initial velocity difference \( \Delta \vec{u}_0 \) is set up one would find at later times \( \Delta \vec{u}(t) = \Delta u_0 \exp(-t/\tau_u) \) where \( \tau_u \) is the velocity relaxation time. The effect of diffusion on the acoustic propagation can be expected to change character at acoustic frequencies.
\[ \omega \text{ such that } \omega \tau_u \sim 1. \]

Goldman \cite{62, 63} has considered the propagation of high frequency sound in a gas mixture applying a general two fluid model of a gas mixture developed by Goldman and Sirovich \cite{64, 65}. These authors, starting from the coupled kinetic equations (eqs. 1.5) and using a modified Chapman-Enskog procedure have obtained a set of hydrodynamic equations for a binary gas mixture which include the effects of the above mentioned relaxation of the velocity difference of the two components as well as the relaxation of the temperature difference. The application of this theory to the calculation of the acoustic dispersion relation \cite{62} shows a distinct relaxation of the diffusion contribution to the attenuation at frequencies such that \( \omega \tau_u \sim 1 \). We have studied this relaxation in the helium-xenon mixture.

The helium-xenon mixture with xenon dilute is particularly attractive for the study of the effects of diffusion on sound propagation because the diffusive contribution to the attenuation is very large in this system, a result of the large molecular mass ratio of xenon to helium. We have made a limited number of preliminary measurements of the Brillouin splitting and linewidths in the helium-xenon mixture at frequencies \( \omega \approx 1/\tau_u \) and have compared these to the theory of Goldman and Sirovich. Partial agreement is obtained.

C. Summary

We may summarize the significant contributions of this work as follows: 1) We have demonstrated experimentally the appropriateness of the exact solution of the Boltzmann equation via the method of the kinetic model for describing the time dependence of density fluctuations in a dilute monatomic gas, throughout the kinetic-hydrodynamic transition. 2) We have studied the phenomenon of collision narrowing by measuring the shape of the inelastic light scattering spectrum \( S_{xx}(\vec{K}, \omega) \) of xenon gas in a helium-xenon mixture. This study shows the solution of a linearized kinetic equation, with a soft collision approximation to account for xenon-helium collisions and the kinetic model approximation to account for xenon-xenon collisions, describes the kinetic-diffusion transition of \( S_{xx}(\vec{K}, \omega) \) very well. 3) We have made a preliminary study of high frequency acoustic propagation in a binary gas mixture.
References: Chapter 1

1. Summaries of the history of the kinetic theory can be found in references 2, 3 and 4 of this chapter. A delightful account of the developments in the early 1900's is given by Sidney Chapman, "Kinetic Theory 50 Years Ago," in Lectures in Theoretical Physics Vol. IX-C, edited by W.E. Britten (Gordon and Breach, New York, 1968).


23. This connection between the hydrodynamic equations and spontaneous fluctuations has been on a firm basis by means of linear response theory: R. Kubo in Lectures in Theoretical Physics (Interscience Publishers, Inc., New York, 1959) I, Chapter 4.


40. The evolution of the spectrum from the Gaussian kinetic form to the three component hydrodynamic form was first pointed out by Landau and Placzek in reference # 16 of this chapter.


CHAPTER II: THEORY - ONE COMPONENT MONATOMIC GASES

A. Introduction

In this chapter we discuss the theoretical apparatus necessary to interpret and calculate the inelastic light scattering spectrum of a dilute monatomic gas. This is largely an effort to review theoretical work which has already been done and to collect in one place information relevant to our subject.

We begin by relating the scattered light spectrum \( S(\vec{k}, \omega) \) to the density-density correlation function \( G(\vec{r}, t) \) of the system. This correlation function is the particle number density at \( (\vec{r}, t) \) given that some particle was at \( (0, 0) \). In general, we may write \( G(\vec{r}, t) \) as the sum of a "self" and "other" contribution: \( G(\vec{r}, t) = P_{s}(\vec{r}, t) + G_{o}(\vec{r}, t) \). Here \( P_{s}(\vec{r}, t) \), the "self" part, is the probability of finding the same particle at \( (\vec{r}, t) \) which was at \( (0,0) \) and \( G_{o}(\vec{r}, t) \), the "other" part, is the density of particles at \( (\vec{r}, t) \) excluding the one which was at \( (0,0) \). We discuss the space-time properties of \( G(\vec{r}, t) \), \( P_{s}(\vec{r}, t) \) and \( G_{o}(\vec{r}, t) \) and their contributions to the scattered light spectrum. We do this to illustrate the processes contributing to the spectrum and to introduce some ideas necessary to the discussion of the gas mixture experiment. We then discuss the applicability of the Boltzmann equation and present calculations of \( S(\vec{k}, \omega) \) based on the Boltzmann equation, emphasizing the exact solution via the kinetic model. We also discuss the calculation of \( S(\vec{k}, \omega) \) in the hydrodynamic limit. In the concluding section we present calculations of the self correlation function \( P_{s}(\vec{r}, t) \) in a one component gas, based on a hard collision model and on a soft collision model of interparticle collisions.

B. Rayleigh Scattering from Pure Monatomic Gases

1. Introduction

In this section we present a discussion of various properties of the light scattered by a dilute monatomic transparent gas. Of primary
concern is the spectral distribution of the scattered light, with monochromatic, collimated light incident on the gas. We shall show that this spectral distribution is related to the space-time behavior of density fluctuations in the scattering system, and describe the space-time properties of the density fluctuations. We shall also discuss the effects on the scattered light spectrum of the finite spatial extent of the incident illumination. Rationalized MKS units will be used throughout.

The experimental situation is depicted in fig. (2.1).

Figure 2.1: Experimental geometry
Monochromatic light of wave vector $\mathbf{k}_0$ in the medium and frequency $\omega_0/2\pi$ Hz illuminates a region $v_I$ in the gas of $N$ particles in a volume $V >> v_I$. The incident electric field can be well approximated by

$$\mathbf{E}_0(r, t) = \mathbf{e}_0 \mathbf{e}^{-i(\mathbf{k}_0 \cdot \mathbf{r} - \omega_0 t)}$$

(2.1)

where $\mathbf{E}_0(r, t)$, the macroscopic field in the medium, is polarized along $\mathbf{e}_0$, and $\mathbf{E}_0(r)$ determines the extent of the illuminated region. This field induces in each of the atoms a radiating dipole moment giving rise to scattered light. At a point $P$ in the focal plane of a lens in the far field, scattered light at a scattering angle $\Theta$, and wave vector $\mathbf{k}_S$ is collected and frequency analyzed. The field $\mathbf{E}(\Theta, t)$ at point $P$ may be written

$$\mathbf{E}(\Theta, t) = \sum_{j=1}^{N} \mathbf{E}'(\mathbf{r}_j) e^{i(\phi_j(t) - \omega_0 t)}$$

(2.2)

Here $\mathbf{E}'(\mathbf{r}_j)$ is the amplitude of the field scattered by particle $j$, and $\phi_j(t)$ is the phase at the detector of the wave scattered by particle $j$. The phase $\phi_j(t)$ depends on particle position $\mathbf{r}_j(t)$ and may be measured relative to that for a particle at some arbitrary origin, since only relative phases will be of interest. The phase $\phi_j(t)$ is $2\pi/\lambda_0$ (where $\lambda_0 = 2\pi/k_0$), times the difference in path length between particle $j$ and a

---

**Figure 2.2:** Geometry for determining $\phi_j(t)$. 

---
particle at the origin and referring to fig. (2.2) is given by

\[ \varphi_j(t) = \frac{2\pi}{\lambda_0} (\mathbf{CPD} - \mathbf{AOB}) = \mathbf{k}_0 \cdot \mathbf{r}_j - \mathbf{k}_s \cdot \mathbf{r}_j = (\mathbf{k}_0 - \mathbf{k}_s) \cdot \mathbf{r}_j. \quad (2.3) \]

It is thus convenient to define the scattering vector \( \mathbf{K} \):

\[ \mathbf{K} = \mathbf{k}_s - \mathbf{k}_o \quad (2.4) \]

so that

\[ \varphi_j(t) = -\mathbf{K} \cdot \mathbf{r}_j(t). \quad (2.5) \]

Since the frequency shifts involved are small we have \( k_s \approx k_o \) and from fig. (2.3) the magnitude of the scattering vector is given by

\[ K = 2k_o \sin(\Theta/2). \quad (2.6) \]

We then characterize the scattering process by the scattering vector \( \mathbf{K} \)

\[ \mathbf{K} = \mathbf{k}_s - \mathbf{k}_o \]

\[ K = 2k_o \sin(\Theta/2) \]

Figure 2.3: Determination of \( \mathbf{K} \).
and we have for the scattered field from eq. (2.2)

\[ \vec{E}(\vec{k},t) = \sum_{j=1}^{N} \vec{E}_o'(\vec{r}_j) e^{-i(\vec{k}\cdot\vec{r}_j + \omega_0 t)} \]  

(2.7)

The scattered field due to particle \( j \) is given in terms of the induced atomic dipole moment \( \vec{p}(\vec{r}_j) \).

\[ \vec{E}_o'(\vec{r}_j) = \left( \frac{k_o^2}{4\pi \varepsilon_o R} \right) \left\{ \left[ \vec{P}(\vec{r}_j) \cdot \frac{\vec{E}_o}{\varepsilon} \right] X \vec{k}_s \right\} X \vec{k}_s \]  

(2.8)

Here \( \varepsilon_o \) is the vacuum permittivity, \( \varepsilon \) is the dielectric constant of the gas, \( \frac{\vec{p}(\vec{r}_j)}{\varepsilon_o/\varepsilon} \) is the induced atomic dipole moment, reduced by \( \varepsilon_o/\varepsilon \) since it is immersed in a medium of dielectric constant \( \varepsilon \), and \( R \) is the distance from \( v_I \) to the detector. The induced atomic dipole moment \( \vec{p}(\vec{r}_j) \) is given by

\[ \vec{p}(\vec{r}_j) = \frac{\vec{P}(\vec{r}_j)}{n_o} \]  

(2.9)

where \( \vec{P}(\vec{r}) \) is the macroscopic polarization per unit volume of the medium at \( \vec{r} \), and \( n_o \) the particle number density. \( \vec{P}(\vec{r}) \) can be written in terms of the incident macroscopic field \( \vec{E}_o(\vec{r}) \)

\[ \vec{P}(\vec{r}) = \varepsilon_0 \chi \vec{E}_o(\vec{r}) \]  

(2.10)

where \( \chi \) is the average electric susceptibility and is given by

\[ \chi = \varepsilon/\varepsilon_o - 1. \]  

Assuming the medium to be nonmagnetic so that \( \mu = \mu_o \) we have \( n^2 = \varepsilon/\varepsilon_o \) and

\[ \chi = n^2 - 1 \]  

(2.11)

where \( n \) is the index of refraction of the gas. Letting \( k_o \) be the incident wave length in a vacuum we find
For a monatomic gas the induced moment $\vec{p}$ is along $\vec{E}_0$ so that

$$k_o^2 = \frac{\epsilon}{E_0} (k_o \nu)^2.$$ \hspace{1cm} (2.12)

Using eqs. (2.9) - (2.13) in eq. (2.8) we obtain

$$E'(\vec{r}_j) = \frac{(k_o \nu)^2}{4 \pi R} \sin \varphi \left( \frac{n^2 - 1}{n_o} \right) E_0(\vec{r}_j) \equiv Z E_0(\vec{r}_j),$$ \hspace{1cm} (2.14)

and the scattered field amplitude becomes

$$E(\vec{K}, t) = Z \sum_{j=1}^{N} E_0(\vec{r}_j) \ e^{-i(\vec{K} \cdot \vec{r}_j + \omega_o t)}.$$ \hspace{1cm} (2.15)

where

$$Z = \left( \frac{(k_o \nu)^2}{4 \pi R} \right) \left( \frac{n^2 - 1}{n_o} \right) \sin \varphi.$$ \hspace{1cm} (2.16)

We can now proceed to calculate the spectral power distribution of the scattered field, $E(\vec{K}, t)$. Because the phase of the wave scattered by each atom varies randomly in time as it moves about in the gas, it is impossible to predict the exact time dependence of $E(\vec{K}, t)$. Such information is in fact not necessary since one can obtain those temporal properties of $E(\vec{K}, t)$ of interest here statistically by forming the two time field correlation function $< \langle E(\vec{K}, t) \ E^*(\vec{K}, t+\tau) \rangle$. This field correlation function is obtained by measuring $E(\vec{K}, t)$ and $E^*(\vec{K}, t+\tau)$ for many similarly prepared systems and ensemble averaging their product. The ensemble of all possible sample functions defines a random process. Since the experimental conditions under which the average is carried out are time independent, the random process $E(\vec{K}, t)$ will be stationary and the field correlation function will be independent of starting time $t$ so that we may define the correlation function $R_E(\tau)$:
\[ R_E(\tau) = \left\langle E(\mathbf{r}, t) E^*(\mathbf{r}, t + \tau) \right\rangle. \] (2.17)

For such a stationary random process the spectral power density \( S_E(\mathbf{r}, \omega) \), is defined by (2)

\[ S_E(\mathbf{r}, \omega) = \int_{-\infty}^{\infty} d\tau \ e^{-i\omega \tau} R_E(\tau) \] (2.18)

and is the quantity of direct physical interest here since \( S_E(\mathbf{r}, \omega) d\omega \) is proportional to the optical power in the field \( E(\mathbf{r}, t) \) in the frequency interval \( (\omega, \omega + d\omega) \). The constant of proportionality is established by noting that

\[ \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} S_E(\mathbf{r}, \omega) = R_E(0) = \left\langle |E(\mathbf{r}, t)|^2 \right\rangle = \frac{2I(\mathbf{r})}{\varepsilon C_m} \] (2.19)

where \( C_m \) is the velocity of light in the medium and \( I(\mathbf{r}) \) the total scattered intensity in the direction \( \mathbf{k}_s = \mathbf{k}_o + \mathbf{K} \). Defining \( I(\mathbf{r}, \omega) d\omega \) to be the optical power per unit area lying between \( \omega \) and \( \omega + d\omega \) we have

\[ I(\mathbf{r}, \omega) = \frac{\varepsilon C_m}{4\pi} S_E(\mathbf{r}, \omega). \] (2.20)

The spectral intensity distribution of the scattered light can thus be obtained from the two time correlation function and eq. (2.17).

We now proceed to relate \( R_E(\tau) \) to density correlations in the scattering medium. Using eq. (2.15) we have

\[ R_E(\tau) = \left\langle E(\mathbf{r}, t) E^*(\mathbf{r}, t + \tau) \right\rangle = \sum_{j=1}^{N} \sum_{k=1}^{N} \left\langle E_o(\mathbf{r}_j(t)) e^{-i(\mathbf{k}_j \cdot (t + \tau_k) + \omega_k t)} \right\rangle \] (2.21)
The double sum consists of \( N \) identical terms for which \( j = k \) and \( N(N-1) \) identical terms for which \( j \neq k \) so that

\[
R_E(t) = \mathcal{Z}^2 N \ e^{i \omega_0 t} \left\{ \langle E_0(\vec{r}_1(t)) E_0(\vec{r}_2(t+t)) \rangle e^{-i \vec{r}_1 \cdot (\vec{r}_1(t) - \vec{r}_1(t+t))} \right. \\
\left. + (N-1) \langle E_0(\vec{r}_1(t)) E_0(\vec{r}_2(t+t)) \rangle e^{-i \vec{r}_1 \cdot (\vec{r}_1(t) - \vec{r}_2(t+t))} \right\}. \tag{2.22}
\]

The correlation function, \( R_E(\tau) \), for the scattered field thus depends on ensemble averages of functions of the particle positions only. The particle positions \( \vec{r}_1(t) \) and \( \vec{r}_2(t) \) will, in general, take on a range of values in the various systems of the ensemble. It is convenient to express this range in terms of probability distributions of particle positions. Ensemble averages such as in eq. (2.22) are then given by integrals over the appropriate probability distributions. The evaluation of the ensemble averages in eq. (2.22) requires joint probability distributions \( P_{11}(\vec{r}', \vec{r}, \tau) \) and \( P_{21}(\vec{r}', \vec{r}, \tau) \). These are defined as follows:

\[
P_{21}(\vec{r}', \vec{r}, \tau) \ d^3r \ d^3r' = \text{probability of finding particle 1 in } d^3r \text{ at } (\vec{r}, t) \text{ and particle 2 in } d^3r' \text{ at } (\vec{r}', t + \tau). \tag{2.23}
\]

\[
P_{11}(\vec{r}', \vec{r}, \tau) \ d^3r \ d^3r' = \text{probability of finding particle 1 in } d^3r \text{ at } (\vec{r}, t) \text{ and in } d^3r' \text{ at } (\vec{r}', t + \tau). \tag{2.24}
\]

The ensemble averages in eq. (2.22) may be expressed in terms of \( P_{11}(\vec{r}', \vec{r}, \tau) \) and \( P_{21}(\vec{r}', \vec{r}, \tau) \) as:

\[
R_E(t) = \mathcal{Z}^2 N \ e^{i \omega_0 t} \left\{ \int \int \ E_0(\vec{r}) E_0(\vec{r}') \ e^{-i \vec{r}_1 \cdot (\vec{r} - \vec{r}')} \right. \\
\left. \left[ P_{11}(\vec{r}', \vec{r}, \tau) + (N-1) P_{21}(\vec{r}', \vec{r}, \tau) \right] \right\}. \tag{2.25}
\]
The integrals are performed over the volume \( V \), but since \( V \) is arbitrary we may let \( V, N \to \infty \), with \( N/V = n_0 \), and extend the limits of integration to infinity. Under these conditions the system is homogeneous in space and the joint probability distributions \( P_{11}(\mathbf{r}', \mathbf{r}, \tau) \) and \( P_{21}(\mathbf{r}', \mathbf{r}, \tau) \) depend only on the relative position vector \( \mathbf{r}' - \mathbf{r} \). It is convenient then to express \( P_{11} \) and \( P_{21} \) in terms of conditional probability distributions defined as follows:

\[
P_s(\mathbf{r}, \tau) = \text{probability of finding a particle in } d^3r \text{ at } (\mathbf{r}, \tau) \text{ given that the same particle was at } (0,0). \tag{2.26}
\]

\[
P_o(\mathbf{r}, \tau) = \text{probability of finding particle } i \text{ at } (\mathbf{r}, \tau) \text{ given that particle } j \text{ was at } (0,0) \text{ where } i \neq j. \tag{2.27}
\]

We may in fact write

\[
P_{11}(\mathbf{r}', \mathbf{r}, \tau) = P_s(\mathbf{r}' - \mathbf{r}, \tau) P(\mathbf{r}) \tag{2.28}
\]

\[
P_{21}(\mathbf{r}', \mathbf{r}, \tau) = P_o(\mathbf{r}' - \mathbf{r}, \tau) P(\mathbf{r}) \tag{2.29}
\]

where \( P(\mathbf{r}) \, d^3r \) is the probability of finding particle 1 in \( d^3r \) at \( \mathbf{r} \), that is

\[
P(\mathbf{r}) = \frac{1}{V}. \tag{2.30}
\]

Using eqs. (2.25), (2.28), (2.29), and (2.30) and making the change of variable \( \mathbf{r}' - \mathbf{r} = \mathbf{s} \), we find for \( R_E(\tau) \)

\[
R_E(\tau) = \sum_{n=2}^\infty n_0 e^{i \omega \tau} \int d^3s \left\{ \left[ \int d^3r E_0(\mathbf{r}) E(\mathbf{r} + \mathbf{s}) \right] e^{i \mathbf{K} \cdot \mathbf{s}} \left[ P_s(\mathbf{s}, \tau) + (N-1) P_o(\mathbf{s}, \tau) \right] \right\}.
\]

The integral in curly brackets is the spatial folding of the incident field distribution with itself and is a function of \( \mathbf{s} \) only so that we may write
\[ A(\vec{s}) \equiv \int d^3 r \ E_o(\vec{r}) E_o(\vec{r} + \vec{s}) \]  

(2.32)

and

\[ R_E(\tau) = Z^2 n_0 e^{i\omega \tau} \int d^3 s \ A(\vec{s}) e^{i\vec{K} \cdot \vec{s}} [\bar{P}_s(\vec{s}, \tau) + (N-1) P_0(\vec{s}, \tau)]. \]  

(2.33)

We shall demonstrate in sec (II B A) that the configuration of the illuminated region in our experimental arrangement is such that it is safe to replace \( A(\vec{s}) \) in eq. (2.33) by \( A(0) \), so that we obtain for \( R_E(\tau) \):

\[ R_E(\tau) = Z^2 n_0 A(0) e^{i\omega \tau} \int d^3 s \ e^{i\vec{K} \cdot \vec{s}} [\bar{P}_s(\vec{s}, \tau) + (N-I) P_0(\vec{s}, \tau)]. \]  

(2.34)

The scattered light spectrum \( S_E(\vec{K}, \omega) \) may then be obtained from eqs. (2.34) and (2.18) and we find:

\[ S_E(\vec{K}, \omega + \omega_o) = Z^2 n_0 A(0) \int d^3 s \int d\tau \ e^{i(\vec{R} \cdot \vec{s} - \omega \tau)} [\bar{P}_s(\vec{s}, \tau) + (N-I) P_0(\vec{s}, \tau)]. \]  

(2.35)

where \( \omega_o \) is the shift in frequency from \( \omega \). Apart from constants, then, the spectral distribution of the scattered light is determined by the space-time behavior of the conditional probability distributions \( P_s(\vec{r}, \tau) \) and \( P_0(\vec{r}, \tau) \). Eq. (2.35) may be written more succinctly in terms of the conditional density distribution \( G(\vec{r}, \tau) \) defined as follows:

\[ G(\vec{r}, \tau) = P_s(\vec{r}, \tau) + (N-I) P_0(\vec{r}, \tau). \]  

(2.36)

From the definition of \( P_0(\vec{r}, \tau) \) the quantity \((N-1) P_0(\vec{r}, \tau)\) is the number density of the particles \(2\ldots N\) at \((\vec{r}, \tau)\) subject to \#1 being at \((0, 0)\). Also \( P_s(\vec{r}, \tau) \) is the number density of particle \#1 at \((\vec{r}, \tau)\). The conditional density distribution \( G(\vec{r}, \tau) \) then has the following meaning:
G (\vec{r}, \tau) = \text{average number of particles in } d^3 r \text{ at } (\vec{r}, \tau) \text{ given that a particle was at } (0,0). \quad (2.37)

so that

\[ S_E(\vec{K}, \omega_0 + \omega) = Z n_o A(0) \int d^3 s \int dt \ e^{i(\vec{K} \cdot \vec{s} - \omega t)} G(\vec{s}, t). \quad (2.38) \]

Thus the spectral power density of the scattered field with a momentum transfer of \( K \) and energy transfer of \( \omega \) is proportional to the space-time Fourier transform of the conditional density distribution \( G(\vec{r}, \tau) \) evaluated at \( \vec{K} \) and \( \omega \).

2. Properties of the Particle Distributions and Scattered Light Spectrum

a) The Conditional Density Fluctuation Distribution

We now turn to discuss specific space time properties of \( P_s (\vec{r}, \tau) \), \( P_o (\vec{r}, \tau) \) and \( G (\vec{r}, \tau) \). We do this to further simplify the expression for the total scattered intensity, and to clarify the contributions of the various distributions to the observed spectrum. We consider first the limit \( \tau \to \infty \). In general, as we shall see, the particle density at \( (\vec{r}, \tau) \) is influenced to some extent by the initial placement of a particle at \( (0,0) \), which produces a time dependent density disturbance in the medium. As time \( \tau \) increases, however, this disturbance dies away and in the limit \( \tau \to \infty \), the system retains no "memory" of the initial condition. In this limit then the conditional density \( G (\vec{r}, \tau) \) becomes spatially constant approaching the average particle density \( n_o \):

\[ \lim_{\tau \to \infty} G(\vec{r}, \tau) = n_o. \quad (2.39) \]

The conditional density \( G(\vec{r}, \tau) \) is, then, a space-time constant, \( n_o \), plus a distribution \( \rho(\vec{r}, \tau) \) which approaches zero at \( t \to \infty \):

\[ \rho(\vec{r}, \tau) \equiv G(\vec{r}, \tau) - n_o \quad (2.40) \]

where

\[ \lim_{\tau \to \infty} \rho(\vec{r}, \tau) = 0. \quad (2.41) \]
So defined, \( \rho (\vec{r}, \tau) \) is the deviation in the density from \( n_0 \) at \( (\vec{r}, \tau) \) given that a particle was located at \((0, 0)\). We shall refer to \( \rho (\vec{r}, \tau) \) as a conditional density fluctuation distribution. The separation of \( G (\vec{r}, \tau) \) into a constant \( n_0 \) plus an \( (\vec{r}, \tau) \) dependent part is convenient because the constant term does not contribute to the scattering as may be seen by substituting \( G (\vec{r}, \tau) = \rho (\vec{r}, \tau) + n_0 \) into eq. (2.28) from which we find

\[
S_E (\vec{k}, \omega + \omega) = Z^2 n_0 A(0) \left[ n_0 (2\pi)^4 \delta (\omega) \delta (\vec{k}) + \int d^3 \vec{s} \int d\tau e^{i(\vec{k} \cdot \vec{s} - \omega \tau)} \rho (\vec{s}, \tau) \right].
\]

Thus the term arising from \( \rho \) contributes a component unshifted in frequency only in the forward (\( \vec{K} = 0 \)) direction. Since only finite scattering angles are of interest this term will be deleted and we have

\[
S_E (\vec{k}, \omega + \omega) = Z^2 n_0 A(0) S_\rho (\vec{k}, \omega),
\]

where we define

\[
S_\rho (\vec{k}, \omega) \equiv \int d^3 \vec{r} d\tau e^{i(\vec{k} \cdot \vec{r} - \omega \tau)} \rho (\vec{r}, \tau).
\]

b) Extinction Coefficients

Before discussing further the space-time properties of the various distribution functions it will be convenient to obtain expressions for the energy angle extinction \( h (\vec{K}, \omega) \) and the solid angle extinction \( h (\vec{K}) \) defined as follows:

\[
h (\vec{K}, \omega) d\Omega = \text{fraction of incident power scattered into a solid angle element } d\Omega \text{ with a frequency shift in the interval } (\omega, \omega + d\omega) \text{ per unit length of scattering volume}.
\]
\[ h(\vec{K}) \, d\Omega = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} d\omega h(\vec{K}, \omega) \, d\omega \, d\Omega \]

fraction of incident power scattered into a solid angle element \( d\Omega \) per unit length of the scattering volume.

(2.46)

To obtain \( h(\vec{K}, \omega) \) in terms of \( S^p(\vec{K}, \omega) \) we must evaluate \( A(0) \) in eq. (2.43). From Eq. (2.32) we have for \( A(0) \)

\[ A(0) = \int d^3 r \, E^2_o(r^2). \]

(2.47)

Let us assume for the illuminated region a focused laser beam of length \( L \) with a uniform Gaussian intensity distribution normal to the beam axis so that the incident field amplitude \( E_o(r^2) \) depends only on \( r \), the distance from the beam axis. Using \( E_o^2(r) = 2I(r)/c_m\varepsilon \), where \( I(r) \) is the radial intensity distribution and integrating over the beam cross section \( (d^3 r = L \, da) \) we then have

\[ A(0) = \frac{2L}{c_m\varepsilon} \int I(r) \, da. \]

The total incident power, \( P \), is given by

\[ P = \int I(r) \, da \]

(2.48)

and we have

\[ A(0) = \frac{2LP}{c_m\varepsilon}. \]

(2.49)

The energy angle extinction by its definition is given in terms of the scattered intensity \( I(\vec{K}, \omega) \) by
Using eqs. (2.16), (2.20), (2.43), and (2.49) we may write the scattered intensity

\[
I(\vec{k}, \omega) = \frac{L \rho}{2\pi} \left\{ \frac{(k^0)^2 (n^2 - 1) \sin \phi}{4\pi R^2 n_0} \right\}^2 n_0 \ S_\rho (\vec{k}, \omega) .
\]  

(2.51)

Thus

\[
h(\vec{k}, \omega) = \frac{h_0}{2\pi} \ S_\rho (\vec{k}, \omega) \quad (2.52)
\]

where

\[
h_0 \equiv \left\{ \frac{(k^0)^2 \sin \phi}{4\pi} \right\}^2 \frac{(n^2 - 1)^2}{n_0} .
\]  

(2.53)

Thus the probability for scattering with momentum transfer \( \vec{k} \) and energy transfer \( \omega \) is the space-time Fourier transform, evaluated at \((\vec{k}, \omega)\), of the of the conditional fluctuation distribution \( \rho(\vec{r}, \tau) \).

We may obtain the extinction per unit solid angle, \( h(\vec{k}) \) by integrating \( h(\vec{k}, \omega) \) over all frequencies in the scattered light:

\[
h(\vec{k}) = \int_{-\infty}^{\infty} d\omega \ h(\vec{k}, \omega) .
\]  

(2.54)

We find from eqs. (2.52) and (2.44) that
So defined, \( h(\vec{K}) \) is the probability that a photon will be scattered into a solid angle element \( d\Omega \) about \( \vec{k}_s = \vec{k}_o + \vec{K} \), per unit length of travel in the medium. Eq. (2.55) shows that \( h(\vec{K}) \), and thus the scattered intensity, depends only on the \( \tau = 0 \) form of the conditional density fluctuation distribution, \( \rho(\vec{r},0) \).

c) The Properties of \( P_s(\vec{r},\tau) \), \( P_0(\vec{r},\tau) \), and \( \rho(\vec{r},\tau) \).

We now proceed to discuss further the properties of \( P_s(\vec{r},\tau) \), \( P_0(\vec{r},\tau) \), and \( \rho(\vec{r},\tau) \). Eqs. (2.40) and (2.36) may be used to express \( \rho \) in terms of \( P_s \) and \( P_0 \):

\[
\rho(\vec{r},\tau) = P_s(\vec{r},\tau) + N P_0(\vec{r},\tau) - n_0. \tag{2.56}
\]

We have set \( N = N-1 \) here and will continue to do so since the limit \( N, V \rightarrow \infty \) is assumed. We shall discuss separately the properties of \( P_s \) and \( P_0 \) and use eq. (2.56) to obtain \( \rho \).

The physical situation which the distributions \( P_s \) and \( P_0 \) pertain to is the following. Suppose we have a dilute monatomic gas in a large container. Imagine, at some time, stopping the molecular motion. We call this time \( \tau = 0 \) and set the spatial origin of coordinates to be at the center of a particle, chosen at random, which we will call particle #1. We now have the initial condition of particle #1 being at \((0,0)\). We now let the gas continue in its motion and measure the density of particle #1 and of the other particles for \( \tau > 0 \). Repeating this operation many times and averaging the
measured density distribution of particle \#1 yields \( P_S(\vec{r}, \tau) \).
Averaging the measured density distribution of the other particles yields \( N_P(\vec{r}, \tau) \). Because the gas is isotropic the distributions \( P_S \), \( P_O \), and \( \rho \) have spherical symmetry about \( \vec{r} = 0 \), depending only on \( r = |\vec{r}| \).

We discuss first the evolution of \( P_S \). At \( \tau = 0 \) the self distribution, \( P_S(\vec{r}, 0) \), is a Dirac delta function at the origin since particle \#1 is known to be at \((0, 0)\). We now define \( \tau_c \), the average time between collisions for a given particle. Particle \#1 will, on the average, not undergo a collision with another particle until \( \tau \sim \tau_c \). For short times \((0 < \tau < \tau_c)\) particle \#1 is in free flight and \( P_S(\vec{r}, \tau) \) is a Gaussian spatial distribution, falling to \( 1/e \) of its peak value at \( r = v_m \tau \), where \( v_m = \sqrt{2k_BT/m} \) is the most probable molecular speed. The Gaussian spatial distribution of \( P_S \) is a result of the Gaussian distribution of molecular speeds. At long times \((\tau > \tau_c)\) particle \#1 collides with the other particles and executes Brownian motion. In this limit the self distribution is still Gaussian in space but now with a \( 1/e \) width given by \( r = \sqrt{4D\tau} \) where \( D \) is the self diffusion constant for the gas.\(^{(3)}\) Note that the volume integral of \( P_S \) is always unity. In the limit \( \tau \to \infty \) particle \#1 is found anywhere in \( V \) with equal probability so that in this limit \( P_S \to 1/V \equiv 0 \). Fig. (2.4a) shows the evolution of \( P_S(\vec{r}, \tau) \). The forms of the distributions in the various regimes are given in Table (2.1).

We now consider the evolution of \( N_P(\vec{r}, \tau) \), the density of the other particles given that particle \#1 was at the origin at \((0, 0)\). At \( \tau = 0 \), \( N_P \) will be influenced by the presence of particle \#1 since the other particles will be deflected from about \( \vec{r} = 0 \) by collisions with particle \#1. The probability of a particle being found at a position, \( \vec{r} \), will depend on its energy of interaction with particle \#1, with the distribution in energy having the Maxwell-Boltzmann form. If we assume a pair potential energy, \( \phi(r) \), for an interatomic separation of \( r \), then
NP₀(\vec{r}, 0) will be given by

\[ NP₀(\vec{r}, 0) = n₀ e^{\frac{-\Phi(\vec{r})}{k_BT}}. \] (2.57)

For small \( r \), where \( \varphi(r) \) is large and positive, we have \( NP₀ = 0 \).
For large \( r \), outside of the range of molecular interaction we find \( \varphi(r) = 0 \) and \( NP₀ = n₀ \), its equilibrium value.

It is convenient to define the net correlation function \( \mathcal{g}(r) \) by

\[ n₀ \mathcal{g}(r) \equiv NP₀(\vec{r}, 0) - n₀ \] (2.58)

so that \( n₀ \mathcal{g}(r) \) is the deviation of \( NP₀(\vec{r}, 0) \) from its equilibrium value.

From eqs. (2.57) and (2.58) we have for the dilute monatomic gas:

\[ \mathcal{g}(r) = e^{\frac{-\Phi(\vec{r})}{k_BT}} - 1. \] (2.59)

A vast amount of experimental evidence indicates that \( \varphi(r) \) for a monatomic gas is well approximated by the Lennard-Jones form

\[ \varphi(r) = 4\epsilon \left\{ \left( \frac{a}{r} \right)^{12} - \left( \frac{a}{r} \right)^6 \right\} \]

where \( \epsilon \) and \( a \) are the attractive potential well depth and the interaction range respectively. Fig. (2.5) shows \( \varphi(r) \) for xenon gas (\( \epsilon \approx 220 \, ^0\text{K}, \, a \approx 4.1 \, \text{Å} \)) and the resulting \( \mathcal{g}(r) \) at room temperature.

We have drawn the contribution, \( n₀ \mathcal{g}(r) \), to \( NP₀(\vec{r}, 0) \), arising because the other particles distribute themselves according to \( \exp[-(\varphi(r)/k_BT)] \), as the shaded region in fig (2.4b).

Fig (2.5) shows that \( \mathcal{g}(r) \) is small for \( r > 2a \). This allows us to simplify the expression for \( h(\vec{r}) \), the extinction per unit solid angle by using eqs. (2.55, 6, and 8), from which we find

\[ h(\vec{r}) = h₀ \int d^3 \vec{r} \, e^{i\vec{k} \cdot \vec{r}} \left[ P₀(\vec{r}, 0) + n₀ \mathcal{g}(r) \right] \] (2.60)
Table 2.1: The Distributions $P_3(r, \tau)$, $NP_0(r, \tau)$, and $\rho(r, \tau)$

$P_3(r, \tau)$:

$\tau = 0$:
$$P_3(r, 0) = \delta(r)$$

$\tau < \tau_c$:
$$P_3(r, \tau) = (\pi \nu_m \tau)^{\frac{3}{2}} \exp\left[-\left(\frac{r}{\nu_m \tau}\right)^2\right], \text{ where } \nu_m = \sqrt{\frac{2kT}{m}}$$

$\tau > \tau_c$:
$$P_3(r, \tau) = (4\pi D \tau)^{\frac{3}{2}} \exp\left[-\left(\frac{r}{\sqrt{4D\tau}}\right)^2\right]$$

$$\lim_{\tau \to \infty} P_3(r, \tau) = \frac{1}{\nu} \equiv 0$$

$NP_0(r, \tau)$:

$\tau = 0$:
$$NP_0(r, 0) = n_0 + n_0 \chi(r)$$

$\tau < \tau_c$:
$$NP_0(r, \tau) = n_0 + n_0 \chi(r) \otimes P_3(r, \tau)$$

$\frac{a}{\nu_m} < \tau < \tau_c$:
$$NP_0(r, \tau) = n_0 + n_0 \chi(r) P_3(r, \tau) \text{ where } \chi(r) = \frac{1}{4\pi D \tau}$$

$\tau > \tau_c$:
$$NP_0(r, \tau) = n_0 - P_3(r, \tau) + (1 + n_0 \chi(r)) H(r, \tau)$$

$$\lim_{\tau \to \infty} NP_0(r, \tau) = n_0$$

$\rho(r, \tau)$:

$\tau = 0$:
$$\rho(r, 0) = \delta(r) + n_0 \chi(r)$$

$\tau < \tau_c$:
$$\rho(r, \tau) = P_3(r, \tau) + n_0 \chi(r) \otimes P_3(r, \tau)$$

$\frac{a}{\nu_m} < \tau < \tau_c$:
$$\rho(r, \tau) = (1 + n_0 \chi(r)) P_3(r, \tau)$$

$\tau > \tau_c$:
$$\rho(r, \tau) = (1 + n_0 \chi(r)) H(r, \tau)$$

$$\lim_{\tau \to \infty} \rho(r, \tau) = 0$$
Figure 2.4a: Temporal evolution of $P_s(\mathbf{r}, \tau)$. 
The scale in $\vec{r}$ has been reduced for $\tau > \tau_c$ in order to fit everything on the page. The distribution $NP_0$ is broadest in space in this limit.

Figure 2.4b: Temporal evolution of $NP_0(\vec{r}, \tau)$
The scale in $\vec{r}$ has been reduced for $\tau > \tau_c$ in order to fit everything on the page. The distribution $\rho$ is broadest in space in this limit.

Figure 2.4c: Temporal evolution of $\rho(\vec{r}, \tau)$
for Xe at $T = 295^\circ K$:

$a = 4.1\,\text{Å}$

$\frac{\varepsilon}{k_B T} = 0.74$

$$\gamma(r) = e^{-\frac{\Phi(r)}{k_B T}} - 1$$

Figure 2.5: The net correlation function for xenon gas.
or

\[ h(\mathbf{K}) = h_0 \left[ 1 + n_o \int d^3 r e^{i \mathbf{K} \cdot \mathbf{r}} \mathscr{A}(r) \right] \]  \hspace{1cm} (2.61)

where we have used \( \mathcal{P}_s(\mathbf{r}, 0) = \delta(\mathbf{r}) \). If the incident wavelength is 6328 Å we will have \( K < 2 \times 10^5 \text{ cm}^{-1} \) and \( Kr \lesssim 10^{-2} \) where \( \mathscr{A}(r) \) is appreciable so that we may make the approximation \( \exp[iK \cdot \mathbf{r}] = 1 \) in eq. (2.61) and we find

\[ h(\mathbf{K}) = h_0 \left[ 1 + n_o \int d^3 r \mathscr{A}(r) \right]. \]  \hspace{1cm} (2.62)

The total scattered intensity per unit solid angle is independent of \( \mathbf{K} \) and thus independent of scattering angle, \( \theta \). This is in accord with the experimental results of Watson and Clark (7) who found \( h(\mathbf{K}) \) for nitrogen gas at 1 atm. to be independent of \( \theta \).

Eq. (2.62) shows that the total scattered intensity is proportional to \( 1 + n_o \int d^3 r \mathscr{A}(r) \), the effective number of particles localized near the origin at \( \tau = 0 \). Particle #1 contributes the \( 1 \) and, by definition of \( \mathscr{A}(r) \) in eq. (2.58), \( n_o \int d^3 r \mathscr{A}(r) \) is the number of other particles displaced from about the origin by particle #1. Since, in the absence of particle #1, the other particles would have a density of \( n_o \), we see that \( \int d^3 r \mathscr{A}(r) \) is the effective molecular volume, \( v^* \), of particle #1

\[ v^* \equiv \int d^3 r \mathscr{A}(r). \]  \hspace{1cm} (2.63)

The effective volume, \( v^* \), may be positive or negative depending, respectively, whether the molecular attraction or repulsion predominates. In a dilute gas particles occupy only a small fraction of the total volume so that \( |n_o v^*| \ll 1 \).++ In this limit eq. (2.62) shows that the net correlation has only a small effect on the scattered intensity.

++ For xenon at STP we have \( n_o v^* \approx -2 \times 10^{-2} \).
We now consider \(NP_0(r, \tau)\) for \(0 < \tau < \tau_0\). We are still concerned with short times such that particle \#1 has, on the average, not yet collided with any of the other particles. The situation, then, is essentially the same as at \(\tau = 0\) except that particle \#1 is not localized at \(r = 0\) but has a Gaussian spatial distribution of width \(\sim \tau\). If particle \#1 is distributed in space the probability, \(P_0(r, \tau)\), of finding another particle at \(r\) will be the probability, \(P(r' - r)\), of finding a particle at \(r\), given that particle \#1 was at \(r'\), times the probability, \(P_s(r'; \tau)\), of finding \#1 at \(r'\), summed over all \(r'\). From eq. (2.58) we find that \(P(r' - r)\), the probability of finding another particle at \(r\) if particle \#1 is known to be at \(r'\), is given by

\[
P(r' - r) = \frac{n_0}{N} (1 + n_0 \mathcal{L}(r' - r')).
\]

We thus find for \(NP_0(r, \tau)\)

\[
NP_0(r, \tau) = \int d^3r' P(r' - r) P_s(r'; \tau)
\]

and therefore

\[
NP_0(r, \tau) - n_0 = n_0 \mathcal{L}(r) \otimes P_s(r, \tau)
\]

(2.64)

where \(\otimes\) denotes convolution. For \(\tau\) such that \(v_m \tau > a\), where \(a\) is the molecular diameter, the distribution \(P_s(r, \tau)\) will be broad compared to \(\mathcal{L}(r)\) and

\[
n_0 \mathcal{L}(r) \otimes P_s(r, \tau) = n_0 v^* P_s(r, \tau)
\]

so that

\[
NP_0(r, \tau) - n_0 = n_0 v^* P_s(r, \tau).
\]

(2.65)

This contribution to \(NP_0\), due to the Boltzmann distribution of the other particles around particle \#1, will be called the "direct" contribution to \(NP_0\) and is depicted as the shaded region in fig. (2.4b). The volume integral of the shaded region is \(n_0 v^*\) as was the case for \(\tau = 0\). From eq. (2.56), the conditional density fluctuation dis-
tribution, \( \rho(\vec{r}, \tau) \), is given by

\[
\rho(\vec{r}, \tau) = \left(1 + n_0 v^*\right) P_s(\vec{r}, \tau)
\]  \hspace{1cm} (2.66)

and is shown in fig. (2.4c). Since \(|n_0 v^*| \ll 1\), the distribution \( \rho(\vec{r}, \tau) \) is dominated by the contribution of particle \#1 for \( 0 \leq \tau < \tau_c \).

We now consider \( N P_0(\vec{r}, \tau) \) and \( \rho(\vec{r}, \tau) \) for times long compared to the collision time \( (\tau > \tau_c) \). The distribution of particle \#1, \( P_s(\vec{r}, \tau) \), is Gaussian in space but, because for long times particle \#1 is in diffusion, has a width in space which increases as \( \sqrt{\tau} \), as stated above. The direct (shaded) portion of \( NP_0 \), just discussed, will still be present having the same shape as \( P_s \) and a volume integral of \( n_0 v^* \) as was the case for \( a/v_m < \tau < \tau_c \). It, however, is not shown in fig. (2.4b) for \( \tau > \tau_c \) to avoid cluttering. The direct (shaded) contribution to \( NP_0 \) will then be

\[
N P_0^{dir}(\vec{r}, \tau) = n_0 v^* P_s(\vec{r}, \tau).
\]  \hspace{1cm} (2.67)

For \( \tau > \tau_c \), there will be an additional contribution to \( NP_0 \) which arises from collisions of particle \#1 with the other particles. For lack of a better name we call this the "indirect" contribution to \( NP_0 \) and denote it by \( NP_0^{in}(\vec{r}, \tau) \). The indirect contribution to \( NP_0 \) is the disturbance in the density of the other particles produced by collisions with particle \#1 as it diffuses among them. The adjustment of the density of the other particles under the influence of diffusing particle \#1 may be viewed as occurring in two stages, so that the indirect contribution \( NP_0^{in} \) will be the sum of two parts. During the first, or local, stage, the other particles come into local equilibrium with particle \#1. In diffusing among them particle \#1 will exert on the other particles an average force per unit volume, \( \vec{F}(\vec{r}, \tau) \), related to its distribution, \( P_s(\vec{r}, \tau) \). This force arises because the density of particle \#1 is spatially nonuniform, and will be calculated in the next section. In the establishment of local equilibrium, the density of the other particles adjusts itself so as
to set up a pressure gradient which cancels $\vec{F}(\vec{r}, \tau)$. This is the local equilibrium condition. If collisions conserve momentum and energy the disturbance in the density of the other particles due to the establishment of local equilibrium, $N_{P_o}^{loc}$, is

$$N_{P_o}^{loc}(\vec{r}, \tau) = - (1 + n_o v^*) \rho_o(\vec{r}, \tau)$$

(2.68)

as will be shown in the next section. This contribution to $N_{P_o}$, since it is negative, represents a decrease in the density of the other particles from about $\vec{r} = 0$. This is so because particle #1, in spreading out from $\vec{r} = 0$, pushes some of the other particles along with it. Volume integration of $N_{P_o}^{loc}$ shows that a total of $1 + n_o v^*$ particles are displaced by particle #1.

The spreading of particle #1, therefore, removes the available space for $1 + n_o v^*$ of the other particles, creating an apparent excess of $1 + n_o v^*$ particles distributed about $\vec{r} = 0$. The second stage of equilibration is the relaxation of this excess density. The temporal evolution of the excess density, if we limit our consideration to time intervals long compared to the collision time, $\tau_c$, is governed by the laws of hydrodynamics. The perturbation from equilibrium due to the excess density will excite the normal modes of the system which, in the hydrodynamic limit, are entropy change at constant pressure and pressure change at constant entropy. The space-time behavior of these collective modes will determine the space-time behavior of the excess density. The contribution of the excess density to $N_{P_o}$ will be called the "collective" contribution and denoted by $N_{P_o}^{coll}$. The collective contribution to $N_{P_o}$ is obtained by solving the hydrodynamic equations for the temporal evolution of the initial density disturbance and is found to be well approximated by

$$N_{P_o}^{coll}(\vec{r}, \tau) = (1 + n_o v^*) H(\vec{r}, \tau)$$

(2.69)
where
\[ H(r, t) = \left(1 - \frac{1}{\gamma}\right) \left[ (4\pi D_T)^{-\frac{3}{2}} \exp \left\{ \left(\frac{r}{\sqrt{4D_T t}}\right)^2 \right\} \right] \]
(2.70)
\[ + \frac{(4\pi B_T)^{3/2}}{\gamma} \left[ (1 + \frac{c_T}{r}) \exp \left\{ \left(\frac{r\eta_0 c_T}{4\beta c_T}\right) \right\} + (1 - \frac{c_T}{r}) \exp \left\{ \left(\frac{r - c_T}{\sqrt{4\beta c_T}}\right)^2 \right\} \right] \]

and
\[ D_T = \text{thermal diffusivity} = \frac{\chi}{\eta_0 c_T} \]
\[ B = \frac{1}{2} \left\{ \frac{4\eta}{3\eta_0} + \left(1 - \frac{1}{8}\frac{\chi}{\eta_0 c_T} \right) \right\} \]

with the quantities \( \chi, \eta, c_T, c_v, c_0, \) and \( \gamma \) being defined in sec. (II C 3).

The collective contribution to \( \text{NP}_0 \) is shown as the dashed and solid line in fig. (2.4b). It consists of two parts. The first is a Gaussian distribution with a 1/e width of \( \sqrt{4D_T t} \), where \( D_T \) is the thermal diffusivity. This distribution arises from the dissipation, by thermal conduction, of the excess entropy carried by the initial excess density. There is, in addition, a propagating density disturbance arising from the response of the pressure to the initial excess pressure. Referring to fig. (2.4b), the zero crossing of the bipolar impulse is at \( r = c_0 \) and its width is of the order of \( \sqrt{4B_T} \), where \( B \) is proportional to the acoustic attenuation and \( c_0 \) is the adiabatic sound speed.

The net "indirect" contribution to \( \text{NP}_0 \) is the sum of the "collective" contribution, \( \text{NP}_0^{\text{coll}} \), plus the contribution from the local stage of equilibration, \( \text{NP}_0^{\text{loc}} \). Using eqs. (2.67, 8) we find for the "indirect" contribution
\[ \text{NP}_0^{\text{ind}}(r, t) = \text{NP}_0^{\text{loc}}(r, t) + \text{NP}_0^{\text{coll}}(r, t) \]
(2.71)
\[ = -(1 + \eta_0 u^*) P_S(r, t) + (1 + \eta_0 u^*) H(r, t). \]
The distribution $N_0$, which we are now in a position to determine, is the sum of the equilibrium density of the other particles, $n_0$, plus the "direct" and "indirect" contributions to the density of the other particles due to the presence of particle #1. Using eq. (2.67) for the "direct" contribution, $N_0^{\text{dir}}$, and eq. (2.71) for the "indirect" contribution, $N_0^{\text{in}}$, we find for $N_0$

$$N_0(r', \tau) = n_0 + N_0^{\text{dir}}(r', \tau) + N_0^{\text{in}}(r', \tau)$$

$$= n_0 + n_0 u^* P_s(r', \tau) + (1 + n_0 u^*) [P_s(r', \tau) + H(r', \tau)]$$

$$= n_0 - P_s(r', \tau) + (1 + n_0 u^*) H(r', \tau).$$

The resulting $N_0$, for $\tau > \tau_c$, is plotted in fig. (2.4b). The conditional density fluctuation distribution, $\rho(r, \tau)$, may now be evaluated using eq. (2.56), from which we find

$$\rho(r', \tau) = (1 + n_0 u^*) H(r', \tau).$$

(2.74)

This result is plotted in fig. (2.4c). Note that for $\tau > \tau_c$, contributions to $\rho(r, \tau)$ having the diffusion form of $P_s(r', \tau)$ are cancelled.

The cancellation from $\rho(r, \tau)$ of the diffusion contribution arises from two conditions: (i) Particle #1 has the same scattering cross section as the other particles. For a gas mixture it will be necessary to consider the distribution of particles of kind B, given that a particle of kind A was at (0, 0). If the components A and B have different extinction coefficients, the cancellation of the self term will not be complete and a diffusion contribution will be observed. (ii) Particle #1 moves among particles of its own kind. We have discussed above the case where particle #1 diffuses among other particles of its own kind. The conservation of momentum in inter-particle collisions requires the transfer of the full momentum of particle #1 to the other particles. The transfer of all the momentum
of particle #1 to the other particles leads to the appearance of the "indirect" contribution to \( N P_0 \) which, as we have discussed, cancels in \( \rho \) the self distribution, \( P_s' \), and produces the excitation of collective modes and thereby the appearance in \( \rho \) of the collective response, \( H \). If all of the momentum transferred by particle #1 is not taken up by the other particles then the "indirect" contribution to \( N P_0 \) will not exactly cancel \( P_s' \), and \( P_s \) will appear in \( \rho \). Such is the case for a system of particles 1 to N mixed with other particles (kind X).

If the particles 1 to N are dilute, particle #1 transfers momentum to, and sets up collective motion in the particles of kind X, which only weakly influences the particles 2 to N. In this case there is no "indirect" contribution to \( N P_0 \) and only the self distribution, \( P_s' \), appears in \( \rho \). Such is the case for a dilute suspension of colloidal particles in water, \(^9\) and, as we shall see in Chapter III, for a binary gas mixture with one component dilute.

d) Calculation of \( N P_0^{loc}(\mathbf{r},\tau) \)

We would now like to calculate \( N P_0^{loc}(\mathbf{r},\tau) \), the modification of the density of the other particles in the establishment of local equilibrium with particle #1. The particle flux vector, \( \mathbf{j} \), associated with particle #1 is given by

\[
\mathbf{j}(\mathbf{r},\tau) = -D \nabla P_s(\mathbf{r},\tau)
\]

(2.77)

where \( D \) is the self diffusion coefficient and \( P_s \) is given in Table (2.1).

In the presence of a flux, \( \mathbf{j} \), due to particle #1, there will be a net force exerted on the medium in which particle #1 is diffusing. If a single particle moves with a velocity, \( \mathbf{v} \), and has a friction constant, \( \zeta \), the force, \( \mathbf{f} \), exerted on the medium by the particle will be

\[
\mathbf{f} = \zeta \mathbf{v} = \frac{k_B T}{D} \mathbf{v}
\]

(2.78)

where \( \zeta = k_B T/D \) is the relationship between the friction and diffusion constants for a particle in Brownian motion. \(^{10}\) The force per unit volume, \( \mathbf{F} \), in the presence of a flux, \( \mathbf{j} \), will then be
\[ \vec{f} = \int n_d \, dV = \frac{k_B T}{D} \vec{v} n_d = \frac{k_B T}{D} j \]  

(2.79)

where \( n_d \) is the number density of diffusing particles. The force per unit volume exerted by particle #1, having a density \( P_s(\vec{r}, \tau) \) is, from eqs. (2.77) and (2.79)

\[ \vec{F}(\vec{r}, \tau) = \frac{k_B T}{D} \vec{v} P_s(\vec{r}, \tau) = -k_B T \nabla P_s(\vec{r}, \tau). \]  

(2.80)

In the establishment of local equilibrium this force will be balanced by a pressure gradient, \( \nabla p(\vec{r}, \tau) \), in the other particles. If collisions between particles conserve momentum the pressure gradient will be given by \( \nabla p = \vec{F} \) and we will have from eq. (2.80)

\[ \nabla p(\vec{r}, \tau) = -k_B T \nabla P_s(\vec{r}, \tau). \]  

(2.81)

Associated with the pressure gradient will be a density gradient, \( \nabla n(\vec{r}, \tau) \), in the other particles. If collisions conserve energy then locally the temperature cannot be altered by collisions and the density gradient \( \nabla n \) will be established isothermally, that is, the relation between \( \nabla n \) and \( \nabla p \) will be

\[ \nabla n(\vec{r}, \tau) = n_o \kappa_T \nabla p(\vec{r}, \tau). \]  

(2.82)

where \( n_o \) is the average density and \( \kappa_T \) is the isothermal compressibility. Using eqs. (2.81) and (2.82) and defining

\[ \kappa_T = 1/(n_o k_B T), \]  

the isothermal compressibility of an ideal gas we find

\[ \nabla n(\vec{r}, \tau) = -\frac{\kappa_T}{\kappa_T^*} \nabla P_s(\vec{r}, \tau). \]  

(2.83)

It can be shown using statistical mechanics (11) that, in general,

\[ \frac{\kappa_T}{\kappa_T^*} = 1 + n_o \int d^3 \zeta \mathcal{H}(\zeta) = 1 + n_o \vartheta^* \]  

(2.84)

where \( \mathcal{H}(\zeta) \) is the net correlation function from eq. (2.58). Using eq. (2.84) in (2.83) we find for \( \nabla n \)

\[ \nabla n(\vec{r}, \tau) = -(1+n_o \vartheta^*) \nabla P_s(\vec{r}, \tau). \]  

(2.85)

Spatial integration of this equation yields the contribution to the density of the other particles due to the establishment of local equilibrium with particle #1 which was given in eq. (2.68):

\[ \nabla P_o^{loc} = -(1+n_o \vartheta^*) P_s(\vec{r}, \tau). \]  

(2.86)
e) The Spectra $S_{p}(K, \omega)$ and $S_{D}(K, \omega)$

We close the discussion of the correlation functions with a few words about the observed spectral density $S_{p}(K, \omega)$. In the limit of large $K$, the space-time Fourier transform of eq. (2.44) couples most strongly to the portion of $\rho(\mathbf{r}, \tau)$ which varies most rapidly in space and time. The most rapid variation of $\rho(\mathbf{r}, \tau)$ in both space and time occurs for $\tau < \tau_{c}$ where $\rho(\mathbf{r}, t)$ falls off within a few mean free paths, $t \sim v_{m} \tau_{c}$, of the origin. We then expect the form of $\rho(\mathbf{r}, \tau)$ for $\tau < \tau_{c}$ to dominate for $K > 1/t_{c}$. From Table (2.1) we find

$$S_{p}(K, \omega) = (1 + n_{0}v^{*}) \int d^{3}r d\tau e^{i(\mathbf{K} \cdot \mathbf{r} - \omega \tau)} e^{-\frac{(\mathbf{K} \cdot \mathbf{r})^{2}}{\nu_{m}^{2}}} \left\{ \begin{array}{ll}
K > \frac{1}{K_{c}} \\
\omega > \frac{1}{\tau_{c}} \end{array} \right. (2.88)$$

$$S_{p}(K, \omega) = (1 + n_{0}v^{*}) \left( \frac{2\pi}{K_{c}v_{o}} \right) e^{-\left( \frac{\nu_{m}^{2}}{K} \right)} \left\{ \begin{array}{ll}
K > \frac{1}{K_{c}} \\
\omega > \frac{1}{\tau_{c}} \end{array} \right. (2.89)$$

This is the kinetic, collisionless, or ideal gas limit wherein the observed spectrum is Gaussian of $1/e$ width $K v_{m}$, since the scattered light is simply Doppler shifted from molecules with a Gaussian distribution of speeds, and a particle moving along $K$ with a speed $v$ Doppler shifts the light by a frequency $\Delta \omega = K v$. For small $K$ and $\omega$, on the other hand, the slowly varying $H(\mathbf{r}, \tau)$ for $\tau > \tau_{c}$ couples most strongly to $S_{p}(K, \omega)$ and

$$S_{p}(K, \omega) = (1 + n_{0}v^{*}) \int d^{3}r d\tau e^{i(\mathbf{K} \cdot \mathbf{r} - \omega \tau)} H(\mathbf{r}, \tau) \left\{ \begin{array}{ll}
K < \frac{1}{K_{c}} \\
\omega < \frac{1}{\tau_{c}} \end{array} \right. (2.90)$$

The resulting $S_{p}(K, \omega)$, the hydrodynamic or long-wavelength limit, is given in eq. (2.247) and consists of three components, an unshifted line from the entropy fluctuations at constant pressure of width $\Gamma_{c} = D_{T}K^{2}$ and a pair of lines split by $\omega_{0} = Kc_{o}$ and of width $\Gamma_{B} = BK^{2}$ due to propagation of adiabatic pressure fluctuations.
We may also consider the long-wavelength limit of \( P_s(\vec{r}, \tau) \) which is observable in gas mixtures as mentioned above. The space-time Fourier transform of \( P_s(\vec{r}, \tau) \) will be called the diffusion spectrum \( S_D(\vec{K}, \omega) \). We have in this case, from Table (2.1)

\[
S_D(\vec{K}, \omega) = \int d^3 r d\tau e^{i(\vec{K}, \vec{r} - \omega \tau)} (4\pi D\tau)^{-\frac{3}{2}} e^{-\left(\frac{r}{\sqrt{4D\tau}}\right)^2}
\]  
(2.91)

\[
S_D(\vec{K}, \omega) = \frac{2DK^2}{\omega^2 + (DK^2)^2}
\]  
(2.92)

The diffusion spectrum is a Lorentzian line of HWHH given by \( DK^2 \). It is possible to understand simply why the spectrum \( S_D(\vec{K}, \omega) \) has a width \( DK^2 \) in the diffusion limit. As was discussed in sec. (II B 1) the phase at the detector of light scattered by a given particle depends on the particle's position and changes as the particle moves. The phase coherence of the scattered light is lost if the particle moves in such a way as to change the phase by \( \pi \) radians. Using eq. (2.5), in order to change the phase by \( \pi \) radians the particle must move a distance \( \pi/K \) along the direction of \( \vec{K} \). In the case of a diffusing particle, however, the mean square distance, \( \langle \Delta x^2 \rangle \), moved in a time, \( t \), in a particular direction (call it the x direction) is \( \langle \Delta x^2 \rangle = 6Dt \). (3) If this mean square distance is chosen to be \( (\pi/K)^2 \) we see that the time, \( \tau \), required for a loss of phase correlation in the scattered light is

\[
\tau \sim \left(\frac{\pi^2}{6}\right) \left(\frac{1}{DK^2}\right) \sim \frac{1}{DK^2}
\]

The spectral width, \( \Delta \omega \), of scattered light is just the inverse phase coherence time, i.e. \( \Delta \omega \sim DK^2 \), in agreement with the rigorous result of eq. (2.92).

This completes the discussion of the correlation functions and resulting spectra.
3) Numerical Calculation of the Extinction

The extinction coefficient \( h(\mathbf{R}) \) may be expressed in terms of the molecular polarizability \( \alpha \) using the Clausius Mossotti relation:\(^{(12)}\)

\[
\frac{n^2 - 1}{n^2 + 2} = \frac{\alpha n_0}{3} . \tag{2.93}
\]

For a dilute gas \( n \approx 1 \) so we can write

\[
n^2 - 1 \approx \alpha n_0 . \tag{2.94}
\]

from which we obtain using eq. (2.51)

\[
h(\mathbf{R}) = \left[ \frac{(k_o^2 \sin^2 \theta)}{4\pi} \right]^2 \alpha^2 n_0 \left[ 1 + n_0 \int d^3 r \mathcal{G}(r) \right] . \tag{2.95}
\]

Thus the scattered intensity has, in general, a nonlinear dependence on the on the average density, \( n_0 \). The term in \( h(\mathbf{R}) \) proportional to \( n_o^2 \) may be estimated accurately by relating it to the second virial coefficient \( \beta(T) \) in the equation of state relating the pressure \( P \) to the average density \( n_0 \)\(^{(13)}\)

\[
\frac{P}{k_B T} = n_0 \left[ 1 + n_0 \beta(T) + \ldots \right] . \tag{2.96}
\]

One finds\(^{(14)}\)

\[
\beta(T) = -\frac{1}{2} \int d^3 r \mathcal{G}(r) = -\frac{1}{2} v^* \tag{2.97}
\]

so that \( h(\mathbf{R}) \) may be written in terms of the virial coefficient \( \beta(T) \):
The measured values of $\beta(T)$ agree well with those calculated for the Lennard-Jones potential, which Hirschfelder, Curtiss, and Bird have tabulated.\footnote{15} For xenon one finds

$$1 - 2 n_o \beta(T) = 1 + 0.0117 [n_o \text{(amagats)}]$$

and since $n_o < 1.0$ amagat for our experiments the nonlinear dependence of intensity on density is small and will be neglected so that

$$h(\vec{r}) = h_o = \left[\frac{(k^o)^2 \sin \phi}{4 \pi}\right]^2 \alpha^2 n_o.$$  \hspace{1cm} (2.99)$$

The integral of $h(\vec{r})$ over all solid angle elements gives $h_t$, the probability that a photon while propagating in one centimeter of the gas will be scattered. One finds

$$h_t = \frac{8 \pi}{3} \frac{h_o}{\sin^2 \phi} = \frac{2}{3 \pi} \left(\frac{k^o}{n^2 - 1}\right) \frac{(n^2 - 1)^2}{n^2} \hspace{1cm} (2.100)$$

so that $h_t$ may be readily evaluated from index of refraction data. The values of $h_t$ for xenon and helium gas at STP, and benzene liquid for comparison with $\lambda_o = 6328\text{Å}$ are given in Table (2.2).

<table>
<thead>
<tr>
<th></th>
<th>$n - 1$</th>
<th>$h_t$ (cm.$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Xenon at STP</td>
<td>7.00 x $10^{-4}$</td>
<td>3.76 x $10^{-7}$</td>
</tr>
<tr>
<td>Helium at STP</td>
<td>0.36 x $10^{-4}$</td>
<td>0.995 x $10^{-9}$</td>
</tr>
<tr>
<td>Benzene liquid</td>
<td>5.0 x $10^{-5}$ (b)</td>
<td></td>
</tr>
</tbody>
</table>

(a) International Critical Tables (Mc Graw Hill Book Co., Inc., 1930) Vol VII.
4. The Effect of a Finite Illuminated Region

We now return to consider the effect of the finite dimension of the illuminated region on the spectral density of the scattered field, initially brought up in going from eq. (2.33) to eq. (2.34). Using eqs. (2.33) and (2.56) we may obtain $R_E(\tau)$ in the form

$$R_E(\tau) = \mathbb{Z}^2 \eta_o e^{i \omega \tau} \int d^3 s \ e^{i \hat{k}_0 \cdot \hat{s}} A(\hat{s}) \left[ \eta_o + \rho(\hat{s}, \tau) \right]. \quad (2.101)$$

The integrals over $\hat{s}$ can be carried out and the physical significance of $A(\hat{s})$ clarified by starting with the following relations:

$$A(\hat{r}) = \int d^3 r \ e^{i \hat{k}_0 \cdot \hat{r}} A(\hat{r}) \quad (2.102)$$

$$E_o(\hat{r}) = \int d^3 r \ e^{i \hat{k}_0 \cdot \hat{r}} E_o(\hat{r}) \quad (2.103)$$

$$B(\hat{r}) \equiv \frac{A(\hat{r})}{A(0)} \quad (2.104)$$

and eq. (2.32) so that we have

$$B(\hat{r}) = \frac{|E_o(\hat{r})|^2}{\int d^3 K (2\pi)^3 |E_o(\hat{r})|^2 \delta(K)} \quad (2.105)$$

The function $B(\hat{r})$, thus defined, is normalized in $\hat{r}$ space ($\int B(\hat{r}) d^3 K / 2\pi = 1$) and represents the distribution of incident intensity about $\hat{r}_o$. This can be seen by expanding the spatial dependence of the incident field as a superposition of plane waves

$$E_o(\hat{r}) e^{i \hat{k}_0 \cdot \hat{r}} = \int \frac{d^3 K}{(2\pi)^3} \ e^{i (\hat{k}_0 + \Delta \hat{k}) \cdot \hat{r}} E_o(\Delta K) \quad (2.106)$$
wherein the intensity associated with the component of wave vector \( \mathbf{k}_0^+ \) will be proportional to \( |E_0(\Delta \mathbf{k})|^2 \) and thus \( B(\Delta \mathbf{k}) \). Using eqs. (2.101), (2.102), and (2.104) we may write

\[
R_{E}(\tau) = \mathbb{Z} n_0 e^{i\omega_0 \tau} A(\omega) \left[ \eta_0 G(\mathbf{k}) + \frac{d^3 k'}{(2\pi)^3} B(\mathbf{k}') \rho(\mathbf{k} - \mathbf{k}'', \tau) \right]
\]  

(2.107)

where

\[
\rho(\mathbf{k}, \tau) = \int d^3 r e^{i\mathbf{k} \cdot \mathbf{r}} \rho(\mathbf{r}, \tau).
\]  

(2.108)

We may now obtain the scattered spectral power density from eqs. (2.107) and (2.17) and we find for \( S_{E}(\mathbf{k}, \omega_0 + \omega) \)

\[
S_{E}(\mathbf{k}, \omega_0 + \omega) = \mathbb{Z} n_0 A(\omega) \left[ 2\pi n_0 G(\mathbf{k}) \delta(\omega) + \frac{d^3 k'}{(2\pi)^3} B(\mathbf{k}') S_P(\mathbf{k} - \mathbf{k}'', \omega) \right]
\]  

(2.109)

where again \( \omega \) is the shift in frequency from \( \omega_0 \).

The first term in \( S_{E}(\mathbf{k}, \omega_0 + \omega) \) is due to the average density and contributes a component to the scattered spectrum at the incident frequency. The intensity of this component, however, depends strongly on \( \mathbf{k} \) and thus on scattering angle through the distribution \( B(\mathbf{k}) \). The spatial variation of the source intensity along the direction of \( \mathbf{k} \) determines the distribution \( B(\mathbf{k}) \) and is very slow compared to the spatial frequency \( \lambda = 2\pi/K \), except in the extreme forward direction where \( K \to 0 \) and \( \lambda \) can approach the dimensions of the illuminated region. The amplitude \( B(\mathbf{k}) \) then is small unless \( \lambda > d \), where \( d \) is the dimension of the illuminated region along \( \mathbf{k} \). At small scattering angles \( d \) is the transverse dimension of the illuminated region which, for this experiment, was \( d \sim 1 \text{mm} \), and \( \lambda \sim d \) occurs for a scattering angle \( \theta \sim 10^{-3} \text{rad} \). Thus \( B(\mathbf{k}) \) is sharply peaked about \( \mathbf{k} = 0 \). For scattering \( \theta = 10.6^\circ \), \( B(\mathbf{k}) \sim \exp(-10^8) \) and consequently the first term may be neglected. The effect of \( B(\mathbf{k}) \) on the angular dependance of the intensity for scattering from small illuminated regions has been discussed
by Theimer (16) and possibly observed by George et al. (17).

The fluctuation contribution to \( S_E (\vec{K}, \omega_o + \omega) \) is the convolution of the incident \( \vec{K} \) distribution \( B(\vec{K}) \) with the space-time Fourier transform \( S_p (\vec{K}, \omega) \) of the conditional fluctuation distribution \( \rho (\vec{r}, \tau ) \). Since \( B(\vec{K}) \) is sharply peaked about \( \vec{K} = 0 \), one observes in the scattered spectrum the average of \( S_p (\vec{K}, \omega) \) over a small range of \( \vec{K} \) values, determined by the size and shape of the illuminated region along \( \vec{K} \). We shall consider the effect of this averaging for the optical arrangement employed in these experiments in section (IV C 2), and it will be shown to be very small. In such a case we can set

\[
B(\vec{K}) = (2\pi)^3 \delta (\vec{K})
\]

which one would obtain in the limit of a boundless illuminated region. With these approximations we find that the exact expression for \( S_E (\vec{K}, \omega_o + \omega) \) in eq. (2.109) reduces to that obtained above in eq. (2.43):

\[
S_E (\vec{R}, \omega+\omega_o) = \frac{\mathcal{Z}^2 n_o A(\delta) S_p (\vec{R}, \omega)}. \tag{2.111}
\]

5) Fluctuations in the Dielectric Constant

It will be convenient later, when considering the calculation of spectra in the continuum limit and in gas mixtures, to have the energy angle extinction expressed in terms of the correlation function for the fluctuations in the dielectric constant \( \varepsilon \). We will write \( \varepsilon (\vec{r}, t) = \bar{\varepsilon} + \delta \varepsilon (\vec{r}, t) \) where \( \bar{\varepsilon} \) is the average part and \( \delta \varepsilon (\vec{r}, t) \) the fluctuating part of the dielectric constant. Since the dielectric constant depends only on the density

\[
\langle \delta \varepsilon (\vec{r}, t) \delta \varepsilon (\vec{r}, 0) \rangle = \left( \frac{\partial \bar{\varepsilon}}{\partial n_o} \right)^2 \langle \delta n (\vec{r}, t) \delta n (\vec{r}, 0) \rangle \tag{2.112}
\]
where \( \delta n(\mathbf{r}, t) \) is the number density fluctuation defined by

\[
n(\mathbf{r}, t) = n_0 + \delta n(\mathbf{r}, t).
\] (2.113)

Since \( \langle \delta n(\mathbf{r}, t) \rangle = 0 \) we have

\[
\langle \delta n(\mathbf{r}, t) \delta n(0, 0) \rangle = \left( \frac{\partial \rho}{\partial n_0} \right)^2 \left\{ \langle n(\mathbf{r}, t) n(0, 0) \rangle - n_0^2 \right\}
\] (2.114)

where \( \langle n(\mathbf{r}, t) n(0, 0) \rangle \) is the density-density correlation function. The quantity \( \langle n(\mathbf{r}, t) n(0, 0) \rangle d^3 r d^3 r_0 \) is the average of measurements of the product of the number \( N_o \) of particles found in \( d^3 r_0 \) at \((0, 0)\) and the number \( N_1 \) of particles found in \( d^3 r \) at \((\mathbf{r}, t)\). If we let \( d^3 r_0 \) become infinitesimally small, \( N_0 \) will be either 0 or 1 for a given measurement and only those measurements for which \( N_0 = 1 \) are included in the average. Such is the case in a fraction \( n_0 d^3 r_0 \) of the measurements. However, if \( N_0 \) is known to be 1 then, by the definition of \( G(\mathbf{r}, t) \), we have, on the average,

\[
N_1 = G(\mathbf{r}, t) d^3 r \text{ when } N_0 = 1.
\] Thus

\[
\langle N_1 N_0 \rangle = \langle N_1 \rangle_{N_0 = 1} n_0 d^3 r_0 = G(\mathbf{r}, t) n_0 d^3 r d^3 r_0.
\] (2.115)

Since

\[
\langle N_1 N_0 \rangle = \langle n(\mathbf{r}, t) n(0, 0) \rangle d^3 r d^3 r_0
\] (2.116)

we have

\[
G(\mathbf{r}, t) = \frac{\langle n(\mathbf{r}, t) n(0, 0) \rangle}{n_0}.
\] (2.117)
Using eqs. (2.40), (2.113), and (2.117) we find

\[ \rho(\vec{r}, t) = \frac{\langle \delta n(\vec{r}, t) \delta n(0, 0) \rangle}{n_0} \]  

(2.118)

so that from eq. (2.114)

\[ \langle \delta \varepsilon(\vec{r}, t) \delta \varepsilon(0, 0) \rangle = n_0 \frac{\partial \varepsilon}{2n_0} \rho(\vec{r}, t). \]  

(2.119)

The derivative \( \frac{\partial \varepsilon}{\partial n} \) may be evaluated from eq. (2.56) by recalling that \( n^2 = \varepsilon/\varepsilon_0 \) and it is

\[ \frac{\partial \varepsilon}{\partial n} \approx \alpha \varepsilon_o \approx \varepsilon_o \left\{ \frac{n^2 - 1}{n_0} \right\} \]  

(2.120)

Substituting eqs. (2.119) and (2.120) into eq. (2.51) we find the desired expression for \( h(\vec{k}, \omega) \):

\[ h(\vec{k}, \omega) = \frac{1}{2\pi} \left[ \frac{(k_0^\gamma)^2 \sin \theta}{4\pi} \right]^2 S_{\delta\varepsilon}(\vec{k}, \omega) \]  

(2.121)

where

\[ S_{\delta\varepsilon}(\vec{k}, \omega) = \int d^3r \int dt \ e^{i(\vec{k} \cdot \vec{r} - \omega t)} \langle \delta \varepsilon(\vec{r}, t) \delta \varepsilon(0, 0) \rangle. \]  

(2.122)

Eqs. (2.51) and (2.121), which relate the power spectrum of the scattered light to the power spectra of fluctuations in density and dielectric constant in a monatomic gas, are the basis for the interpretation of the experiments to be described.
C. Density Fluctuations in Dilute Monatomic Gases

1. The Boltzmann Equation (BE)

a) Validity of the Boltzmann Equation

The basis for the microscopic study of the dilute monatomic gas is the Boltzmann equation

\[
\left( \frac{\partial}{\partial t} + \vec{v} \cdot \nabla \right) f(\vec{r}, \vec{v}, t) = \left( \frac{\partial f}{\partial \vec{v}} \right)_{\text{coll}}
\]

which, with appropriate boundary conditions allows one to calculate the temporal evolution of \( f(\vec{r}, \vec{v}, t) \), the particle density in the six dimensional space (\( \mu \) space) determined by the coordinates \( (\vec{r}, \vec{v}) \), \( f(\vec{r}, \vec{v}, t) d^3r d^3v \) being the ensemble average number of particles found in volume \( d^3r d^3v \) at \( (\vec{r}, \vec{v}) \) at time \( t \).

In general, particles are carried out of the \( \mu \) space volume element at \( \vec{r}, \vec{v} \) by streaming (motion of the particle in \( \vec{r} \) due to its velocity \( \vec{v} \)) and collisions. The BE accounts exactly for the effects of streaming \( (\partial f/\partial t)_{\text{streaming}} = - (\vec{v} \cdot \nabla)f \), but assumes that only binary collisions are important in determining the rate of change of \( f \) due to collisions, \( (\partial f/\partial t)_{\text{coll}} \). Furthermore, the BE collision term depends only on the binary collision cross section, that is it treats the gas as a collection of point particles having a finite cross section. These two approximations (binary collisions and point particles) limit the application of the BE to dilute systems where triple (and higher order) collisions, and spatial correlation due to finite particle size are not important. Before proceeding to relate the propagation of density fluctuations to the BE we will first discuss the applicability of the BE to our experimental situation.

The range of validity of the Boltzmann equation is a complex subject but there is general agreement that it is applicable under the following conditions:

(i) When one is interested in the change of \( f(\vec{r}, \vec{v}, t) \) over times long compared to the duration of an interatomic collision.

(ii) When one is interested in the change of \( f(\vec{r}, \vec{v}, t) \) over distances
long compared to the range of the molecular interaction.

(iii) When \( n_0 v^* \ll 1 \); that is when the atomic volume \( (v^*) \) is small compared to the volume per atom in the gas \( (1/n_0) \).

For a neutral gas at room temperature (i) and (ii) present little practical limitation to the use of the BE because of the short collision times \( (\tau_c \sim 10^{-13} \text{ sec.}) \) and small molecular diameters \( (a \leq 5\text{Å}) \) involved. Starting from the Liouville theorem, Van Leeuwen and Yip \(^{20}\) have derived a more general kinetic equation, valid only for small deviations from equilibrium, but which can explicitly treat collisions of finite duration between particles of finite size. They show that their kinetic equation reduces to the linearized BE when conditions (i) and (ii) are satisfied. For our experiments, times \( (\gtrsim 10^{-9} \text{ sec}) \) and distances \( (\gtrsim 10^{-4} \text{ cm}) \) over which \( f(r, v, t) \) is sampled are such that the limitations (i) and (ii) are of no importance.

Condition (iii) indicates the accuracy of the implicit assumption of the BE that only binary collisions need be accounted for in the evaluation of the transport coefficients \( \kappa \) (thermal conductivity) and \( \eta \) (shear viscosity). Assuming only binary collisions, the mean free path \( \lambda \) goes inversely with density \( (\lambda \sim 1/n_0) \). This fact, since \( \kappa, \eta \sim n_0 \lambda \), leads directly to the prediction of the BE that the transport coefficients \( \kappa \) and \( \eta \) are independent of density. For triple or higher order collisions \(^{21}\)

\[ \lambda \sim 1/n_0 (1 + C_1 n_0 + C_2 n_0^2)^{-1} \]

so that

\[ \eta = \eta_0(\tau) \left[ 1 + n_0 \eta_1(\tau) + \ldots \right] \] (2.124)

\[ \kappa = \kappa_0(\tau) \left[ 1 + n_0 \kappa_1(\tau) + \ldots \right], \] (2.125)

more terms being required with increasing density. The measured density dependance of the viscosity of xenon at STP \(^{22}\) shows that \( \eta_1 \sim 5 \times 10^{-4} / \text{amagat} \), a very small correction. A similar result can be
expected for the thermal conductivity. Therefore under the conditions of our experiment \( n_0 < 0.7 \) amagat only binary collisions need be considered in the calculation of \( \eta \) and \( \kappa \) and the BE should adequately describe transport properties of the gas.

Condition (iii) also indicates the importance of imperfect gas corrections in determining the thermodynamic parameters of the gas. As we saw in sec. (II B 2c), because the molecules interact over a finite range, \( a \), the placement of particle \# 1 at \( \vec{r} = 0 \) modifies the distribution of the other particles, effectively removing a fraction \( n_0 v^* \sim n_0 a^3 \) of a particle from the vicinity of \( \vec{r} = 0 \). Such spatial correlation leads to deviations of the thermodynamic behavior of the gas from that predicted by the kinetic theory of an ideal gas. The equation of state, for example, is no longer \( P = n_0 k_B T \) but is given by

\[
P = n_0 k_B T \left( 1 - \frac{1}{2} n_0 v^* + \ldots \right)
\]

as was stated in eqs. (2.96, 7). Similar "virial" expansions can be obtained for the internal energy, specific heats \( C_p \) and \( C_v \), and \( C_p / C_v = \gamma \), with the actual quantities differing from those predicted by ideal gas theory by fractional corrections of order \( n_0 v^* \). These are termed "imperfect gas corrections." The BE, because it implicitly assumes point particles \( (v^* = 0) \) yields ideal gas thermodynamic parameters and cannot account for a finite \( n_0 v^* \). For the BE to be applicable then, \( n_0 v^* \) must be small enough so that modifications of the spectra due to imperfect gas corrections are too small to be observed. The most important correction to be contended with is the correction to the adiabatic sound speed, \( c_o \), for which we have the following virial expansion

\[
c_o = \sqrt{\frac{5k_B T}{3m}} \left( 1 - 0.0043[n_0 \text{ (amagat)}] \right) \tag{2.126}
\]

where \( \sqrt{5k_B T/3m} \) is the value given by the BE and ideal gas theory. For our experiments \( n_0 < 0.7 \) am) the imperfect gas correction to \( c_o \) is \( \sim 0.4\% \) and is not observable. Similar results are found for \( C_p \), \( C_v \) and \( \gamma \).
In summary, at the highest density studied here ($n \sim 0.7$ amagat), in the hydrodynamic limit, condition (iii) is satisfied such that deviations of the actual thermodynamic parameters which determine the spectrum ($\eta, \kappa, c_0, C_p, C_v, \gamma$) from those given by the kinetic theory of the ideal gas and the BE are not observable. Conditions (i), (ii), and (iii) are satisfied to such an extent under the present experimental conditions that a proper solution of the BE should be adequate to describe the density fluctuation spectrum. Our experiments then serve to test the method of solution of the BE rather than the validity of the BE. We will now proceed to discuss density fluctuations and the BE.

b) Density Fluctuations and the Boltzmann Equation

Writing out the collision term in eq. (2.123) we have for the BE:

$$\left( \frac{\partial}{\partial t} + \vec{v} \cdot \nabla \right) f(\vec{r}, \vec{v}, t) = \left( \frac{\partial f}{\partial t} \right)_{\text{coll}}$$

$$= \int d\Omega \int d^3 \vec{r} \ I(\theta, \vec{v} \cdot \vec{v}) \left[ f(\vec{v}') f(\vec{v}^{'*}) - f(\vec{v}) f(\vec{v}') \right], \quad (2.127)$$

where $I(\theta, \vec{v})$ is the collision cross section defined such that if there are $N_0$ particles per unit area incident with a velocity $\vec{V}$ on a scattering center, then the number of particles scattered into $d\Omega$ through an angle $\theta$ is $N_0 I(\theta, \vec{v}) d\Omega$. The form of the intermolecular potential chosen determines the functional dependence of $I(\theta, \vec{v})$ on $\theta$ and $\vec{v}$. The collision term of the BE gives the rate of change of $\mu$ space particle density at $\vec{V}$ due to binary collisions. The $\mu$ space density at $\vec{V}$ increases because of collisions which result in a particle with velocity $\vec{V}'$, i.e. collisions for which particles upon entering have velocities $\vec{V}_1'$ and $\vec{V}'$ and upon exiting have velocities $\vec{V}_1$ and $\vec{V}$. Because of the conservation of energy and momentum in a collision the entering velocities $\vec{V}_1'$ and $\vec{V}'$ are determined uniquely by specifying the exiting velocities $\vec{V}_1$ and $\vec{V}$, and the angle $\theta$ through which the relative velocity $\vec{V}_1 - \vec{V}$ turns in the collision, i.e. $\vec{V}_1' = \vec{V}_1 (\vec{V}, \vec{V}_1, \theta)$ and $\vec{V}' = \vec{V}' (\vec{V}, \vec{V}_1, \theta)$. The rate of increase of $\mu$ space particle density at $\vec{V}$ is given by
Here, because \( \vec{v}_1' \) and \( \vec{v}' \) are specified by \( \vec{v}_1, \vec{v}, \) and \( \theta \), all collisions which result in a particle with velocity \( \vec{v} \) are accounted for by the integrations over \( \vec{v}_1 \) and \( \theta \). The \( \mu \) space particle density at \( \vec{v} \) is decreased because of collisions of particles with a velocity \( \vec{v} \) with other particles. The remaining term of the Boltzmann collision operator gives this decrease.

Since we consider here only small deviations from equilibrium the linearized form of the BE is adequate, as has been shown by Van Leeuwen and Yip. We can obtain the linearized form by setting

\[
f(\vec{r}, \vec{v}, t) = f_0(\vec{v}) \left[ n_0 + h(\vec{r}, \vec{v}, t) \right]
\]

(2.128)

where \( f_0(\vec{v}) \) is the equilibrium Maxwellian distribution

\[
f_0(\vec{v}) = \left( \frac{2\pi v_0} {\nu_0^2} \right)^{3/2} \exp\left( -\frac{\nu^2} {2\nu_0^2} \right)
\]

(2.129)

and we have defined

\[
\nu_0^2 \equiv \frac{k_B T}{m}
\]

(2.130)

with \( k_B = \) Boltzmann's constant, \( T = \) temperature and \( m = \) particle mass. Assuming that \( h(\vec{r}, \vec{v}, t) \ll n_0 \) and neglecting all terms \( \sim \hbar^2 \) we obtain the linearized form of the BE:
where

\[ C(h) = n_0 \int d\Omega \int d^3 \vec{r}_0 \int d^3 \vec{r} \int d^3 \vec{r}' \int d^3 \vec{r}'' \left| \eta(\vec{r}_0 \vec{r}' \vec{r} \vec{r}'') \right| \delta(\vec{r}_0) \left[ h(\vec{r}') + h(\vec{r}'') - h(\vec{r}) - h(\vec{r}) \right]. \]  

(2.132)

To obtain the scattered light spectrum we must calculate from the BE the conditional density fluctuation distribution \( \rho(\vec{r}, t) \), the deviation of the average number density from its equilibrium value under the condition that a particle was known to be at \((0, 0)\). The distribution \( \rho(\vec{r}, t) \) is obtained from \( f_0(v) h(\vec{r}, \vec{v}, t) \), the deviation from equilibrium in \( \mu \) space, by averaging over all velocities

\[ \rho(\vec{r}, t) = \int d^3 \vec{v} f_0(v) h(\vec{r}, \vec{v}, t). \]  

(2.133)

Here \( h(\vec{r}, \vec{v}, t) \) is the solution of the linearized BE (eq. (2.158)) with the appropriate initial condition. This initial condition has been shown by van Leeuwen and Yip to be

\[ f_0(v) h(\vec{r}, \vec{v}, 0) = f_0(v) \delta(\vec{r}). \]  

(2.134)

Thus the initial \( \mu \) space density disturbance is \( f_0(v) \delta(\vec{r}) \), i.e. the addition of a thermalized particle at \((\vec{r} = 0, t = 0)\). This initial condition in \( \mu \) space may be understood by considering the evolution of \( \rho(\vec{r}, t) \) for times short compared to a collision time \( \tau_c \). Recalling eq. (2.56) we have for \( \rho(\vec{r}, t) \)
\rho(\vec{r}, t) = P_s(\vec{r}, t) + N P_o(\vec{r}, t) - n_0. \hspace{1cm} (2.56)

We are seeking here the evolution of \( \rho(\vec{r}, t) \) at short times in the system which is described by the Boltzmann equation, i.e. a gas of particles which undergo instantaneous binary collisions (point particles). In this system there is no interaction between the particle which is at \( \vec{r} = 0, t = 0 \) and the other particles for short times. That is, the probability that the particle at \( \vec{r} = 0, t = 0 \) will experience a collision over the time interval from \( t = 0 \) to \( t = t' \) goes to zero in the limit \( t' \to 0 \). In this limit, then, there is no interaction between the particle at \( \vec{r} = 0, t = 0 \), and the other particles and the distribution of the other particles takes on the value it would have in the absence of the particle at \( \vec{r} = 0, t = 0 \), i.e. \( \lim_{t \to 0} N P_o(\vec{r}, t) = n_0 \). Thus we have for short times

\[ \rho(\vec{r}, t) = P_s(\vec{r}, t). \hspace{1cm} (2.139) \]

Since in the absence of collisions particle velocities are constant, given that a particle was at \( (0, 0) \) and had an initial velocity \( \vec{v} \), the probability \( P_s(\vec{r}, t/0, 0; \vec{v}) \) that it will be found at \( \vec{r}, t \) is

\[ P_s(\vec{r}, t/0, 0; \vec{v}) = \delta(\vec{r}-\vec{v} t). \hspace{1cm} (2.140) \]

We may in general write

\[ P_s(\vec{r}, t) = \int d^3 \vec{v} P_s(\vec{r}, t/0, 0; \vec{v}) P(\vec{v}) \hspace{1cm} (2.141) \]

where \( P(\vec{v}) \) is the probability that a particle will have a velocity \( \vec{v} \). This is just the equilibrium Maxwellian distribution.
\[ P(\mathbf{v}) = f_0(\mathbf{v}). \quad (2.142) \]

We then have for short times

\[ \rho(r^2, t) = \int d^3v f_0(v) \delta(r^2 - \mathbf{v}^2 t). \quad (2.143) \]

A comparison of eqs. (2.143) and (2.133) shows that for short times the solution of the linearized Boltzmann equation is

\[ h(\mathbf{r}, \mathbf{v}, t) = \delta(\mathbf{r} - \mathbf{v} t) \quad (2.144) \]

and verifies the initial condition in eq. (2.134).

The scattered power spectrum from eq. (2.52) will be proportional to \( S_\rho(\mathbf{K}, \omega) \):

\[ S_\rho(\mathbf{K}, \omega) = \int_{-\infty}^{\infty} dt \int d^3r e^{i(\mathbf{K} \cdot \mathbf{r} - \omega t)} \rho(r^2, t) \quad (2.52) \]

and since \( \rho(r^2, t) = \rho(r^2, -t) \) we have:

\[ S_\rho(\mathbf{K}, \omega) = 2Re \int_{-\infty}^{\infty} dt \int d^3r e^{i(\mathbf{K} \cdot \mathbf{r} - \omega t)} \rho(r^2, t). \quad (2.145) \]

Defining the Laplace-Fourier transform \( h(\mathbf{R}, \mathbf{v}, \omega) \) of \( h(\mathbf{r}, \mathbf{v}, t) \)

\[ h(\mathbf{v}, \omega) = \int d\mathbf{r} \int d^3r e^{i(\mathbf{K} \cdot \mathbf{r} - \omega t)} h(\mathbf{r}, \mathbf{v}, t), \quad (2.146) \]
we obtain the spectrum directly as a velocity integral:

$$\mathcal{S}_\rho(k,\omega) = 2\Re \int d^3\hat{v} f_0(\hat{v}) h(k,\hat{v},\omega).$$

(2.147)

Applying the Laplace transform to the linearized BE (eqs. 131, 2) we find

$$(i\omega - k \cdot \hat{v}) h(k,\hat{v},\omega) - h(k,\hat{v},t=0) = C [h(k,\hat{v},\omega)]$$

(2.148)

where $h(k,\hat{v},t=0) = \int d^3r \exp(iK \cdot \vec{r}) \delta(\vec{r}) = 1$, so that

$$i (\omega - k \cdot \hat{v}) h(k,\hat{v},\omega) = 1$$

$$+ n_0 \int d\omega \int d^3\hat{v} \int f_0(\hat{v}) \left[ h(\hat{v}) + h(\hat{v}) - h(\hat{v}) - h(\hat{v}) \right].$$

(2.149)

We shall consider here two forms of the intermolecular potential, $\phi(r)$:

$$\Phi(r) = \frac{\lambda}{4\pi a}$$

Maxwell molecule

$$\Phi(r) = \begin{cases} 0, & r > d \\ \infty, & r \leq d \end{cases}$$

Hard Spheres

where $r$ separates the particle centers. For these potentials the product

$$Q = I(\theta, |\hat{v} - \hat{v}_1|) |\hat{v} - \hat{v}_1|$$

may be shown to be respectively

$$Q = \sqrt{\frac{\lambda}{\pi}} \mathcal{H}(\theta)$$

(Maxwell Molecules)

(2.150)
where $H(\theta)$ is a dimensionless function of scattering angle only, and

$$ Q = \frac{d^2}{4} |\mathbf{v} - \mathbf{v}'|, \quad \text{(Hard Spheres)} \tag{2.151} $$

These both can be written in the form *

$$ Q = \sqrt{2} \sigma \nu_0 H(\theta; |\mathbf{v} - \mathbf{v}'|), \quad \text{(2.152)} $$

where $\mathbf{v}$ is the scaled velocity

$$ \mathbf{v} = \frac{\nu}{\sqrt{2\nu_0^*}}, \quad \text{(2.153)} $$

$H(\theta, |\mathbf{v} - \mathbf{v}'|)$ is a dimensionless function of $\theta$ and $|\mathbf{v} - \mathbf{v}'|$, and $\sigma$ is the effective collision cross sectional area given by

$$ \sigma_{\text{Max}} = \frac{1}{\sqrt{2\nu_0^*}} \sqrt{\frac{\nu}{m}} = \sqrt{\frac{\nu}{2k_B T}} \quad \text{(Maxwell)} \tag{2.154} $$

$$ \sigma_{\text{hs}} = \frac{d^2}{4} \quad \text{(Hard Spheres)} \tag{2.155} $$

The transformed BE, equation (2.149), can be put in a dimensionless form by defining the dimensionless frequency parameter, $\chi$, and distribution, $a(\mathbf{k}, \mathbf{v}, \omega)$:

*Eq. (2.152) may be written for an arbitrary intermolecular potential and, in general, both $\sigma$ and $H(\theta, |\mathbf{v} - \mathbf{v}'|)$ will be temperature dependent.
\[ x = \frac{\omega}{\omega_x} = \frac{\omega}{\sqrt{2} k v_0} \quad (2.156) \]

\[ a(\vec{R}, \vec{r}, \omega) = \frac{\sqrt{2} k v_0}{2\pi} h(\vec{R}, \vec{r}, \omega) \quad (2.157) \]

The variable \( x \) then measures frequency in units of \( \sqrt{2} k v_0 \) which physically is the Doppler frequency shift for light scattered by a particle moving along the direction \( \vec{K} \) with a velocity of magnitude \( \sqrt{2} v_0 \), the most probable speed of the gas molecules. With these latter definitions and eqs. (2.129), (2.131), and (2.132) we find a linear integral equation for \( a(\vec{K}, \vec{r}, x) \)

\[ i(\nu - \hat{\chi}, \vec{\epsilon}) a(\vec{R}, \vec{r}, x) = \frac{1}{2\pi} + \frac{n_o \sigma}{k} J(a), \quad (2.158) \]

where

\[ J(a) = \int d\Omega \int d^2 \vec{r} \int H(\Theta, |\vec{\epsilon} - \vec{\epsilon}_i|) \phi(\vec{\epsilon}) \times \left[ a(\vec{R}, \vec{r}, \vec{\epsilon}_i, x) + a(\vec{R}, \vec{r}, \vec{\epsilon}, x) - a(\vec{R}, \vec{r}, \vec{\epsilon}_i, x) - a(\vec{R}, \vec{r}, \vec{\epsilon}, x) \right], \quad (2.159) \]

and

\[ \phi(\vec{\epsilon}) = \pi^{-3/2} \exp(-\epsilon^2) \quad (2.160) \]

is the Maxwellian normalized to unity in \( \vec{\epsilon} \) space. Eq. (2.158) determines the dependence of \( a(\vec{K}, \vec{r}, x) \) on the variables \( \vec{K}, \vec{r}, \) and \( x \). The variable \( \vec{K} \) occurs only in the combination \( n_o \sigma / k \) so that the solution \( a(\vec{K}, \vec{r}, x) \) will be of the form \( a(\vec{K}, \vec{r}, x) \). Thus the form of the dependence of \( a \) on the variables \( \vec{\epsilon} \) and \( x \) is determined only by the single parameter, \( n_o \sigma / k \sim \)
This scaling property of the BE is a consequence of the assumption of point particles, leaving the mean free path $\ell$ as the only characteristic length of the gas.

It is convenient then to express the scattered spectrum in terms of $n_o \sigma / K$ and the reduced frequency $x$. We define a uniformity parameter

$$\gamma \propto \frac{n_o \sigma}{K}, \quad (2.161)$$

where the constant of proportionality depends on the particular intermolecular potential. We also define a spectrum $S(x, y)$, normalized in $x$ to unit area

$$\int_{-\infty}^{\infty} dx \ S(x, y) = 1. \quad (2.162)$$

Since $1/2\pi \int S_\rho (K, \omega) d\omega = 1$ we find

$$S(x, y) = \frac{\sqrt{2} Ku_o}{2\pi} \ S_\rho (K, \omega) \quad (2.163)$$

and from eqs. (2.147) and (2.157)

$$S(x, y) = 2Re \int d^3 \varphi (\xi) a (k, \xi, \psi) \quad (2.164)$$

Since $y \sim n_o \sigma / K \sim 1/K \ell \sim \lambda / \ell$, as $y$ decreases the kinetic regime is approached. We may calculate immediately $S(x, 0)$ in the extreme kinetic limit ($n_o \sigma / K = 0$) using eqs. (2.158) and (2.164), from which we find

$$S(x, 0) = 2Re \int d^3 \varphi (\xi) \left\{ \frac{1}{2\pi (i \nu - i \xi^2)} \right\}, \quad (2.165)$$
where we have chosen \( \hat{K} \) along the z direction. The integral over \( \epsilon_z \) may be evaluated by substituting \( x + i \delta x \) for \( x \) and integrating in the complex plane over a contour which follows the real axis and is closed in the upper half plane. Upon evaluating the residue of the pole at \( \epsilon_z = x + i \delta x \) and letting \( \delta x \to 0 \) we find:

\[
S(\nu, 0) = \frac{1}{\sqrt{\pi}} \exp(-\nu^2) \quad (2.166)
\]

The spectrum in the kinetic limit then is a Gaussian which falls to 1/e of its maximum at \( x = 1 \). From eq. (2.156) this corresponds to a 1/e width in frequency of \( \Delta \omega = \sqrt{2KV_0} \).

2. Solution of the Linearized BE

a) The Polynomial Expansion

We shall now outline the solution of the linearized Boltzmann equation for the spectrum \( S(x, y) \) using the Wang Chang-Uhlenbeck method and the method of the kinetic model. These two techniques both employ a polynomial expansion for the distribution function, \( a(y, \vec{\epsilon}, x) \), originally introduced by Wang Chang and Uhlenbeck \(^{24} \), which we shall now discuss. Wang-Chang and Uhlenbeck expanded \( a(y, \vec{\epsilon}, x) \) in a complete orthonormal set of polynomial functions of the velocity

\[
a(y, \vec{\epsilon}, \nu) = \sum_{j=1}^{\infty} a_j(y, \nu) \psi_j(\vec{\epsilon}) \quad (2.167)
\]

where the \( \psi_j(\vec{\epsilon}) \) are orthonormal with respect to the weight function \( \phi(\epsilon) \) in the sense that

\[
(\psi_i, \psi_j) = \int d^3 \vec{\epsilon} \phi(\epsilon) \psi_i(\vec{\epsilon}) \psi_j(\vec{\epsilon}) = \delta_{ij} \quad (2.168)
\]
and

$$a_j(x,y) = (\psi_j, a) = \int d^3 \varepsilon \phi(\varepsilon) \psi_j(\varepsilon) a(y, \varepsilon, x). \quad (2.169)$$

Such an expansion is useful because it converts the linearized Boltzmann equation (eq.(2.158)) into an inhomogeneous set of linear equations which, with suitable approximations, can be solved. The expansion of the distribution function in terms of functions of the velocity only is useful in the solution of the Boltzmann equation because the Boltzmann collision operator $J$, defined by eq. (2.159), operates in velocity space only. Thus

$$J(a_j(x,y) \psi_j(\varepsilon)) = a_j(x,y) J(\psi_j(\varepsilon))$$

and we need consider the operation of $J$ on the functions $\psi_j(\varepsilon)$ only. Since the $\psi_j(\varepsilon)$ form a complete set of functions we may write

$$J(\psi_j) = \sum_{l=1}^{\infty} \lambda_{j,l} \psi_l \quad (2.170)$$

where from eq. (2.159)

$$\lambda_{j,l} = (\psi_j, J \psi_l) = \int d^3 \varepsilon \phi(\varepsilon) \psi_j(\varepsilon) \int d\Omega \int d^2 \varepsilon_i \ H(\varepsilon_i, |\varepsilon - \varepsilon_i|) \times$$

$$\phi(\varepsilon) \left[ \psi_l(\varepsilon_i) + \psi_l(\varepsilon_i') - \psi_l(\varepsilon) - \psi_l(\varepsilon) \right] \quad (2.171)$$
Wang Chang and Uhlenbeck\(^{(25)}\) have derived a set of velocity functions \(\psi^M_i\) and the matrix elements \(\lambda^M_{ij}\) of the collisions operator \(J^M\) for Maxwell molecules. In this case the matrix \(\lambda_{ij}\) is diagonal, i.e. the \(\psi^M_i\) are the eigenfunctions of the Maxwell collision operator:

\[
(\psi^M_i, J^M \psi^M_j) = \lambda^M_{ij} \delta_{ij}.
\]

Later Mott-Smith used the same \(\psi^M_i\) to calculate the matrix elements \(\lambda_{ij}\) of the collision operator for hard spheres.\(^{(26)}\) In Table (2.3) we tabulate the first few of these eigenfunctions, \(\psi^M_i(\vec{v})\), of \(J^M\) and the corresponding diagonal matrix elements, \(\lambda_{ij}\), for Maxwell and hard sphere molecules. The polynomials, \(\psi^M_j(\vec{v})\), expressed in spherical coordinates in velocity space, are of the form \(\psi^M_{r\ell m}(\vec{v}) \sim R_{r\ell}(\epsilon) Y\ell m(\theta, \phi)\) where \(R_{r\ell}(\epsilon)\) are the Sonine polynomials and \(Y\ell m(\theta, \phi)\) are spherical harmonics. The functions \(\psi^M_i\) then are specified by a set of three indices \((r, \ell, m)\) to which we assign the single index \(j\). The sets \((r, \ell, m)\) are generally ordered according to the increasing magnitude of the diagonal matrix elements \(\lambda_{ij}\). The diagonal matrix elements, \(\lambda_{r\ell m, r\ell m}\), are independent of the index \(m\), because the operator \(J\) is isotropic in velocity space. It can be shown directly from the Boltzmann equation that the diagonal elements, \(\lambda_{ii}\), are always negative or zero.\(^{(27)}\)

There are five functions \(\psi^M_j(\vec{v})\) for which the diagonal matrix elements are zero. These are \(\psi^M_{000} = 1\), \(\psi^M_{01m} = \vec{v}\), and \(\psi^M_{100} = \epsilon^2 - 3/2\).

The diagonal matrix elements of these functions are zero because of the respective conservation of particle number, momentum, and energy in a collision, i.e. for each of these and only these functions we have

\[
\psi^M_j(\vec{v}') + \psi^M_j(\vec{v}) = \psi^M_j(\vec{v}) + \psi^M_j(\vec{v})
\]  

(2.172)
Table 2.3: Maxwell molecule Eigenfunctions and Diagonal Matrix Elements for Maxwell and Hard Sphere Molecules.

\[ \psi_{r \ell m}^{M}(\epsilon) \]

\[ \lambda_{r \ell, r \ell} \]

<table>
<thead>
<tr>
<th>( \psi_{r \ell m}^{M} )</th>
<th>( \lambda_{r \ell, r \ell} )</th>
<th>Maxwell</th>
<th>Hard Sphere</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \psi_{000}^{M} = \epsilon )</td>
<td>0</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>( \psi_{01m}^{M} = \epsilon )</td>
<td>( m = 0, \pm 1 )</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>( \psi_{100}^{M} = \epsilon - 3/2 )</td>
<td>0</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>( \psi_{11m}^{M} = \epsilon(\epsilon - 5/2) )</td>
<td>( m = 0, \pm 1 )</td>
<td>-0.4</td>
<td>-0.396</td>
</tr>
<tr>
<td>( \psi_{02m}^{M} = \epsilon_{i} \epsilon_{j} -(1/3) \delta_{ij} \epsilon )</td>
<td>( m = 0, \pm 1 \pm 2 )</td>
<td>-0.6</td>
<td>-0.590</td>
</tr>
</tbody>
</table>
for any possible collision with initial velocities $\vec{\xi}_1', \vec{\xi}_1''$ and final velocities $\vec{\xi}_1, \vec{\xi}$. The collision conservation laws $J(M_j) = 0$ will be employed in sec. (II C 2d) in the Boltzmann equation to obtain the macroscopic conservation laws for number density, momentum density and energy density.

Denoting by $\psi_1(\vec{\xi})$ the eigenfunction $\psi_{000}$ we have $\psi_1 = 1$ and from eq. (2.169)

$$a_1(x, y) = \int d^3 \xi \phi(\xi) a(y, \vec{\xi}, \xi)$$  \hspace{0.5cm} (2.173)

so that the desired spectrum from eq. (2.164) is given simply by

$$S(x, y) = 2\text{Re} \ a_1(x, y).$$ \hspace{0.5cm} (2.174)

b) The Method of Wang-Chang and Uhlenbeck

Inserting the expansions (2.167) and (2.170) into eq. (2.158) we find from the linearized BE

$$\sum_{j=1}^{\infty} a_j(x, y) \left[ i(x - \epsilon z) \psi_j(\vec{\xi}) - \frac{\eta_0 \sigma}{k} \sum_{l=1}^{\infty} \lambda_{jl} \psi_l(\vec{\xi}) \right] = \frac{1}{2\pi}$$ \hspace{0.5cm} (2.175)

where we taken $\hat{K}$ along the z direction. Forming the scalar product with $\psi_n$ we find

$$i \n \ a_n - \sum_{j=1}^{\infty} \left[ i a_j(\psi_n, \epsilon_z \psi_j) + \frac{\eta_0 \sigma}{k} \lambda_{jn} \right] = \frac{(\psi_n, 1)}{2\pi}, \ \ n = 1, 2, \ldots$$ \hspace{0.5cm} (2.176)

an infinite set of coupled linear equations for the $a_j$'s, which cannot be exactly solved. Ranganathan and Yip \cite{28} following Wang Chang and
Uhlenbeck, were able to obtain a solution for Maxwell molecules by truncating the matrix \( \lambda_{jn} \) which in this case is diagonal (\( \lambda_{jn} = \delta_{jn} \)). As a result, \( a_j = 0 \) for \( j > N \) and one has \( N \) coupled linear equations for the remaining \( a_j \)'s, which can be solved. Solutions were obtained for larger and larger \( N \) until the resulting spectra ceased to change. These spectra are the exact solution of the BE if convergence is obtained. The truncation of the polynomial expansion, however, results in poorer convergence of this procedure as \( n_0 \sigma/K \) decreases, that is in the kinetic regime. This can be understood by expanding the nontransformed distribution \( h(r, \mathbf{v}, t) \) and comparing it with the known solution for \( y = 0 \) from eq. (2.144)

\[
h(r, \mathbf{v}, t) = \sum_{j} h_j(r, t) \psi_j(\mathbf{v}) = \delta(\mathbf{r} - \mathbf{v}, t). \tag{2.177}
\]

At \( y = 0 \) for a fixed \( r \) and \( t \), the solution \( h(r, \mathbf{v}, t) \) is a \( \delta \) function in \( \mathbf{v} \) and requires all orders of the polynomials in the expansion. Thus \( y \) decreases \( h(r, \mathbf{v}, t) \) becomes a rapidly varying function in velocity space and higher order eigenfunctions are required in the solution of the BE.

c) The Kinetic Model

The kinetic model approximation is an extension of the method of Wang Chang and Uhlenbeck which remedies this defect, and is obtained from the following approximation of the effect of the collision operator from eq. (2.170)\(^{(29)}\)

\[
J(a) = \sum_{j,k=1}^{\infty} a_j \lambda_{jk} \psi_k \quad \text{(exact)} \tag{2.179}
\]

\[
\approx \sum_{j,k=1}^{N} a_j \lambda_{jk} \psi_k - \sum_{j=N+1}^{\infty} a_j \lambda_j \psi_j \quad \tag{2.180}
\]
Adding and subtracting the term \( \sum_{j=1}^{n} a_j \psi_j \) we have

\[
J(a) = \sum_{j,k=1}^{N} (\lambda_{jk} + \delta_{jk}\lambda) a_j \psi_k - \lambda \sum_{j=1}^{\infty} a_j \psi_j
\]

(2.180)

\[
= \sum_{j,k=1}^{N} (\lambda_{jk} + \delta_{jk}\lambda) a_j \psi_k - \lambda a.
\]

(2.181)

This approximation preserves the matrix \( \lambda_{ij} \) intact for \( i, j < N \), sets all off-diagonal elements for \( i, j \geq N \) to zero, and approximates the diagonal elements for \( i \geq N \) by a single constant: \(-\lambda\). The preservation of diagonal elements of all orders allows convergent solutions at all values of \( y \).

Inserting \( J(a) \) from eq. (2.181) into the linearized Boltzmann equation (eq. (2.158)) we find

\[
[i(\nu - \nu_0) + \frac{n_0 \sigma}{k} \lambda] \sum_{j=1}^{\infty} a_j \psi_j = \frac{1}{2\pi} + \frac{n_0 \sigma}{k} \lambda \left[ \sum_{j,k=1}^{N} \beta_{jk} a_j \psi_k \right]
\]

(2.182)

where

\[
\beta_{jk} = \frac{\lambda_{jk}}{\lambda} + \delta_{jk}.
\]

(2.183)

It is convenient to specify the proportionality constant in eq. (2.132) to be \(-\lambda_{11}\) so that

\[
y = -\lambda_{11} \left( \frac{n_0 \sigma}{k} \right).
\]

(2.184)
Dividing through by \( \left[ i(x - \epsilon_z) + (n_0 \sigma/K) \lambda \right] \) and taking the inner product with \( \psi_n \) we obtain an inhomogeneous set of coupled linear equations

\[
a_n(x, y) = \frac{1}{2\pi} \gamma_n - \gamma \left( \frac{\lambda}{\lambda_n} \right) \sum_{j=1}^{N} \beta_{jk} \lambda_k a_j(x, y), \quad n = 1, 2, \ldots
\]

(2.185)

where

\[
\gamma_{ij} = \left( \psi_{ij}, \frac{\psi_i}{[i(z - \epsilon_z) - \frac{\gamma\lambda}{\lambda_n}]} \right) = \int d\gamma \left[ \frac{\phi(\gamma)}{\psi_i(\gamma)} \frac{\psi_j(\gamma)}{[i(z - \epsilon_z) - \frac{\gamma\lambda}{\lambda_n}]} \right].
\]

Eqs. (2.185) for \( n = 1, 2, \ldots, N \) form a closed set of \( N \) equations for \( N \) unknowns which can be solved for \( a_n \) with \( n = 1, 2, \ldots, N \). Eqs. (2.185) for \( n = N + 1, N + 2, \ldots \) may then be employed to calculate the remaining \( a_n \), i.e. for \( n \geq N + 1 \).

Sugawara has followed the convention in choosing \( \lambda = \lambda_N + 1 \) so that once the matrix elements \( \lambda_{ij} \) and the scalar products \( \gamma_{ij} \) are determined, eqs. (2.186) may be numerically solved for \( a_1(x, y) \) and thus \( S(x, y) \) via eq. (2.174). That the KM yields the proper kinetic limit can be seen by setting \( y \sim n_0 \sigma/K = 0 \) in eqs. (2.185) for \( n = 1 \), thereby obtaining \( a_1(x, 0) \). Using eq. (2.174) one finds the correct result for \( S(x, 0) \), given in eq. (2.165).

The KM procedure has been carried out (30) for Maxwell and hard sphere molecules for order \( N \) up to \( N = 21 \) at which convergence is obtained for all values of \( x \) and \( y \). That is, \( S(x, y) \) does not change significantly as successive orders are included beyond \( N = 21 \). Since the KM method, when convergent, yields exact solutions of the BE, the resulting spectra \( S(x, y) \) are exact.

Although this completes the review of the calculation of the spectra, we shall postpone discussion of the results for \( S(x, y) \) until after we have related \( y \) to measurable properties of the gas, and discussed the calculation of \( S(x, y) \) from the hydrodynamic equations. The parameter \( y \) for a
particular intermolecular potential may be obtained from the transport coefficients calculated for the same intermolecular potential, via the Chapman-Enskog procedure.

We close the discussion of the kinetic model by pointing out the relationship of the density fluctuation spectrum to the dispersion relation for forced sound propagation. Sirovich and Thurber\(^{(31)}\) have applied the kinetic model to the calculation of the dispersion relation for forced sound propagation in a dilute monatomic gas. They show that this dispersion relation is obtained from eqs. (2.185) by solving their characteristic equation

\[
D(x, y) = Det \left[ \delta_{\alpha \beta} + \psi(\frac{\lambda}{\lambda_0}) \sum_{k \alpha \beta} \sum_{k \beta \beta} \frac{\lambda}{\lambda_0} y_{\alpha \beta} \right] = 0.
\]

The dispersion relation for forced sound propagation is obtainable from eqs. (2.185) because these are the equations of motion of the gas for small deviations from equilibrium. To calculate the dispersion relation for forced sound propagation one seeks solutions of the Boltzmann equation that correspond to density disturbances which are periodic in time but which die away in space. Thus, the characteristic equation \(D(x, y) = 0\) is solved for the complex spatial propagation constant \(y(x)\) as a function of real frequency \(x\). The spectrum \(S(x, y)\), on the other hand, is determined by the time dependence of disturbances in the gas which are periodic in space. This time dependence is governed by the dispersion relations obtained when \(D(x, y) = 0\) is solved for \(x(y)\) where \(x\) is imaginary and \(y\) is real.

The density fluctuation spectrum and the dispersion relations for forced sound propagation are thus closely related. The solution of \(D(x, y) = 0\) determines the acoustic propagation constant as well as the time dependence of each of the normal modes of the system and thus the nature of the spectral contribution of each mode. The calculation of the spectrum requires, in addition, the inhomogeneous terms in eqs. (2.185) which arise from the initial condition and determine the extent to which each mode must be excited to yield the spectrum.
d) The Chapman-Enskog Procedure

Starting from the BE the Chapman-Enskog procedure (CEP)\(^{(32),(33)}\) enables one to obtain a set of hydrodynamic equations which determine the behavior of the average number density \(n(\vec{r}, t)\), temperature \(T(\vec{r}, t)\) and velocity \(\vec{u}(\vec{r}, t)\) in the long wavelength limit \((1/K \gg t)\). These hydrodynamic equations consist of the conservation laws for mass, momentum and energy flux and equations for the heat flux vector and stress tensor in terms of temperature and velocity gradients respectively. The latter relations involve the transport coefficients for energy \((\kappa = \text{thermal conductivity})\) and momentum \((\eta = \text{shear viscosity})\) which can be calculated from the properties of the constituent particles.

The CEP dictates that the distribution function \(f(\vec{r}, \vec{v}, t)\) depends on \(\vec{r}\) and \(t\) only through the local number density, temperature, and velocity, so that

\[
f(\vec{r}, \vec{v}, t) = f(n(\vec{r}, t), \vec{u}(\vec{r}, t), T(\vec{r}, t), \vec{v}) . \tag{2.187}
\]

The initial approximation of the CEP is to replace the \(f(\vec{r}, \vec{v}, t)\) by the local Maxwellian equilibrium distribution,

\[
f(\vec{r}, \vec{v}, t) = f^{(o)}(\vec{r}, \vec{v}, t) = n(\vec{r}, t) \left( \frac{m}{2k_B T(\vec{r}, t)} \right) \exp \left[ \frac{-m}{2k_B T(\vec{r}, t)} (\vec{v} - \vec{u}(\vec{r}, t))^2 \right] , \tag{2.188}
\]

where \(n(\vec{r}, t)\), \(T(\vec{r}, t)\), \(\vec{u}(\vec{r}, t)\) are assumed to be slowly varying spatial functions. The distribution, \(f^{(o)}(\vec{r}, \vec{v}, t)\), being spherically symmetric in velocity space about local conditions, does not describe dissipative energy or momentum transport. This may be seen by calculating from \(f^{(o)}(\vec{r}, \vec{v}, t)\) the heat flux vector \(\vec{q}\) and the pressure tensor \(P_{ij}\):

\[
\vec{q}(\vec{r}, t) = m^2 n_o \int d^3 \vec{v} f^{(o)}(\vec{r}, \vec{v}, t) (\vec{v} - \vec{u}) (\vec{v} - \vec{u}) = 0 \quad (2.189)
\]
\[ P_{ij}(r^2,t) = m n \int d^3 \nu f^{(o)}(r^2,\nu,t) \delta(\nu_i - \nu_j) = n_0 k_B T_{ij}^b \]  \hspace{1cm} (2.190)

Furthermore \( f^{(o)} \) does not solve the BE since \( (\partial f^{(o)}/\partial t)^{\text{coll}} = 0 \) (collisions cannot relax \( f^{(o)}(r^2,\nu,t) \)), but, in general, streaming alone cannot account for the change of \( f^{(o)}(r^2,\nu,t) \)

\[ \left( \frac{\partial}{\partial t} + \vec{\nu} \cdot \nabla \right) f^{(o)}(r^2,\vec{\nu},t) \neq 0 . \]  \hspace{1cm} (2.191)

A solution of the BE can be obtained by assuming that the temperature and velocity gradients in the system produce small deviations from local equilibrium and thus that \( f(r^2,\nu,t) = f^{(o)}(r^2,\nu,t) + g(r^2,\nu,t) \) where \( g(r^2,\nu,t) \ll 1 \). Linearizing the BE one obtains an equation for \( g(r^2,\nu,t) \)

\[ \left( \frac{\partial}{\partial t} + \vec{\nu} \cdot \nabla \right) f^{(o)}(r^2,\vec{\nu},t) = f^{(o)} C(g) , \]  \hspace{1cm} (2.192)

where \( C \) is the collision operator of the linearized Boltzmann equation from eq. (2.132). The left hand side of this equation may be simplified using the conservation equations. These are obtained by using the laws for conservation of particle number, momentum, and energy in a collision. As was discussed in eq. (2.172) these conservation laws are expressed by \( J(\psi_j(\vec{\epsilon})) = 0 \) where \( J \) is the linearized Boltzmann collision operator and \( \psi_j(\vec{\epsilon}) \) an eigenfunction of \( J \) with zero eigenvalue. As was pointed out in Table (2.3) these eigenfunctions of \( J \) which have zero eigenvalues are \( \psi_j(\vec{\epsilon}) = 1, \vec{\epsilon}, \vec{\epsilon}^2 / 2 - 3/2 \) for which the relation \( J(\psi_j(\vec{\epsilon})) = 0 \) expresses respectively conservation of particle number, momentum, and energy in a collision. The conservation law \( J(\psi_j(\vec{\epsilon})) = 0 \) can be shown to be equivalent to the following relation for the full Boltzmann collision operator \( (\partial f/\partial t)^{\text{coll}} \)
in eq. (2.127)

\[
\int d^3 \mathbf{v} \, \psi_j(\mathbf{v}) \left( \frac{\partial f_j}{\partial t} \right)_{\text{coll}} = 0.
\]

Using the Boltzmann equation (eq. 2.127) we have further that

\[
\int d^3 \mathbf{v} \left( \frac{2}{\partial t} + \mathbf{v} \cdot \nabla \right) f(\mathbf{p}, \mathbf{v}, t) \psi_j(\mathbf{v}) = 0 \tag{2.193}
\]

for the functions \( \psi_j(\mathbf{v}) \) so that \( J(\psi_j(\mathbf{v})) = 0 \). The macroscopic laws for the conservation of number density, momentum density and energy density are obtained from eq. (2.193) by substituting \( \psi_j(\mathbf{v}) = 1, \mathbf{v}, \) and \( v^2 - 3/2 \) respectively. These are

(number) \hspace{1cm} \frac{\partial n}{\partial t} + \nabla \cdot (n \mathbf{u}) = 0 \tag{2.194}

(momentum) \hspace{1cm} m n \left( \frac{\partial}{\partial t} + \mathbf{v} \cdot \nabla \right) \mathbf{u} = - \nabla \cdot \mathbf{P} \tag{2.195}

(energy) \hspace{1cm} m n \left( \frac{\partial}{\partial t} + \mathbf{v} \cdot \nabla \right) k_B T = - \frac{2}{3} \mathbf{v} \cdot \mathbf{q} - \frac{2m}{3} \frac{\mathbf{P} \cdot \mathbf{D}}{\rho} \tag{2.196}

where the rate of strain tensor, \( D_{ij} \), is

\[
D_{ij} = \frac{1}{2} \left( \frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} \right).
\]
Using the conservation equations, the effect of the streaming operator, 
$(\partial / \partial t + \overrightarrow{v} \cdot \nabla)$, on $f^{(o)}$ in eq. (2.192) may be expressed in terms of the spatial gradients of $T(\overrightarrow{r}, t)$ and $\overrightarrow{u}(\overrightarrow{r}, t)$ as follows

$$
\left( \frac{\partial}{\partial t} + \overrightarrow{\nabla} \overrightarrow{v} \right) f^{(o)}(\overrightarrow{r}, \overrightarrow{u}, t) = f^{(o)}(\overrightarrow{r}, \overrightarrow{u}, t) \left\{ \frac{1}{T} \nabla T \cdot \overrightarrow{U} \left( \frac{m}{2k_B T} - \frac{5}{2} \right) + \frac{m}{k_B T} \delta_{ij} \left( U_i U_j - (\frac{1}{3}) \delta_{ij} U^2 \right) \right\} \tag{2.198}
$$

where $\overrightarrow{U} = \overrightarrow{v} - \overrightarrow{u}$ and repeated indices are summed over. Introducing the normalized variable $\overrightarrow{c} = \overrightarrow{U} / 2 v_o$ we find from eq. (2.192)

$$
\frac{1}{T} \nabla T \cdot \overrightarrow{U} \left( c^1 - \frac{5}{2} \right) + \frac{2 \delta_{ij}}{2v_o} \left( c_i c_j - \frac{1}{3} \delta_{ij} c^2 \right) = n_0 \sigma \overrightarrow{J}(\overrightarrow{c}) \tag{2.199}
$$

where $J$ is the dimensionless collision operator of eq. (2.159). For Maxwell molecules the solution of this equation for $g$ is particularly simple because the velocity functions $\overrightarrow{c} (c^2 - 5/2)$ and $c_i c_j - (1/3) \delta_{ij} c^2$ are eigenfunctions $\psi_i(\overrightarrow{c})$ of the collision operator $J$, as may be noted in Table (2.3). Therefore

$$
\overrightarrow{J}(\overrightarrow{c} (c^2 - 5/2)) = \lambda_{ij} \overrightarrow{c} (c^2 - 5/2) \tag{2.200}
$$

and

$$
\overrightarrow{J}(c_i c_j - \frac{1}{3} \delta_{ij} c^2) = \lambda_{ij} (c_i c_j - \frac{1}{3} \delta_{ij} c^2) \tag{2.201}
$$

so that the perturbation $g(\overrightarrow{r}, \overrightarrow{t}, t)$ of the distribution $f^{(o)}$ under the influence of temperature and velocity gradients is
\[ q(\vec{r}, t) = \frac{1}{n_o \sigma \lambda_n} \left[ \frac{1}{T} \nabla T \cdot \mathcal{E} \left( c^2 - \frac{S}{2} \right) \right] \]

\[ + \frac{2}{n_o \sigma \lambda_{o2}} \left( \frac{1}{T_0} \right) D_{ij} \left( c_i c_j - \frac{1}{3} \delta_{ij} c^2 \right), \quad (2.202) \]

The absolute magnitude of \( g \) may be estimated by noting that for an oscillatory temperature gradient \( \delta T \sim \exp(i \vec{K} \cdot \vec{r}) \), we have \( |\nabla T/T| \sim K \) so that \( g \sim K/n_o \sigma \lambda_{11} \sim 1/y \). Since the linearization of the BE in eq. (2.192) requires the condition \( g \ll 1 \), we can expect the first order (Navier-Stokes) approximation, which we have just carried out, to become poorer as \( y \) decreases much below \( y = 10 \). Evaluating the heat flux vector and pressure tensor from \( f = f(0) [1 + g] \) we find

\[ q(\vec{r}, t) = \frac{n_o m}{2} \int d^3 \nu \, f(0) \, \phi \Phi U^2 = n_o m \left( \frac{2 k_B T}{m} \right)^{3/2} \int d^3 \phi (c) \, g(\vec{r}, \overline{z}, t) \, \mathcal{E} \, c^2 \]

\[ (2.203) \]

\[ q(\vec{r}, t) = \frac{5}{4} \frac{m k_B}{\sigma \lambda_{11}} \left( \frac{2 k_B T}{m} \right)^{1/2} \nabla T(\vec{r}, t) \]

\[ (2.204) \]

and similarly

\[ P_{ij}(\vec{r}, t) = n_o k_B T(\vec{r}, t) \delta_{ij} + 2 n_o k_B T(\vec{r}, t) \int d^3 \phi (c) \, g(\vec{r}, \overline{z}, t) c_i c_j \]

\[ (2.205) \]

\[ P_{ij}(\vec{r}, t) = n_o k_B T(\vec{r}, t) \delta_{ij} + \frac{m}{\sigma \lambda_{o2}} \left( \frac{2 k_B T}{m} \right)^{1/2} \left( D_{ij}(\vec{r}, t) - \frac{1}{3} D_{kk}(\vec{r}, t) \delta_{ij} \right) \]

\[ (2.206) \]

Eqs. (2.194-6), (2.204) and (2.206) constitute the hydrodynamic equations in the long wavelength limit.

From the definitions of thermal conductivity, \( \kappa \), and shear viscosity,
\[ \kappa = - \frac{5}{4} \frac{k_B}{\sigma \lambda_{11}} \left( \frac{2k_BT}{m} \right)^{\frac{1}{2}} = - \frac{5}{6} \left( \frac{m C_v}{\sigma \lambda_{11}} \right) \sqrt{2} \nu_0, \]  
\[ \eta = - \frac{m}{2 \sigma \lambda_{02}} \sqrt{2} \nu_0, \]  
(2.207)  
(2.208)

where \( C_v = 3k_B/2m \) is the heat capacity per unit mass. Since from Table (2.3), \( \lambda_{11}/\lambda_{02} = 2/3 \), the Eucken ratio, \( \kappa / \eta C_v \) for Maxwell molecules is

\[ E = \frac{\kappa}{\eta C_v} = \frac{5}{2}. \] : Maxwell. (2.209)

Since, as shown in Table (2.3), the eigen values \( \lambda_{11} \) and \( \lambda_{02} \) for hard sphere molecules differ slightly from the Maxwell molecule values, a gas of hard spheres has an Eucken ratio of 2.52:

\[ E = 2.52. \] hard spheres. (2.210)

Eqs. (2.207 and 2.208) are the desired expressions for the transport coefficients \( \eta \) and \( \kappa \) in terms of thermodynamic and molecular parameters. Before relating \( \eta \) and \( \kappa \) to \( \gamma \), however, we shall briefly discuss the physical significance of the eigenfunctions \( \psi_i \) and the eigenvalues \( \lambda_i \).

e) Discussion of the Eigenfunctions and Eigenvalues

The evaluation of the moments \( \mathbf{c}^2 \) and \( c_i c_j \) of the distributions in eqs. (2.203) and (2.205) shows that the part of \( g \) corresponding only to \( \psi_{11} \) couples to \( \mathbf{c}^2 \) and that corresponding to \( \psi_{02} \) couples only to \( c_i c_j \), that is

\[ \int d^3 \mathbf{c} \, \phi(c) \mathbf{c}^2 \psi_{02}(c) = \int d^3 \mathbf{c} \, \phi(c) c_i c_j \psi_{02}(c) = 0. \]
The eigenfunction $\psi_{11}(c)$ then is that modification of the distribution function which produces heat flow and $\psi_{02}(c)$ that which produces velocity gradients.

The physical significance of the eigenvalues $\lambda_i$ can be understood more clearly if we solve eq. (2.131) in the spatially uniform case. With no $\vec{r}$ dependence we can write

$$h(\vec{v}, t) = \prod_i h_i(t) \psi_i(\vec{v})$$

and we find from eq. (2.131)

$$h_i(t) = h_i(0) e^{-t/\tau_i} \quad (2.211)$$

where the $1/\tau_i$ are the eigenvalues of $C$:

$$C \psi_i = -\frac{1}{\tau_i} \psi_i \quad (2.212)$$

In terms of the dimensionless eigenvalues $\lambda_i$ of the operator $J$ (see eq. (2.159))

$$\frac{1}{\tau_i} = -\sqrt{2} \eta_0 \sigma v_o \lambda_i \quad (2.213)$$

The inverse eigenvalues $\tau_i$ then are relaxation times for the various perturbations $\psi_i(\vec{v})$ to the equilibrium distribution function, and the moments which couple to them. There are 5 infinite relaxation times (see Table (2.3)) corresponding to the perturbations $1, \vec{v}$, and $v^2$ which cannot be relaxed by collisions because of the conservation of particle number, momentum and energy respectively. From the discussion above it is clear that $\tau_{11}$ and $\tau_{02}$
are relaxation times for the moments which correspond to heat flux and momentum flux respectively. In the present approximation (Navier-Stokes) these are the highest velocity moments required to describe the nonequilibrium state. For more rapidly varying phenomena higher velocity moments are required and the CEP must be carried to a higher order of approximation. (34)

The kinetic model method treats all relaxation times \( \tau_i \) for \( i \leq N + 1 \) exactly and sets all \( \tau_i \) for \( i > N + 1 \) to an arbitrary constant, usually \( \tau_{N+1} \). The lowest order KM approximation is for \( N = 6 \) since the conservation laws require \( \tau_i = \infty, i = 1, \ldots, 5 \). This is the Bhatnagar-Gross-Krook (BGK) model or the single relaxation time model since all \( \tau_i = \tau_5 \) for \( i > 5 \). Thus the BGK model equates the relaxation times for heat flow and velocity gradients, producing an incorrect Eucken ratio and thus an incorrect ratio of central to Brillouin width in the resulting spectrum. For higher order models however \( \tau_{11} / \tau_{02} \) is preserved and the correct hydrodynamic limit obtained.

f) Kinetic Model Wrapup

We may now express \( \kappa \), \( \eta \) and \( \gamma \) terms of the relaxation times \( \tau_{11} \) and \( \tau_{02} \) using eqs. (2.184), (2.213), (2.207), and (2.208):

\[
\gamma = \frac{1}{\sqrt{2kT_0} \tau_{11}} \quad (2.214)
\]

\[
\kappa = \frac{5}{3} \zeta' \rho \tau_{11} \quad (2.215)
\]

\[
\eta = \rho \tau_{02} \quad (2.216)
\]
where \( P = n_0 k_B T \). The parameter \( y \) may then be determined from either the thermal conductivity, \( \kappa \), or viscosity, \( \eta \). This determination will be unique, however, only if the measured values of \( \kappa, \eta, \) and \( C_v \) satisfy the Eucken ratio for the intermolecular potential being employed. This same condition is required if the kinetic model is to accurately provide the linewidths of both central and Brillouin lines in the hydrodynamic limit. It is of interest then to compare the measured Eucken ratio of real gases with those given in eqs. (2.209) and (2.210) of the models which we intend to use. The Eucken ratio was calculated at 25°C from the measured viscosity\(^{35}\) and thermal conductivity\(^{36}\) of the simple gases: xenon, krypton, argon, neon and helium. The ideal gas value of \( C_v \) was used in all cases.\(^{37}\) These results are summarized on Table (2.4). Measured values of \( E \) at \( T = 25^\circ C \) and \( P = 1 \) atm. were found to be \( E = 2.50 \) within experimental error for xenon, krypton, argon and neon. The determination of \( y \) therefore, for either the Maxwell molecule or hard sphere gas is unambiguous for these gases at 25°C. The experimental values of \( E \) at 25°C for xenon, krypton, argon and neon are also in good agreement with the value of \( E = 2.50 \) calculated from the Lennard-Jones potential.\(^{38}\) For helium at 25°C an Eucken ratio of \( E = 2.42 \) is observed. Measurements of \( E \) for all of the simple gases show that \( E \) tends to decrease with increasing \( T/T^* \), where \( T^* \) is the attractive well depth of the intermolecular potential. This is evident from Table (2.4) and arises from deviations of the intermolecular potential from the Lennard-Jones form.

Since available measurements of \( \eta \) are more accurate than those of \( \kappa \) we shall use \( \eta \) to determine \( y \). We find from eqs. (2.214) and (2.216) for \( y \) in the case of Maxwell molecules (\( \tau_{11}/\tau_{02} = 3/2 \))

\[
y = \sqrt{\frac{2}{3}} \frac{m n_0 \nu_c}{\eta \kappa}.
\]

\( y \) is defined as

Maxwell

(2.217)
Table 2.4: Attractive Well Depth, Thermal Conductivity, Shear Viscosity and Eucken Ratio of Simple Gases at 25°C and 1 atm.

<table>
<thead>
<tr>
<th>T*(°K)</th>
<th>( \kappa ) (Cal/sec-cm-°C)(^{(36)} )</th>
<th>( \eta ) (μ poise)(^{(35)} )</th>
<th>E</th>
</tr>
</thead>
<tbody>
<tr>
<td>Xe 229</td>
<td>1.316 ± 1%</td>
<td>231.02 ± 0.06%</td>
<td>2.509 ± 0.025</td>
</tr>
<tr>
<td>Kr 190</td>
<td>2.265 ± 1%</td>
<td>253.22 ± 0.06%</td>
<td>2.515 ± 0.025</td>
</tr>
<tr>
<td>Ar 124</td>
<td>4.22 ± 0.5%</td>
<td>226.38 ± 0.04%</td>
<td>2.498 ± 0.012</td>
</tr>
<tr>
<td>Ne 35.7</td>
<td>11.60 ± 0.5%</td>
<td>317.30 ± 0.05%</td>
<td>2.503 ± 0.012</td>
</tr>
<tr>
<td>He 10.2</td>
<td>35.60 ± 0.5%</td>
<td>198.46 ± 0.05%</td>
<td>2.42 ± 0.012</td>
</tr>
</tbody>
</table>
We define the mean free path \( l = \sqrt{2} v_0 \tau_0 \), so that \( l \) is the distance traveled by a particle with the most probable speed in a time \( \tau_c \), the velocity correlation time. We show in sec. (II C 4) that \( \tau_c = 0.88 \tau_{11} \), so that from eq. (2.214)

\[
\gamma = \frac{1}{k' \xi} \left( \frac{\tau_c}{\tau_{11}} \right) = \frac{0.88}{k' \xi} \approx 0.13 \frac{\Lambda}{\xi}.
\]  

(2.218)

The kinetic model has also been carried out by Sugawara for hard spheres. In this case he defines

\[
\gamma_{HS} = \frac{1}{\sqrt{2} k' v_0 \tau_{11}^{o2}}
\]

so that, since \( \tau_{11}/\tau_{11}^{o2} = 1.5 \), one would expect \( \gamma_{HS}/\gamma_M = 1.5 \) under identical physical conditions in the Maxwell and hard sphere gas. Due to higher order corrections to the eigenvalues in the hard sphere case, however, one finds (see Table (2.3))

\[
(\tau_{11}^{o2})_{HS} = 0.984 (\tau_{11}^{o2})_{Max}
\]

so that

\[
\frac{\gamma_{HS}}{\gamma_{Max}} = \frac{1.5}{0.984} = 1.524
\]

and

\[
\gamma_{HS} = 1.524 \sqrt[3]{\frac{2 m n_0}{\eta k}} \quad \text{(hard spheres)}
\]  

(2.219)
To avoid confusion, for the presentation of all spectra (KM and hydrodynamic) and data here, we shall use the parameter $y$ for both rigid sphere and Maxwell molecules where it is understood that rigid sphere plots are for $y_{HS} = 1.524y$.

Spectra $S(x, y)$, have been calculated$^{(30)}$ from the KM approximation for $N = 21$ and $|x| < 3.0$ for Maxwell molecules at $y = 0, 0.1, 0.328, 0.5, 0.767, 1.312, 1.968, 3.00, 4.65$ and $6.00$. and for hard sphere molecules at $y = 0.328, 0.767, 1.312, 1.968, 3.00$ and $6.00$. Selected spectra are shown plotted in fig. (1.1). In the kinetic limit ($y \to 0$) the spectra approach the Gaussian form of eq. (2.166). As $y$ increases the three component spectrum of a system described by the hydrodynamic equations gradually evolves, the sound peaks appearing first as shoulders on the Gaussian near $x \approx 0.8$. The hydrodynamic limit will be discussed in the next section.

Only the Maxwell molecule results have been plotted here because the spectra are rather insensitive to choice of intermolecular potential differing at most by $\sim 3\%$, even though the Maxwell and hard sphere molecules respectively represent the limits of a soft and hard repulsive force. Tabulations of KM spectra for Maxwell and hard sphere molecules for a few values of $x$ are given in Table (2.5) in the next section, along with corresponding results from hydrodynamic calculations.

In summary, the KM method employed by Sugawara, Yip and Sirovich yields exact solutions of the BE for the spectrum of light scattered by a dilute monatomic gas throughout the hydrodynamic-kinetic transition. The spectral shape is determined by the single parameter $y$, which can be determined exactly from the various parameters of the experiment.

3. Hydrodynamic Limit

a) Introduction

Although the KM method provides an exact means of calculating $S(x, y)$ for any frequency ($x$) and wavelength to mean free path ratio ($y$), it is of interest to calculate $S(x, y)$, in the limit of large $y$, directly from the hydrodynamic equations. We do this for several reasons. The first is that
such a calculation illustrates the structure of \( S(x, y) \) in the hydrodynamic limit and allows the prominent features of the spectrum to be identified in terms of the thermodynamic derivatives and transport coefficients of the gas. Secondly, such a calculation allows one to establish the range of applicability of the hydrodynamic equations to the description of density fluctuations, recalling from the previous section that the first order (Navier-Stokes) hydrodynamic equations obtained from the CEP could be expected to be valid only for \( y > 5 \), that is, in the long wavelength regime. We would also expect the hydrodynamic equations to break down for oscillatory disturbances of frequency \( \omega \) comparable to the relaxation frequencies for transport of momentum, \( 1/\tau_{02} \), and energy, \( 1/\tau_{11} \). Since \( \tau_{11} > \tau_{02} \), this leads to the condition \( \omega < 1/\tau_{11} \) or equivalently, from eqs. (2.156) and (2.214), \( x < y \) for hydrodynamics to apply. Thus hydrodynamics should not be expected to describe the tails of \( S(x, y) \) for \( x > y \).

The hydrodynamic approach to the calculation of the scattered light spectrum is through eq. (2.121), relating \( h(\vec{K}, \omega) \) to fluctuations in the dielectric constant \( \varepsilon \). The dielectric constant fluctuations \( \delta \varepsilon(\vec{r}, t) \) are, in turn, related to fluctuations in the independent thermodynamic state variables of the system, two such variables \( u, v \) being required for a one component system, so that in general

\[
\delta \varepsilon(\vec{r}, t) = \left( \frac{\partial \varepsilon}{\partial u} \right)_v \delta u(\vec{r}, t) + \left( \frac{\partial \varepsilon}{\partial v} \right)_u \delta v(\vec{r}, t).
\]  

(2.220)

The calculation of \( h(\vec{K}, \omega) \) is simplified if one chooses state variables whose fluctuations are spatially uncorrelated at a particular time, i.e.

\( \langle \delta u(\vec{r}, t) \delta v(\vec{r}', t) \rangle = 0 \). For a single component fluid, fluctuations in the pairs of variables, density and temperature \( (n, T) \), and pressure and entropy \( (p, s) \) satisfy this requirement. (39) The choice of density and temperature is convenient for a gas because, as was noted in obtaining eq. (2.112), the dielectric constant is independent of temperature and eq. (2.112) gives \( \langle \delta \varepsilon(\vec{r}, t) \delta \varepsilon(0, 0) \rangle \). We find from eqs. (2.112) and (2.120)
\[
\langle \delta E(\mathbf{r}, t) \delta E(0, 0) \rangle = \left( \frac{\partial E}{\partial n} \right)_T \langle \delta n(\mathbf{r}, t) \delta n(0, 0) \rangle = (\alpha \epsilon_0)^2 \langle \delta n(\mathbf{r}, t) \delta n(0, 0) \rangle
\]
(2.21)

and obtain for \( h(\mathbf{k}, \omega) \) from eqs. (2.118) and (2.121)

\[
h(\mathbf{k}, \omega) = \frac{1}{2\pi} \left[ \frac{(k_0^e)^2 \sin \Phi}{4\pi} \right]^2
S_\omega (\mathbf{k}, \omega) = \frac{1}{2\pi} \left[ \frac{(k_0^e)^2 \sin \Phi}{4\pi} \right]^2 n_o (\alpha \epsilon_0)^2 S_\rho (\mathbf{k}, \omega)
\]
(2.22)

where \( S_\rho (\mathbf{k}, \omega) \) is defined in eq. (2.44)

\[
S_\rho (\mathbf{k}, \omega) = \int d^3 \mathbf{r} dt e^{i(\mathbf{k} \cdot \mathbf{r} - \omega t)} \rho(\mathbf{r}, t) = \int d^3 \mathbf{r} dt e^{i(\mathbf{k} \cdot \mathbf{r} - \omega t)} \frac{\langle \delta n(\mathbf{r}, t) \delta n(0, 0) \rangle}{n_o}
\]
(2.23)

Thus we need concern ourselves only with calculation of correlations in fluctuations, \( \delta n(\mathbf{r}, t) \), in the density, \( h(\mathbf{k}, \omega) \) being proportional to \( S_\rho (\mathbf{k}, \omega) \).

Mountain\(^{40}\) has calculated \( S_\rho (\mathbf{k}, \omega) \) exactly for a simple fluid described by the first order (Navier-Stokes) hydrodynamic equations. We shall review his calculation and consider several approximations to his exact results. We present spectra calculated using the hydrodynamic equations obtained from carrying the Chapman-Enskog procedure to the second order of approximation (Burnett approximation). We also present the results of the generalized hydrodynamic theory of Selwyn.\(^{41}\)

b) Calculation of Approximate and Exact Hydrodynamic Spectra
To calculate \( S_\mathbf{k}(\mathbf{K}, \omega) \) it is more convenient to deal with the Laplace-Fourier transform \( n(\mathbf{K}, s) \) than \( n(\mathbf{r}, t) \) so we define:

\[
n(\mathbf{K}, s) = \mathcal{L}[n(\mathbf{r}, t)] = \int e^{-st} \left[ \int d^3r e^{i\mathbf{K} \cdot \mathbf{r}} \delta n(\mathbf{r}, t) \right],
\]

(2.224)

and also

\[
n(\mathbf{K}) = \int d^3r e^{i\mathbf{K} \cdot \mathbf{r}} \delta n(\mathbf{r}, 0),
\]

(2.225)

with analogous definitions for \( T(\mathbf{K}, s) \) and \( T(\mathbf{K}) \). From eqs. (2.223) and (2.224) we find that

\[
S_\mathbf{k}(\mathbf{K}, \omega) = \frac{1}{n_0 V} 2Re \left\{ \langle n(\mathbf{K}, s) n(-\mathbf{K}) \rangle_{s=i\omega} \right\}
\]

(2.226)

where \( V \) is the system volume which we let become infinite. Since the deviations from equilibrium being considered are small the linearized hydrodynamic equations are applicable and for a dilute monatomic gas are

\[
\frac{\partial (\delta n)}{\partial t} + n_0 \nabla \cdot \mathbf{U} = 0
\]

(continuity) (2.227)

\[
n_0 \frac{\partial \mathbf{u}}{\partial t} + \frac{C_s^2}{\gamma} \nabla (\delta n) + \frac{C_s^2 c_s n_0}{\gamma} \nabla (\delta T)
\]

(\text{Navier-Stokes, longitudinal part})

\[
- \frac{4}{3} \frac{n}{m} \nabla (\nabla \cdot \mathbf{U}) = \frac{F}{m}
\]

(2.228)
\[ n_0 c_v \frac{\partial (\delta t)}{\partial t} + \frac{n_0 c_v (\gamma - 1)}{\alpha_T} \nabla \cdot \vec{u} - \kappa \nabla^2 (\delta t) \]  
(2.229)

(Energy transport)

where we have used and will use:

- \( n_0 \) = average number density
- \( m \) = mass per particle
- \( c_p \) = heat capacity per particle at constant pressure
- \( \gamma \) = \( c_p / c_v \)
- \( \eta \) = shear viscosity
- \( \alpha_T \) = thermal expansion coefficient
- \( c_o \) = adiabatic sound velocity
- \( \kappa \) = thermal conductivity
- \( \vec{F} \) = external force /unit volume
- \( \kappa_T \) = isothermal compressibility
- \( \kappa_T^I \) = \((n \kappa_T)^{-1}\), the isothermal compressibility of an ideal gas.

Since there are no external forces we may set \( \vec{F} = 0 \). We define \( \psi = \nabla \cdot \vec{u} \).

The Laplace-Fourier transformation of eqs. (2.227-9) leads to three simultaneous linear equations for \( n(\vec{K}, s) \), \( T(\vec{K}, s) \), and \( \psi(\vec{K}, s) \) in terms of \( n(\vec{R}) \), \( T(\vec{R}) \), and \( \psi(\vec{R}) \) which may be solved to yield \( n(\vec{K}, s) \) in the form

\[ n(\vec{K}, s) = A(\vec{K}, s)n(\vec{R}) + B(\vec{K}, s)T(\vec{R}) + C(\vec{K}, s)\psi(\vec{R}) \]  
(2.230)

so that the spectral density \( S_p(\vec{K}, \omega) \) is given by...
Thus the frequency dependence of the power spectrum of the density fluctuation of wave vector $\vec{k}$ comes entirely from the response functions $A$, $B$ and $C$ of the equilibrium system but with the respective amplitudes $\langle n(\vec{k})n(-\vec{k}) \rangle$, $\langle T(\vec{k})n(-\vec{k}) \rangle$, and $\langle \psi(\vec{k})n(-\vec{k}) \rangle$, which are related to time independent spatial correlations of $\delta n(\vec{r},t), \delta T(\vec{r},t)$ and $\psi(\vec{r},t)$. We have for $\langle n(\vec{k})n(-\vec{k}) \rangle$:

$$\langle n(\vec{k})n(-\vec{k}) \rangle = \int d^3r d^3r' e^{i(\vec{k}\cdot\vec{r}' - \vec{k}\cdot\vec{r})} \langle \delta n(\vec{r}'_0) \delta n(\vec{r}'_0) \rangle$$

$$= V \int d^3s e^{i\vec{k}\cdot\vec{r}} \langle \delta n(s) \delta n(0,0) \rangle$$

$$= n_0 V \int d^3s e^{i\vec{k}\cdot\vec{s}} \rho(\vec{s},0)$$

$$= n_0 V \int d^3s \left[ \delta(\vec{s}) + n_0 \mathcal{A}(s) \right] ,$$

which from the discussion of sec. (II B 2c) and eq. (2.85) yields

$$\langle n(\vec{k})n(-\vec{k}) \rangle = n_0 V (1 + n_0 u^*) = \frac{\kappa_T}{\kappa_F} n_0 V \approx n_0 V . \quad (2.232)$$

Since density temperature fluctuations are statically independent \(^{39}\) we have $\langle \delta n(\vec{r}) \delta T(\vec{r}) \rangle = 0$ so that $\langle n(\vec{k})T(-\vec{k}) \rangle = 0$. Similarly $\langle \delta n(\vec{r})\psi(\vec{r}) \rangle = 0$ and we have $\langle n(\vec{k})\psi(-\vec{k}) \rangle = 0$. We then find from eq. (2.231)
The response function $A(K, s)$ is given by

\[
S_\rho(K, \omega) = \frac{K^2}{K^2 - \omega} \left\{ A(K, s) \right\}_{\omega = i\omega}.
\] (2.233)

The response function $A(K, s)$ is given by

\[
A(K, s) = \frac{N(s)}{D(s)} = \frac{1 \quad 1 \quad 0 \quad 0 \quad 0 \quad 0 \quad -\omega^2 \gamma}{s + bK^2 \quad -\omega^2 \gamma \quad 0 \quad s + aK^2 \quad 0 \quad s + bK^2 \quad -\omega^2 \gamma \quad 0 \quad s + aK^2}
\] \hspace{1cm} (2.234a)

\[
A(K, s) = \frac{\frac{S^2}{s^3} + \frac{S(a+b)k^2}{s^2} + \frac{abk^4}{s} + \frac{c^2k^2(1-1/\gamma)}{s}}{s^3 + s^2(a+b)k^2 + s(c^2k^2 + abk^4) + ac^2k^2\gamma}.
\] \hspace{1cm} (2.234b)

where

\[
a = \frac{2\eta}{n_0 c}\]
\hspace{1cm} (2.235)

\[
b = \frac{4\eta}{3mn_0}.
\] \hspace{1cm} (2.236)

The denominator $D(s)$ is the characteristic determinant of the transformed hydrodynamic equations. By requiring that $D(s) = 0$ one obtains the dispersion relations
which determine the modes of excitation of the system. The factorization of $D(s)$ also allows a partial fraction expansion of $A(K, s)$

$$A(K, s) = \frac{A_1}{s - a_1} + \frac{A_2}{s - a_2} + \frac{A_3}{s - a_3},$$

which is convenient because it separates the contributions to the spectrum of the various modes. Even though the exact hydrodynamic $S(K, \omega)$ can be calculated from eqs. (2.233) and (2.234), we shall consider expressions of the form (2.238), since here the effects on $S(K, \omega)$ of the various thermodynamic derivatives and transport properties are more explicit. Since the exact determination of the roots is complicated algebraically, we shall consider approximate factorizations of $D(s)$, based on the experimental facts that for $y > 5$, $aK^2 \ll Kc_0$ and $bK^2 \ll Kc_0$. Defining

$$\Gamma_c \equiv \frac{a}{\gamma} K^2 = \frac{2\kappa}{n_0 c_p} K^2$$

and

$$\Gamma_B \equiv \frac{1}{2} \left\{ b + \left( 1 - \frac{1}{\gamma} \right) a \right\} K^2 = \frac{1}{2} \left\{ \frac{4\eta}{3m n_0} + \left( 1 - \frac{1}{\gamma} \right) \frac{\kappa}{n_0 c_v} \right\} K^2$$

and dividing $D(s)$ by $S + \Gamma_c$ one finds that

$$D(s) = (s + \Gamma_c)(s^2 + 2\Gamma_B s + (Kc_0)^2 + \mathcal{O}(abK^4))$$

and since $abK^4 \ll (Kc_0)^2$ we can neglect the terms of order $abK^4$ and obtain the approximate factorization of $D(s)$ :\textsuperscript{(43), (42)}
The root \( S = -\Gamma_C \) corresponds to a nonpropagating mode which relaxes density gradients through thermal conduction. The remaining two roots are complex conjugate pairs having the approximate form \( s = -\Gamma_B \pm iK_c \) and correspond to the relaxation of density gradients by damped propagating fluctuations (sound waves).

With \( D(s) \) in the form (2.242) the spectrum \( S_p(K, \omega) \) is given in terms of a partial fraction expansion for \( A(K, s) \)

\[
S_p(K, \omega) = \frac{\kappa_T}{\kappa_T^2} 2\Re \ A(K, s) = \frac{\kappa_T}{\kappa_T^2} 2\Re \left\{ \frac{B_1}{s + \Gamma_C} + \frac{B_2 s + B_3}{s^2 + 2\Gamma_B s + \omega_0^2} \right\}_{s = i\omega}
\]

where we have used \( \omega_0 = K_c \). Carrying out the required algebra we find to within terms of order \( \alpha e^{-K^4/(K_c)^2} \)

\[
B_1 = 1 - \frac{1}{\gamma} \quad (2.244)
\]

\[
B_2 = \frac{1}{\gamma} \quad (2.245)
\]

\[
B_3 = \frac{2\gamma}{\gamma} + (1 - \frac{1}{\gamma}) \Gamma_C^2 \quad (2.246)
\]

and

\[
S_p(K, \omega) = \frac{2\kappa_T}{\kappa_T^2} \left\{ \frac{(1 - \frac{1}{\gamma}) \Gamma_C^2}{\Gamma_C^2 + \omega^2} + \frac{2\Gamma_B \omega_0^2 - \Gamma_C (\omega^2 - \omega_0^2)(1 - \frac{1}{\gamma})}{(\omega^2 - \omega_0^2)^2 + (2\omega \Gamma_B)^2} \right\}.
\]

(2.247)
This form of the density fluctuation spectrum was originally obtained by Kadanoff and Martin (44) who applied the fluctuation-dissipation theorem to the calculation of time-dependent correlation functions for a fluid described by the Navier-Stokes hydrodynamic equations.

A further simplification of the form of $S_p(K, \omega)$ is possible by a partial fraction expansion of the second term in eq. (2.247). Montrose (42) has demonstrated the factorization of the denominator to be

$$ (\omega^2 - \omega_o^2) + (2\omega\Omega_B)^2 = \left[\frac{\Gamma_B^2}{\Gamma_c^2} + (\omega - \omega_1)^2\right]\left[\frac{\Gamma_B^2}{\Gamma_c^2} + (\omega + \omega_1)^2\right] $$

(2.248)

where $\omega_1^2 = \omega_o^2 - \Gamma_B^2$.

Carrying out the partial fraction expansion yields

$$ S_p(K, \omega) = \frac{\kappa_T}{\kappa_f^2} \left\{ \frac{2(1 - \frac{1}{\gamma})\Gamma_c^2}{\Gamma_c^2 + \omega^2} + \frac{\Gamma_B}{\Gamma_c^2 + (\omega - \omega_1)^2} + \frac{\Gamma_B}{\Gamma_c^2 + (\omega + \omega_1)^2} \right\} $$

+ \left[ \frac{-\Gamma_B}{\gamma} + \frac{\Gamma_c(1 - \frac{1}{\gamma})}{\Gamma_c^2 + (\omega - \omega_1)^2} \right] \left[ \frac{\omega - \omega_1}{\omega_1} \right] + \left[ \frac{-\Gamma_B}{\gamma} + \frac{\Gamma_c(1 - \frac{1}{\gamma})}{\Gamma_c^2 + (\omega + \omega_1)^2} \right] \left[ \frac{\omega + \omega_1}{\omega_1} \right] $$

(2.249)

The spectrum $S_p(K, \omega)$ then consists of three Lorentzian lines centered at $\omega = 0, \pm \omega_1$, plus terms which are antisymmetric about $\omega = \pm \omega_1$. Under conditions such that $\Gamma_C, \Gamma_B \ll \omega_0$ (often encountered for a liquid), the antisymmetric terms contribute negligibly, $\omega_1^2 = \omega_0^2$, and the familiar three component spectrum is obtained:

$$ S_p(K, \omega) = \frac{\kappa_T}{\kappa_f^2} \left\{ \frac{1}{8} \frac{2\Gamma_c}{\omega^2 + \Gamma_c^2} + \frac{\Gamma_B}{\gamma} \left[ \frac{1}{\Gamma_B^2 + (\omega - \omega_0)^2} + \frac{1}{\Gamma_B^2 + (\omega + \omega_0)^2} \right] \right\} $$

(2.250)
This spectrum may also be obtained directly from the following approximate factorization of $D(s)$:

$$D(s) \approx (s + \Gamma_C^*) (s + \Gamma_B^* + i \omega_0) (s + \Gamma_B^* - i \omega_0). \quad (2.251)$$

The (Brillouin) components centered at $\omega = \pm \omega_0$ indicate the presence of propagating density fluctuation modes which are simply thermally driven acoustic waves. The frequency splitting $\omega_0 = Kc_0$ is the frequency of adiabatically propagating sound waves of wave vector $K$, and the HWHH, $\Gamma_B^*$, of the shifted lines is related to the sound absorption coefficient per unit length, $\alpha$, by $\Gamma_B^* = \alpha c_0$. The unshifted (central) line indicates a non-propagating mode and has a HWHH $(\kappa/n_0 c_p) K^2$, proportional to the thermal diffusivity $D_T = \kappa/n_0 c_p$. This mode arises because density fluctuations are accompanied by temperature fluctuations which allow relaxation of the density fluctuations partly through heat flow.

For a dilute gas, since $\kappa$ and $\eta$ are independent of density, $n_0$, eqs. (2.215) and (2.216) show that $\Gamma_C \sim 1/n_0$ and $\Gamma_B \sim 1/n_0$. Since the frequency shift $\omega_0$ is also density independent the ratio of the line widths $\Gamma_C$ and $\Gamma_B$ to the splitting $Kc_0$ increases as $n_0$ is decreased. It is easy to show that $\Gamma_C, \Gamma_B \approx \omega_0/\gamma$ so that the regime where the components begin to overlap is accompanied by the breakdown of the applicability of hydrodynamics.

The ratio of total central intensity $I_C$ to total Brillouin intensity $I_B$ is $I_C/I_B = \gamma - 1$, for the approximations both of eqs. (2.243) and (2.250). For dilute monatomic gas, $\gamma = 5/3$, so the $I_C/I_B = 2/3$. For a dilute monatomic gas the use of the Eucken ratio (eq. (2.209)) in eqs. (2.239) and (2.240) for $\Gamma_C$ and $\Gamma_B$ shows that $\Gamma_C/\Gamma_B = 9/7$.

The extension of the hydrodynamic calculation of $S_p(K, \omega)$ to the second order of the Chapman-Enskog procedure (the Burnett approximation) has been carried out by Ranganathan and Nelkin (45) and by Foch. (46)
In the Navier-Stokes approximation the stress tensor \( P_{ij} \) and heat current \( q_i \) were given by eqs. (2.204) and (2.206) in terms of first order spatial derivatives of the gradients in velocity and temperature respectively. In the Burnett approximation \( P_{ij} \) and \( q_i \) involve higher order spatial velocity, temperature, and density derivatives. For spatial variation in only one direction we have \( P_{ij} \) and \( q_i \) in the Burnett approximation:

\[
P_{ij} = p - \frac{4\eta}{3} \frac{\partial u_i}{\partial x_i} - \frac{2\eta^2}{3\rho} \left\{ \frac{\alpha}{n} \frac{\partial^2 n}{\partial x_i^2} + \frac{\gamma}{T} \frac{\partial T}{\partial x_i^2} \right\}
\]

(2.252)

\[
q_i = \kappa \frac{\partial T}{\partial x_i} + \frac{2\eta^2}{3\rho} \left\{ \beta \frac{\partial^2 u_i}{\partial x_i^2} \right\}
\]

These equations may be compared with the corresponding equations for the Navier-Stokes approximation (eqs. 2.204, 6). Here \( \alpha, \beta, \) and \( \gamma \) are dimensionless transport coefficients which depend on the particular choice of intermolecular potential. The Burnett hydrodynamic equations follow from using \( P_{ij} \) and \( q_i \) from eqs. (2.252) in the conservation equations. Solution of these equations for the Burnett spectrum, \( S_B(K, \omega) \), is similar to that outlined for the Navier-Stokes case and has been carried out in general by Foch and for Maxwell molecules by Ranganathan and Nelkin. We shall present the latter results in the next section.

We also present spectra calculated for a dilute gas of Maxwell molecules using the generalized hydrodynamic theory of Selwyn. Selwyn has obtained from the Liouville equation and linear response theory general expressions for the correlation functions for conserved variables in a simple fluid. If \( A_k(r, t) \) is a conserved variable these expressions take the form

\[
\langle A_j(\vec{r}, \omega)A_k(-\vec{r}) \rangle = \left\{ -i\omega \delta_{ij} + M_{ij}(\vec{r}, \omega) \right\}^{-1} \langle A_j(\vec{r})A_k(-\vec{r}) \rangle
\]
where the matrix $M_{ij}(\vec{K}, \omega)$ contains the interesting dynamical information about the system. If $M_{ij}(\vec{K}, \omega)$ is known, the correlation functions, $<A_j(\vec{K}, \omega)A_k(-\vec{K})>$ can be employed to derive a set of equations in the conserved variables which determine their time behavior (hydrodynamic equations). Selwyn shows that the conservation laws can be used to determine $M_{ij}(\vec{K}, \omega)$ in the form of a power series expansion in about $\vec{K} = 0$ and calculates the first few terms in the series. For $\vec{K} = 0$, $M_{ij}(\vec{K}, \omega) = 0$ and the Euler conservation equations are produced. Retaining the term linear in $\vec{K}$ produces the Navier-Stokes hydrodynamic equations. Carrying his procedure to higher orders he finds hydrodynamic equations which are non-local in time and which, therefore, involve frequency dependent transport coefficients. He has solved these equations for the density-density correlation function of a dilute gas of Maxwell molecules. We present the exact form of Selwyn's density fluctuation spectrum, $S_{\text{SEX}}(x, y)$, as well as an approximate form, $S_{\text{SAP}}(x, y)$, which he has obtained by partial fraction expansion of the exact form. Because of the nature of the expansion in $\vec{K}$ (or equivalently $1/y$) Selwyn's calculation can be expected to be applicable only in the hydrodynamic limit, i.e. $y > 3$.

c) Numerical Comparison of Hydrodynamic and Kinetic Model Spectra

We have rewritten in terms of the reduced variables $x$ and $y$, and the spectrum $S(x, y)$ normalized to unity (see eq. (2.162)) the equations for the exact Navier-Stokes spectrum * (eqs. (2.233, 4)), the Kadanoff-Martin spectrum * (eq. (2.247)), the three Lorentzian spectrum * (eq. (2.250)), the Burnett spectrum, (45) and the exact and approximate forms of the Selwyn spectrum. (41) The resulting equations are:

*The Eucken ratio here was taken to be $E = 2.50$. 
\[
S_{NS}(x, y) = \frac{1}{\pi} \text{Re} \left[ \begin{array}{ccc}
1 & 1 & 0 \\
0 & i x + \frac{4}{\eta y} & -\frac{1}{2} \\
0 & \frac{2}{3} & i x + \frac{5}{6y} \\
\end{array} \right] \\
\]
(2.253a)

\[
S_{NS}(x, y) = \frac{1}{\pi} \text{Re} \frac{-x^2 + i x \left( \frac{23}{18y} \right) + \frac{20}{54y^2} + \frac{1}{3}}{-i x^3 - x^2 \left( \frac{23}{18y} \right) + i x \left( \frac{5}{6} + \frac{20}{54y^2} \right) + \frac{5}{12y}}; \\
\]
(2.253b)

\[
S_{kh}(x, y) = \frac{1}{5\pi y(x^2 + \left( \frac{4}{18y} \right)^2)} + \frac{1}{10\pi y} \left\{ \frac{\frac{50}{9} - 2x^2}{(x^2 - \frac{5}{6})^2 + \left( \frac{7x}{9y} \right)^2} \right\}; \\
\]
(2.254)

\[
S_{3L}(x, y) = \frac{1}{5\pi y(x^2 + \left( \frac{4}{18y} \right)^2)} + \frac{10.5}{90\pi y} \left\{ [(x + \sqrt{\frac{5}{6}})^2 + \left( \frac{7}{18y} \right)^2] \\
+ [(x - \sqrt{\frac{5}{6}})^2 + \left( \frac{7}{18y} \right)^2] \right\}; \\
\]
(2.255)
\[ S_B(x,y) = \frac{1}{\pi} \text{Re} \begin{pmatrix} 1 & 1 & 0 \\ 0 & i\chi + \frac{4}{qy} & -\frac{1}{2} + \frac{4}{5qy^2} \\ 0 & \frac{2}{3} + \frac{14}{5qy^2} & i\chi + \frac{5}{6y} \end{pmatrix} \]

\begin{equation}
S_B(x,y) = \frac{1}{\pi} \text{Re} \left\{ -x^2 + i\chi \left( \frac{23}{18y} \right) + \frac{1}{y^2} \left( \frac{73}{162} - \frac{14}{72qy^2} \right) + \frac{1}{3} \right\};
\end{equation}

\[ S_{\text{sex}}(x,y) = \frac{1}{\pi} \text{Re} \frac{N}{D}, \quad (2.257) \]

where

\[ N = -x^2 + i\chi \left( \frac{23y}{12} + 1.5 i\chi \right) z_1 z_2 + \frac{1}{3} + \frac{z_1 z_2}{q} \]

\[ -i\chi \left\{ \frac{27z_2^2}{S(i\chi + qy)} + \frac{8z_1 z_2^2}{5} + 5z_1^3 + 2z_1^2 z_2 + \frac{7z_1^2}{(ix + qy)} \right\}, \]
\[ D = -i x^3 - x^2 \left( \frac{327}{12} + 5 i x \right) z_1 z_2 + \frac{1}{3} + \frac{z_1 z_2}{q} \]

\[ + \frac{x^2}{q} \left\{ \frac{27 z_1^2}{5 (i x + 3 y)} + \frac{8 z_1 z_2^2}{5} + \frac{5 z_1^3 + 2 z_1^2 z_2 + \frac{7 z_1^2}{(i x + 3 y)}}{12} \right\} \]

\[ + \frac{5 z_1}{12} - \frac{z_1^2}{18} \left\{ 5 z_1 + 2 z_2 + \frac{7}{(i x + 3 y)} \right\} \],

\[ z_1 = (i x + y)^{-1} \]

\[ z_2 = (i x + 3 y)^{-1} ; \]

\[ S_{SAP}(x, y) = \frac{1}{\Pi} \text{Re} \left\{ \frac{A}{i x + y_1} + \frac{B - i C}{i(x-x') + y_2} + \frac{B + i C}{i(x+x') + y_2} \right\} \],

where

\[ A = \frac{2}{5} + \frac{1}{25 y^2} \]

\[ B = \frac{3}{10} - \frac{1}{50 y^2} \]

\[ C = \frac{1}{5} \left\{ \frac{13}{20} - \left( \frac{25}{240} \right) \left( \frac{1}{y^2} \right) \right\} \]

\[ x' = \frac{5}{6} \left\{ 1 + \frac{19}{540} \left( \frac{1}{y^2} \right) \right\} \]

\[ y_1 = \frac{1}{2 y} \left\{ 1 - \frac{1}{2 y^2} \right\} \]

\[ y_2 = \frac{7}{18 y} \left\{ 1 - \frac{53}{189} \left( \frac{1}{y^2} \right) \right\} . \]
For completeness, the dimensionless Brillouin splitting $x_0$, central HWHH, $\gamma_C$, and Brillouin HWHH, $\gamma_B$, are

\[ x_0 = \frac{5}{6} = 0.833 \]  
\[ \gamma_C = \frac{1}{2\gamma} \]  
\[ \gamma_B = \frac{7}{9} \left( \frac{1}{2\gamma} \right). \]  

For purposes of comparison to spectra calculated with the kinetic model, eqs. (2.253-8) were programmed in FORTRAN IV and the hydrodynamic spectra $S_{NS}$, $S_{KdM}$, $S_{3L}$, $S_{B}$, $S_{SEX}$ and $S_{SAP}$ calculated for the following values of $(x, y)$: $|x| < 3.2$; $y = 0.767, 1.312, 3.0, 4.65$ and $6.00$. These spectra are compared in Table (2.5) to the corresponding Maxwell and hard sphere spectra obtained from the exact solution of the Boltzmann equation via the kinetic model. In addition, Table (2.6) gives the location and peak height of the Brillouin peaks for the various calculations.

As can be seen the agreement between the hydrodynamic and kinetic model calculations improves as $y$ increases and is excellent for $y = 6$. For $y < 3$, however, the breakdown of hydrodynamics is evident. The spectra from the KdM approximation agree with the exact Navier-Stokes hydrodynamic spectra to within $\sim 1\%$ for $y > 3$, that is for all values of $y$ for which the Navier-Stokes hydrodynamic approximation can be considered valid. The results of the 3L approximation, however, differ substantially from the exact Navier-Stokes hydrodynamic spectra even when the latter agree well with the kinetic model spectra. This deviation is especially noticeable in the tails ($x > 1$) where the 3L spectra fall off as $x^{-2}$, whereas the KdM and exact Navier-Stokes spectra have a $x^{-4}$ dependence for large $x$. The three Lorentzian approximation does not give accurately the density fluctuation spectrum of a dilute gas except in the limit $y \gg 1$, whereas the Kadanoff-Martin approximation is valid for any value of $y$ for which hydrodynamics
TABLE 2.5: Comparison of Kinetic Model Spectra and Hydrodynamic Spectra

\( y = 0.767 \):

<table>
<thead>
<tr>
<th>( x )</th>
<th>Kinetic Model</th>
<th>Navier-Stokes</th>
<th>Burnett</th>
<th>Selwyn</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Maxwell</td>
<td>Hard Spheres</td>
<td>Exact</td>
<td>Kadanoff-Martin</td>
</tr>
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<td>0.5162</td>
<td>0.5642</td>
<td>0.5273</td>
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Table 2.6: Brillouin Peak Height and Location for Kinetic Model and Hydrodynamic Spectra

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is applicable.

The best agreement of the hydrodynamic spectra with the spectra from the exact solution of the Boltzmann equation is provided by the hydrodynamic theory of Selwyn applied to the Maxwell gas. The agreement for \( y = 6 \) is spectacular, the two calculations differing by < 0.1\%, and is still quite good at \( y = 3 \). For smaller \( y \), however, the Selwyn spectrum develops a large peak near \( x = 0 \).

Selwyn obtained the form \( S_{\text{SAP}}(x, y) \) for his spectrum by approximately expanding the exact spectrum of eq. (2.257), \( S_{\text{SEX}}(x, y) \), in partial fractions to obtain eqs. (2.258). In eqs. (2.258) correction terms of \( 0(1/y^4) \) or smaller were also deleted. The approximations are such that \( S_{\text{SEX}}(x, y) \) and \( S_{\text{SAP}}(x, y) \) are nearly the same in the range of \( y \) where the theory is applicable, i.e., for \( y > 3 \).

The spectra from the Burnett approximation for Maxwell molecules shows somewhat better agreement with the kinetic model Maxwell molecule spectra in the vicinity of the sound propagation peaks than the Navier-Stokes spectra. This is in agreement with the measurements of the dispersion relation for forced sound propagation, \(^{(47)} \) which is provided more accurately by the Burnett equations. The Burnett approximation, however, fails to adequately provide the thermal diffusion mode for \( y > 6 \).

4. Calculation of \( P_s(\mathbf{r}, t) \)
   a) Introduction

   As a prelude to a related calculation for the binary gas mixture, to be taken up in the next section, we now consider, for a single component monatomic gas, the calculation of \( S_D(K, \omega) \), the space-time Fourier transform of the self distribution \( P_s(\mathbf{r}, t) \):

   \[
   S_D(K, \omega) = \iiint d^3r dt e^{i\mathbf{K} \cdot \mathbf{r} - \omega t} P_s(\mathbf{r}, t). \tag{2.282}
   \]

   Kinetic equations of a form similar to the Boltzmann equation:
\[
\left( \frac{\partial}{\partial t} + \mathbf{u} \cdot \nabla \right) f(\mathbf{r}, \mathbf{v}, t) = \left( \frac{\partial f}{\partial t} \right)_{\text{coll}}
\]

(2.283)

will be employed to obtain \( S_D(\mathbf{R}, \omega) \). Here again \( f(\mathbf{r}, \mathbf{v}, t) \) is the \( \mu \) space density and the spectrum predicted by such equations given by

\[
S(\mathbf{R}, \omega) = \int d^3 \mathbf{r} dt \ e^{i(\mathbf{R} \cdot \mathbf{\omega} - \omega t)} \rho(\mathbf{R}, t)
\]

(2.284)

where

\[
\rho(\mathbf{R}, t) = \int d^3 \mathbf{v} f(\mathbf{r}, \mathbf{v}, t) - n_o
\]

(2.285)

with

\[
f(\mathbf{r}, \mathbf{v}, 0) = f_0(\mathbf{v}) \delta(\mathbf{r}).
\]

(2.286)

To obtain \( S_D(\mathbf{R}, \omega) \) for such a formulation it is necessary that the collision term \( (\partial f/\partial t)_{\text{coll}} \) be chosen such that

\[
\rho(\mathbf{r}, t) = P_s(\mathbf{r}, t).
\]

This may be accomplished as follows. It was pointed out in the discussion of the time dependence of the distribution functions in sec. (II B 2c) that \( P_s(\mathbf{r}, t) \) dominates \( \rho(\mathbf{r}, t) \) for times short compared to the collision time, \( t < \tau_c \), but for long times, if collisions conserve momentum and energy, the contribution of \( P_s(\mathbf{r}, t) \) to \( \rho(\mathbf{r}, t) \) is cancelled by an equal and opposite contribution from \( N P_o(\mathbf{r}, t) \). The latter contribution arises because the
collision of particle # 1 with the other particles "pushes a hole", NP₀, in their distribution. The calculation of \( P_s(\vec{r}, t) \) requires a collision term such that the diffusion of particle # 1 does not modify the distribution NP₀(\( \vec{r}, t \)) of the other particles, that is, the other particles must remain in absolute equilibrium, as opposed to local equilibrium, during the diffusion of particle # 1. In this case \( N P_0(\vec{r}, t) = n_0 \) and \( \rho(\vec{r}, t) = P_s(\vec{r}, t) \) from eq. (2.56), where we neglect contributions to NP₀(\( \vec{r}, t \)) containing \( n_0 v^* \) since we are dealing with point particles (\( v^* = 0 \)). The collision operator, \( (\partial f / \partial t)_{\text{coll}} \), which forces particle # 1 to diffuse in a medium at absolute equilibrium is one for which the particles move in a local environment specified by \( T(\vec{r}, t) = T \) and \( \vec{u}(\vec{r}, t) = 0 \). Thus we require a collision operator which relaxes the distribution \( f(\vec{r}, \vec{v}, t) \) directly to \( n(\vec{r}, t)f_o(\vec{v}) \), that is \( (\partial f / \partial t)_{\text{coll}} = 0 \) when

\[
\left\{ \frac{2\pi k_B T}{m} \right\}^{3/2} \exp \left\{ -\frac{(m\vec{v})^2}{2k_B T} \right\}
\]

Such a collision operator cannot conserve momentum or energy. This may be contrasted to the Boltzmann equation which does not constrain \( T(\vec{r}, t) \) and \( \vec{u}(\vec{r}, t) \) and relaxes \( f(\vec{r}, \vec{v}, t) \) to \( f^{(o)}(\vec{r}, \vec{v}, t) \) where

\[
f^{(o)}(\vec{r}, \vec{v}, t) = n(\vec{r}, t) \left( \frac{2\pi k_B T(\vec{r}, t)}{m} \right)^{3/2} \exp \left\{ -\frac{(m\vec{v} - \vec{u}(\vec{r}, t))^2}{2k_B T(\vec{r}, t)} \right\}
\]

An additional requirement on \( (\partial f / \partial t)_{\text{coll}} \) is that it conserve particle number since the volume integral of \( P_s(\vec{r}, t) \) must always be 1.

We shall now discuss two collision operators which satisfy the above two requirements. These are the hard collision model (HCM) and Fokker-Planck model (FPM), which we shall consider in turn.

b) Hard Collision Model

The HCM, employed for the calculation of \( S_D(\vec{K}, \omega) \) by Nelkin and
Ghatak,\(^{(48)}\) is based on the general kinetic equation

$$
\left( \frac{\partial}{\partial t} + \mathbf{u} \cdot \nabla \right) f(\mathbf{r}, \mathbf{v}, t) = \int d^3 v' \: W(\mathbf{v}', \mathbf{v}) f(\mathbf{r}, \mathbf{v}', t) - \frac{1}{\tau_c} \: f(\mathbf{r}, \mathbf{v}, t)
$$

(2.288)

where \(W(\mathbf{v}', \mathbf{v}) d^3 v\) is the transition probability per unit time for an atom of velocity \(\mathbf{v}'\) to be scattered into the volume element \(d^3 v\) at \(\mathbf{v}\). The net scattering probability per unit time, \(1/\tau_c\), is given by

$$
\frac{1}{\tau_c(\mathbf{v}')} = \int d^3 v \: W(\mathbf{v}, \mathbf{v}')
$$

(2.289)

so that the number of particles is conserved in a collision. The hard collision model, first introduced by Bohm and Gross,\(^{(48)}\) is obtained by the approximation

$$
W(\mathbf{v}', \mathbf{v}) = \frac{1}{\tau_c} \: f_0(\mathbf{v})
$$

(2.290)

where \(f_0(\mathbf{v})\) is the absolute Maxwellian distribution defined in eq. (2.129). With this transition probability, particles which exit collisions and enter \(d^3 v\) about \(\mathbf{v}\) are in absolute equilibrium and a collision may be viewed as an absorption of a particle with the re-emission of a thermalized particle. For this model \(\tau_c\) is the average time between collisions for a particle. Since total thermalization occurs for each collision we call this model the hard collision model. This model is appropriate to the calculation of \(S_D(\mathbf{r}, \omega)\) for a single component gas wherein colliding particles have equal masses and thermalization occurs in very few collisions. Inserting eq. (2.290) into eq. (2.288) it is clear that the HCM relaxes \(f(\mathbf{r}, \mathbf{v}, t)\) directly to \(n(\mathbf{r}, t) f_0(\mathbf{v})\) so that the HCM satisfies both requirements on \(\left(\frac{\partial f}{\partial t}\right)_{\text{coll}}\).
The solution of eq. (2.288) for $S_D(K,\omega)$ proceeds initially in a fashion similar to that of the BE, through the introduction of $h(r,\bar{v},t)$ and its Laplace-Fourier transform as given in eqs. (2.128) and eqs. (2.145-7), with which we obtain from eq. (2.288):

\[
[i\omega - i\vec{r} \cdot \vec{v} + \frac{4}{\varepsilon_c}] \xi_0(v) h(r,\bar{v},\omega) - \xi_0(v) = \int d^3\bar{v}' W(\bar{v}',\bar{v}) \xi_0(\bar{v}') h(r,\bar{v}',\omega)
\]

(2.291)

Using eq. (2.290) for $W(\bar{v}',\bar{v})$ and introducing the dimensionless frequency $\epsilon$, velocity $\epsilon$, and distribution $a(K,\epsilon,\nu)$ in analogy to eqs. (2.156), (2.153) and (2.157) respectively, we find

\[
\int d^3\epsilon \phi(\epsilon) a(\vec{K},\epsilon,\nu) = I(\nu,\gamma_D) \left[ \frac{1}{2\pi} + \gamma_D \int d^3\epsilon \phi(\epsilon) a(\vec{K},\epsilon,\nu) \right]
\]

(2.292)

where $\phi(\epsilon)$ the dimensionless Maxwellian is given in eq. (2.160), $\gamma_D$ is defined by

\[
\gamma_D \equiv \frac{1}{\sqrt{2\nu_0} \sqrt{\epsilon_c}}
\]

(2.293)

and

\[
I(\nu,\gamma_D) = \int d^3\epsilon \phi(\epsilon) [i(\epsilon - \vec{K} \cdot \vec{\epsilon} + \gamma_D)^{-1} = i(\epsilon)^{-\gamma_D} \int d\epsilon \nu e^{-\epsilon_\nu^2} [\epsilon_\nu - (\nu - i\gamma_D)]^{-1}
\]

(2.294)

The dimensionless spectrum $S_D(\nu,\gamma_D)$, given as in eq. (2.164) in terms of $a(K,\epsilon,\nu)$, may be algebraically obtained from eq. (2.292) and we find
\[ S_D(x, y_D) = 2 Re \left\{ \frac{I(x, y_D)/2\pi}{1 - y_D I(x, y_D)} \right\} \]  

(2.295)

The integral \( I(x, y_D) \) has the form of the probability integral for complex argument and is a tabulated function \(^{(50)}\) so that eq.(2.295) is the desired solution for \( S_D(x, y_D) \).

As was true for the solution \( S_p \) of the Boltzmann equation the shape in \( x \) of the spectrum \( S_D(x, y_D) \) depends only on a single parameter, in this case \( y_D \), given by

\[ y_D = \frac{1}{\sqrt{2Kv_0} \tau_c} \equiv \frac{1}{\Delta \kappa} \]  

(2.296)

with the mean free path, \( \tau_c = \tau_c \sqrt{2v_0} \) being defined as the distance traveled in a time \( \tau_c \) by a particle with the most probable speed (\( \sqrt{2v_0} \)). In the limit \( y_D \to 0 \) (kinetic limit, \( t > 1/\kappa \)) we find for \( S_D(K, \omega) \) and \( S_D(x, y_D) \):

\[ \lim_{y_D \to 0} S_D(K, \omega) = \frac{\sqrt{2\pi}}{Kv_0} \exp \left\{ - \left( \frac{\omega}{\sqrt{2Kv_0}} \right)^2 \right\} \]  

(2.297)

\[ \lim_{y_D \to 0} S_D(x, y_D) = \frac{1}{\pi} \exp \left\{ - \kappa^2 \right\} \]  

(2.298)

We see by comparing eqs. (2.298) and (2.166) that \( S_D(x, y_D) \) has the same form as \( S(x, y) \) obtained from the Boltzmann equation in the \( y = 0 \) limit. This is to be expected since from the discussion of the distribution functions of sec. (II B 2c) we saw that \( P_s(\vec{r}, t) \) dominates \( \rho(\vec{r}, t) \) for small \( t \).
For large \( y_D \) (diffusion limit, \( t < 1/K \)) the spectra are of the form

\[
\lim_{y_D \to \infty} S_D(k, \omega) = \frac{2Dk^2}{\omega^2 + (Dk^2)^2} \quad (2.299)
\]

\[
\lim_{y_D \to \infty} S_D(k, y_D) = \frac{1}{\pi} \left[ \frac{1/2\gamma_D}{k^2 + (1/2y_D)^2} \right] \quad (2.300)
\]

where we have introduced the diffusion constant \( D \):

\[
D \equiv \frac{k_B T}{m} \tau_c = v_0^2 \tau_c \quad (2.301)
\]

\( m \) being the particle mass. Using eq. (2.296), \( y_D \) is given in terms of the measurable transport coefficient, \( D \), by:

\[
y_D = \frac{v_0}{\sqrt{2Dk}} \quad (2.302)
\]

The identification, in eq. (2.301), of \( v_0^2 \tau_c \) as the diffusion constant, \( D \), may be made by employing the Chapman-Enskog procedure (CEP) for the HCM kinetic equation

\[
\left( \frac{\partial}{\partial t} + \vec{v} \cdot \nabla \right) f(\vec{r}, \vec{v}, t) = \frac{1}{\tau_c} \left[ g(\mu) \int d\vec{v}' f(\vec{r}, \vec{v}', t) - f(\vec{r}, \vec{v}, t) \right] \quad (2.303)
\]

We seek a relationship between particle transport, represented by a non-zero particle flux \( \vec{J}(\vec{r}, t) \):
\[ \vec{J}(\vec{r}, t) = \int d^3 \vec{v} \, \vec{v} \, f(\vec{r}, \vec{v}, t) \]  

(2.304)

and the gradients in the density \( n(\vec{r}, t) \) where

\[ n(\vec{r}, t) = \int d^3 \vec{v} \, f(\vec{r}, \vec{v}, t). \]  

(2.305)

The conservation laws are obtained, as they were in the application of the CEP to the Boltzmann equation, by multiplying the HCM equation (eq. (2.203)) by the collision invariants and averaging over all \( \vec{v} \). In the present case \( \psi(\vec{v}) = 1 \) is the only invariant since only particle number is conserved in a collision by the HCM collision operator. We thus obtain the conservation law for the particle number density \( n(\vec{r}, t) \)

\[ \frac{\partial n(\vec{r}, t)}{\partial t} + \nabla \cdot \vec{J}(\vec{r}, t) = 0. \]  

(2.306)

The zero order CEP approximation in this case is \( f'(\vec{r}, \vec{v}, t) = n(\vec{r}, t)f_0(\vec{v}) \) which yields \( \vec{J} = 0 \) and thus cannot describe particle transport. The first order approximation is obtained by introducing a small deviation from \( f' \):

\[ f(\vec{r}, \vec{v}, t) = f'(\vec{r}, \vec{v}, t) + g(\vec{r}, \vec{v}, t) \]  

(2.307)

where \( g \ll f' \). Eq. (2.305) shows that \( \int d^3 v \, g(\vec{r}, \vec{v}, t) = 0 \). Inserting eq. (2.307) into eq. (2.303) and neglecting small terms we find for \( g \):

\[ g(\vec{r}, \vec{v}, t) = -c_c \left( \frac{\partial}{\partial \vec{r}} + \vec{v} \cdot \nabla \right) n(\vec{r}, t) f_0(\vec{v}). \]  

(2.308)

Employing the conservation law, eq. (2.306), allows us to eliminate the time derivative and
\[ g(\vec{r}, \vec{v}, t) = -\tau_c \int d\vec{v} f_0(\vec{v}) \vec{v} \cdot \nabla n(\vec{r}, t). \] (2.309)

Evaluating the current density \( \vec{j} \) from eqs. (2.309), (2.307) and (2.304) we find

\[ \vec{j}(\vec{r}, t) = \int d\vec{v} \vec{v} g(\vec{r}, \vec{v}, t) = -\tau_c \int d\vec{v} f_0(\vec{v}) (\vec{v} \cdot \nabla n(\vec{r}, t)). \] (2.310)

It is easy to show that

\[ \int d\vec{v} \int d\vec{v} f_0(\vec{v}) = v_0^2 \delta_{ij}; \] (2.311)

so that we have for \( \vec{j} \):

\[ \vec{j}(\vec{r}, t) = -\tau_c v_0^2 \nabla n(\vec{r}, t). \] (2.312)

By standard definition we have \( j(\vec{r}, t) = -\nabla n(\vec{r}, t) \) and eq. (2.301) is proved.

Eq. (2.295) has been programmed in FORTRAN IV and spectra \( S_D(x, y) \) calculated for \( |x| < 3.0 \) and \( 0 < y_D < 10 \). Selected spectra are shown in fig. (2.6), along with corresponding results of the Fokker-Planck model, to be discussed next. As can be seen the spectra evolve from a Gaussian shape at \( y = 0 \) to a narrowing Lorentzian of HWHH = \( 1/2y_D \) as \( y_D \) increases. The spectrum of light scattered from a system of particles in the diffusion limit (suspensions of monodisperse polystyrene spheres or nearly spherical macromolecules in water) has been observed\(^9\) and shown to be accurately Lorentzian.
Figure 2.6: $S_D(x,y_D)$ for the hard collision and Fokker-Planck models
The narrowing of the spectrum as $y_D$ increases or, since $y_D \sim 1/t$ as the mean free path decreases, is known as collision narrowing or motional narrowing and was originally observed in the spectral profile of absorption lines in gases. We shall return to discuss this briefly at the end of the section. We now turn to the Fokker-Planck approximation.

c) Fokker-Planck Model

The Fokker-Planck model (FPM), applied to the calculation of $S_D(K, \omega)$ by Yip and Ranganathan, (51) assumes the evolution in time of the $\mu$ space distribution $f(\vec{r}, \vec{v}, t)$ to be a continuous Markoff random process and is appropriate when there is very small momentum transfer per collision, that is, when the collisions are very soft. This would be the case for a heavy particle diffusing in a sea of light particles. We begin by writing $f(\vec{r}, \vec{v}, t + \tau)$ in terms of $f(\vec{r}, \vec{v}, t)$ using the integral equation

$$f(\vec{r}, \vec{v}, t + \tau) = \int d^3(\delta \vec{v}) f(\vec{r} - \delta \vec{r}, \vec{v} - \delta \vec{v}, t) \Psi(\vec{v} - \delta \vec{v} | \delta \vec{v}, \tau). \tag{2.313}$$

Here $\Psi(\vec{v} - \Delta \vec{v} | \Delta \vec{v}, \tau)$ is the probability that a particle velocity will undergo the change of $\Delta \vec{v}$, from $\vec{v} - \Delta \vec{v}$ to $\vec{v}$, in the time interval $\tau$. Streaming is incorporated by giving the position increment a definite value: $\Delta \vec{r} = \vec{v} \tau$. The Fokker-Planck model is formed by assuming that particle velocities change in a smooth rather than a discontinuous way so that for intervals, $\tau$, over which $f(\vec{r}, \vec{v}, t)$ does not change appreciably, the transition probability, $\Psi(\vec{v} - \Delta \vec{v} | \Delta \vec{v}, \tau)$, will be sharply peaked about $\Delta \vec{v} = 0$. The validity of this assumption requires that the mass, $M$, of the diffusing particle be large compared to the mass, $m$, of the particles in which it is diffusing, such as in the case of dust particles or macromolecules in aqueous solution. If $M \gg m$ then the velocity change of the diffusing particle per collision with the other particles is very small and its trajectory is smooth.
Choosing $\tau$ to be small compared to the time over which $f(r, v, t)$ changes appreciably, the integrand of eq. (2.313) may be expanded in a Taylor's series about $f(r, v, t) \psi(v|\Delta v, \tau)$

\[
f(r-\Delta r, v-\Delta v, t) \psi(v-\Delta v|\Delta v, t) = f(r, v, t) - \mathcal{C} (v \cdot \Delta r, f(r, v, t)) - \Delta v \cdot \nabla_v [f(r, v, t) \psi(v|\Delta v, \tau)]
\]

\[+ \frac{1}{2} \Delta v \cdot \Delta v : \nabla_v \nabla_v [f(r, v, t) \psi(v|\Delta v, \tau)] + \ldots.\]  

(2.314)

With this expansion we obtain from eq. (2.313) a differential equation for $f(r, v, t)$

\[
\left( \frac{\partial}{\partial t} + v \cdot \nabla \right) f(r, v, t) = \nabla_v \left[ -\tilde{a} + b \nabla_v \right] f(r, v, t)  
\]

(2.315)

where $\tilde{a}$ and $b$ are moments of the transition probability

\[
\tilde{a} = \lim_{\tau \to 0} \int d^3(\Delta v) \frac{\Delta v}{2\tau} \psi(v|\Delta v, \tau)  
\]

(2.316)

\[
b = \lim_{\tau \to 0} \int d^3(\Delta v) \frac{(\Delta v)^2}{2\tau} \psi(v|\Delta v, \tau).  
\]

(2.317)

Eqs. (2.316) and (2.317) show that the behavior of $f(r, v, t)$ is determined by moments, $\tilde{a}$ and $b$, of $\psi$. We need not know $\psi$, however, to evaluate $\tilde{a}$ and $b$, as they may be obtained from general arguments. It is clear
from eq. (2.316) that $\ddot{a}$ is the initial acceleration of a particle with a velocity $\vec{v}$. We require eq. (2.315) to describe diffusion for $\tau \gg \tau_c$ by obtaining $\ddot{a}$ from the equation of motion for diffusing particles. If the particles are diffusing in a local environment of average velocity $\bar{u}(\vec{r}, t)$ we have

$$m \ddot{\vec{v}} = -\zeta (\vec{v} - \bar{u}(\vec{r}, t)) \quad (2.318)$$

where $\zeta$ is the force constant. We find for $\ddot{a}$

$$\ddot{a} = -\frac{\kappa}{m} (\vec{v} - \bar{u}(\vec{r}, t)) = -\frac{1}{\tau_c} (\vec{v} - \bar{u}(\vec{r}, t)) \quad (2.319)$$

where $\tau_c = m/\zeta$ is the velocity relaxation time. The second moment $b$ may be most readily obtained by requiring that the collision operator yield zero when the local equilibrium distribution function $f^{(o)}(r, \vec{v}, t)$ given in eq. (2.287) is reached. This requires that

$$(-\ddot{a} + b \nabla \vec{u}) f^{(o)}(r, \vec{v}, t) = 0 \quad (2.320)$$

from which we find

$$b = \frac{1}{\tau_c} \cdot \frac{k_b T(\vec{r}, t)}{m} \quad (2.321)$$

With $\ddot{a}$ and $b$ so specified the collision operator in eq. (2.315) relaxes $f(\vec{r}, \vec{v}, t)$ to $f^{(o)}(\vec{r}, \vec{v}, t)$ in eq. (2.287), as does the Boltzmann collision operator. Thus eq. (2.315), as does the Boltzmann equation, produces hydrodynamic long wavelength behavior. To obtain diffusion behavior, as was stated above, we must place the constraints $T(\vec{r}, t) = T$ and $\bar{u}(\vec{r}, t) = 0$ in eqs. (2.319) and (2.321). We then have
\[
\hat{a} = -\frac{\vec{v}}{\tau_c} \tag{3.322}
\]

\[
b = \frac{l}{\tau_c} \cdot \frac{k_B T}{m} \tag{3.323}
\]

and from eq. (2.315) the Fokker-Planck equation for a diffusing particle

\[
\left( \frac{\partial}{\partial t} + \vec{v} \cdot \nabla \right) f(\vec{r}, \vec{v}, t) = \frac{l}{\tau_c} \nabla_v \cdot \left[ \vec{v} + \frac{k_B T}{m} \nabla_v \right] f(\vec{r}, \vec{v}, t). \tag{3.324}
\]

The solution of this equation for \( S_D(K, \omega) \) has been carried out by Yip and Ranganathan \((51)\) by means of an eigenfunction expansion. Introducing \( h(\vec{r}, \vec{v}, t) \) as we did for the Boltzmann equation (eq. (2.128)) the FP equation becomes

\[
\left( \frac{\partial}{\partial t} + \vec{v} \cdot \nabla \right) h(\vec{r}, \vec{v}, t) = \frac{\nabla_v \cdot \nabla_v}{\tau_c} \left[ \frac{1}{f(\vec{v})} \nabla_v \cdot \left\{ f(\vec{v}) \nabla_v \right\} \right] h(\vec{r}, \vec{v}, t). \tag{3.325}
\]

With the dimensionless frequency, \( \xi \), velocity, \( \vec{\xi} \), Maxwellian, \( \phi(\xi) \), distribution, \( a(K, \vec{\xi}, \xi) \), defined as in eqs. (2.156), (2.153), (2.160), and (2.157), respectively, we find the dimensionless FP equation

\[
i(\nu - \vec{\xi} \cdot \vec{\xi}) a(\vec{K}, \vec{\xi}, \nu) = \frac{1}{2\pi} + \frac{y_D}{2} A_s(a(\vec{K}, \vec{\xi}, \nu)) \tag{3.326}
\]

where

\[
A_s = \frac{1}{\phi(\xi)} \nabla_\xi \left( \phi(\xi) \nabla_\xi \right) \tag{3.327}
\]

and where \( y_D \) is again given by
Analysis of the diffusion limit of the Fokker-Planck equation using the CEP shows that \( D = \frac{v_0^2 \tau_c}{3} \) so that \( \tau_c = \frac{m}{\zeta} \), the velocity relaxation time of the FPM, is the same as \( \tau_c \) of eq. (2.290), the time between collisions for the HCM. A set of eigenfunctions \( \chi_n(\vec{\epsilon}) \) have been obtained for the FPE operator \( A_s \) such that

\[
A_s \chi_n(\vec{\epsilon}) = -n \chi_n(\vec{\epsilon}) \tag{2.329}
\]

where \( \chi_n(\vec{\epsilon}) \) represents the nth order generalized Hermite polynomial tensor

\[
\chi_n(\vec{\epsilon}) = H_i^{(n)}(\epsilon) = \frac{(-1)^n}{\phi(\epsilon)} \frac{\partial}{\partial \epsilon_i} \cdots \frac{\partial}{\partial \epsilon_n} \phi(\epsilon) \tag{2.330}
\]

where \( i_k \) = 1, 2, 3 \((k = 1, \ldots, n)\) denote Cartesian components. With \( a(K, \vec{\epsilon}, x) \) expanded in the eigenfunctions \( \chi_n(\vec{\epsilon}) \)

\[
a(K, \vec{\epsilon}, x) = \sum_{n=0}^{\infty} a_n(\chi) \gamma_0^l \chi_n(\vec{\epsilon}) \tag{2.331}
\]

the dimensionless spectrum \( S_D(x, y_D) \) is given by

\[
S_D(\gamma, y_D) = 2 \Re a_0(\gamma, y_D) \tag{2.332}
\]

in analogy with eq. (2.174). Inserting the expansion into eq. (2.326) one obtains a simple set of coupled linear equations

\[
\gamma_D = \frac{1}{\sqrt{2k \nu_0 \tau_c}}. \tag{2.328}
\]
which may be solved if one requires $a_k$ to be zero for $k > N$. One finds a continued fraction expansion for $a_0(x, y)$ and the spectrum $S_D(x, y_D)$, obtained from eq. (2.333), is given by:

$$
S_D(x, y_D) = \frac{1}{\pi} R e \left\{ \frac{-i}{b_0 - 1} \left( \frac{1}{b_1 - 2} \left( \frac{1}{b_2 - 3} \left( \frac{1}{b_3 \cdots} - \frac{n}{b_n} \right) \right) \right) \right\}
$$

(2.334)

where $b_n = \sqrt{2}(x - iny_D)$.

Eq. (334) was programmed in FORTRAN IV and $S_D(x, y_D)$ calculated for increasing values of $N$. For sufficiently large $N$ the spectra cease to change and one has an exact solution for $S_D(x, y_D)$ in the Fokker-Planck approximation. Since higher order polynomials are required for small $y_D$ (see discussion of Wang Chang-Uhlenbeck method in sec. (II C 2b), the number $N_c$ of terms required for convergence increases as $y_D$ decreases; ($N_c = 26$ at $y_D = 1$; $6$ at $y_D = 10$). Fokker-Planck spectra were calculated for $|x| < 3.0$ and $0.1 \leq y \leq 10$ and selected spectra are shown in fig. (2.6) along with those of the hard collision model. Although both models predict the same spectra in the asymptotic limits ($y_D = 0$, = ), there is considerable difference at intermediate values of $y_D$. This may be understood in view of the approximation which have been made by recalling that $S_D(x, y_D)$ for small $y_D$ arises from $P_s(\vec{r}, t)$ for $t < \tau_c$ and $S_D(x, y_D)$ for large $y_D$ arises from $P_s(\vec{r}, t)$ for $t > \tau_c$. From small $y_D$ the particle velocity is constant, collisions being so rare that the form of the collision operator is of no importance. For large $y_D$ ($t \gg \tau_c$), after many collisions, the net displace-
ment of the particle away from (0, 0) becomes independent of the details of a particular collision, and both models predict the simple diffusion spectrum. Intermediate values of $y_D$ (0.1 $<$ $y_D$ $<$ 3), however, sample $P_s(x, t)$ for $t$ $\sim$ $\tau_c$, the time interval over which the particle will have changed its initial velocity either via one hard collision (HCM) or many soft collisions (FPM). It is over the time interval $t$ $\sim$ $\tau_c$ that the apparent particle trajectories are most different for the two models, as are the resulting spectra.

We have now completed the derivation of the Fokker-Planck diffusion spectrum on the basis of an eigenfunction expansion solution of the kinetic equation, a description which we shall find convenient in the discussion of gas mixtures. It is appropriate to point out here that Rautian and Sobel'man\textsuperscript{[54]} have solved eq. (2, 324) in another way involving Fourier transformation in velocity space. They are able to obtain a closed form expression for $F_D(k, t)$, the spatial Fourier transform of $P_s(x, t)$

$$F_D(k, t) = \int d^3 r \, e^{i k \cdot r} P_s(r, t).$$  \hspace{1cm} (2.335)

They find

$$F_D(k, t) = e^{\frac{t v_0^2}{D}} \left[ e^{-\frac{|k| v_0^2}{D}} - (1 - \frac{|k| v_0^2}{D}) \right]$$ \hspace{1cm} (2.336)

where we have used $D = v_0^2 \tau_c$. Inspection shows the following limiting behavior as $t \to 0$, or $t \to \infty$:

$$\lim_{t \to 0} F_D(k, t) = e^{\frac{t v_0^2}{D}} \left[ -\frac{1}{2} (tkv_0)^2 \right]$$ \hspace{1cm} (2.337)

$$\lim_{t \to \infty} F_D(k, t) = e^{\frac{-Dk^2 t}{2}}.$$ \hspace{1cm} (2.338)
Time Fourier transformation of \( F_D(\vec{K}, t) \) yields the spectrum \( S_D(\vec{K}, \omega) \) and may be carried out in eqs. (2.337, 8) yielding the proper spectra at \( y_D = 0 \) (eq. (2.297)) and \( y_D = 0 \) (eq. (2.299)). Numerical evaluation of \( S_D(\vec{K}, \omega) \) from \( F_D(\vec{K}, t) \) yields spectra identical to those evaluated from the eigenfunction solution. Galatry also has obtained eq. (2.336) for \( F_D(\vec{K}, t) \) starting from \( P_s(\vec{r}, t; 0, 0, \vec{v}) \) the probability that a particle will be at \( (\vec{r}, t) \) given that it was at \( (0, 0) \) with a velocity \( \vec{v} \). This function has been obtained for a diffusing particle in the Fokker-Planck approximation by Chandrasekhar.

\[ d) \ \text{The Mean Free Path} \]

We now briefly discuss the mean free path, \( \ell \), and the relative magnitudes of \( \tau_c \), the velocity correlation time, and \( \tau_{11} \) and \( \tau_{02} \), the relaxation times for energy and momentum transport respectively. In the diffusion limit two time correlation function for the velocity of a diffusing particle, \( \langle \vec{v}(t) \cdot \vec{v}(t+\tau) \rangle \), may be shown to be

\[
\langle \vec{v}(t) \cdot \vec{v}(t+\tau) \rangle = \frac{3k_B T}{m} e^{-\tau/\tau_c} \tag{2.339}
\]

where \( \tau_c \), the velocity correlation time, is given by \( \tau_c = D/v_o^2 \). A natural definition of the mean free path \( \ell \) then is

\[
\ell \equiv \sqrt{2} v_o \tau_c \tag{2.340}
\]

that is, the distance travelled by a particle with the most probable speed \( (\sqrt{2} v_o) \) in a time \( \tau_c \). With this definition of \( \ell \), from eq. (2.328), we have for \( y_D \)

\[
y_D = \frac{1}{\sqrt{2} \sqrt{k} v_o \tau_c} = \frac{1}{k \ell} \tag{2.341}
\]
To obtain $y = \frac{1}{\sqrt[4]{2}} v \tau_{11}$, the parameter for the hydrodynamic spectra, in terms of $Kl$, we must find the ratio $\tau_c/\tau_{11}$. This is done by noting that for a Lennard-Jones gas, the diffusion constant, $D$, and viscosity, $\eta$, are related by

$$D = \frac{6}{5} \frac{\eta}{m n_0} A^*(T)$$

(2.342)

where $A^*(T)$ is nearly 1 and varies slowly with $T$. For xenon at room temperature we have $A^*(T) = 1.097$. Using eqs. (2.217), (2.301) and $\tau_{11} = (3/2) \tau_{02}$ we find

$$\nu_0^2 \tau_c = \frac{6}{5} \nu_0^2 \tau_{02} A^*(T) = \frac{4}{5} \nu_0^2 \tau_{02} A^*(T)$$

so that in a gas the velocity correlation time and the energy and velocity transport relaxation times are nearly equal. We have for $y$

$$y = \frac{\tau_c}{\tau_{11}}$$

(2.344)

We may also point out that the ratio of the HWHH of the diffusion spectrum, $DK^2$, to the HWHH of the component of the hydrodynamic spectrum due to entropy fluctuations, $[\kappa/n_0 c_p]K^2$, is just $\tau_c/\tau_{11}$. This may be seen from eq. (2.215) from which we find

$$\frac{\kappa}{n_0 c_p} = \frac{\nu_0^2 \tau_{11}}{K^2}$$

(2.345)

whereas for diffusion we have

$$D = \nu_0^2 \tau_c$$

(2.346)
e) Collision Narrowing

We conclude the discussion of the scattered light spectrum associated with $P_s(\mathbf{r}, t)$ with a few words about collision narrowing. The narrowing of a spectral profile as the molecular mean free path is decreased is known as collision or motional narrowing and was first discussed by Dicke \cite{60} in connection with the shape of spectral emission or absorption lines in a gas. The condition under which collision narrowing will be observed for an atomic or molecular transition is that the line width, $\Delta \omega$, as determined by effects other than particle motion (i.e., natural line width, broadening due to collision induced transitions, etc.), must be narrow compared to the Doppler width ($\Delta \omega << K_o v_o$), where $K_o$ is the wave vector of the emitted or absorbed radiation. If such is the case then the observed spectral profile $S(\omega)$, where $\omega$ is measured from $\omega_o = K_o c$, will be

$$S(\omega) = \int d^3 r d t \, e^{i(\mathbf{K}_o \cdot \mathbf{r} - \omega t)} P_s(\mathbf{r}, t)$$

(2.347)

where only $P_s$ contributes since the atoms are independent radiators. The profile $S(\omega)$ then is just $S_D(\mathbf{K}_o, \omega)$, but with the emitted wave vector $K_o$ replacing the scattering vector $\mathbf{K}$.

Collision narrowing was first observed by Wittke and Dicke \cite{61} who measured the width of the microwave absorption line corresponding to the hyperfine splitting in ground state hydrogen, obtaining a width $\sim 6$ times narrower than that expected from the Doppler effect. More recently collision narrowing has been observed by Cooper, May, Hara, and Knapp and by Murray and Javan \cite{63} for several Raman lines in gaseous hydrogen. The latter authors have compared the HWHH of the observed spectrum with that of $S_D(x, y_D)$ predicted by both the HCM and FPM, for values of $y_D$ in the range $1 < y_D < 20$. They find that the HCM describes more accurately the dependence on $y_D$ of the spectral HWHH than does the FPM. This is to be expected for a one component system since collisions between like particles are "hard."
References: Chapter 2


6. Reference 5, Appendix I.


8. Reference 5, Chapter 3.


12. Reference 1, p 39.


15. Reference 5, p. 165.


21. Reference 18, Chapter 7


23. Reference 5, Chapter 3, Appendix B.

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CHAPTER III: THEORY - BINARY MONATOMIC GAS MIXTURES

A. Introduction

In this chapter we discuss the study of binary monatomic gas mixtures by inelastic light scattering. Our overall approach will not be a general one, although we do derive some results which are generally applicable to binary gas mixtures. We begin by obtaining the energy angle extinction $h(\mathbf{R}, \omega)$ for a dilute binary gas mixture in terms of the conditional density fluctuation distributions $\rho_{ij}(\mathbf{r}, t)$ of the system and their respective space-time Fourier transforms $S_{ij}(\mathbf{R}, \omega)$. Here, in analogy with the one component gas, $\rho_{ij}(\mathbf{r}, t)$ is the fluctuation in density of particles of kind $i$ given that a particle of kind $j$ was at $(0, 0)$. The calculation of $\rho_{ij}(\mathbf{r}, t)$ under general circumstances in a binary gas mixture requires the solution of a pair of coupled kinetic eqs. (see eq. (3.83)) for the space distributions $f_i(\mathbf{r}, \mathbf{v}, t)$ of each species, subject to appropriate boundary conditions. Such solutions are at present available only in the hydrodynamic limit, where the Chapman-Enskog or other similar procedures can be applied to obtain hydrodynamic equations for the mixture. Recently, Mountain and Deutch (1) have considered the spectrum of light scattered by a general hydrodynamic binary fluid mixture. Their calculation has been applied here to a dilute binary gas mixture and the energy angle extinction $h(\mathbf{R}, \omega)$ has been obtained in the hydrodynamic limit.

Further discussion is limited to the helium-xenon mixture. In the experiments to be described we exploit the peculiar properties of the helium-xenon mixture to study one kind of non-hydrodynamic behavior; namely, the kinetic-hydrodynamic transition of dilute xenon in helium. The experiment may be sketched as follows. We start with pure xenon under nearly kinetic conditions ($t_x > 1/K$), so that a nearly Gaussian scattered light spectrum of $1/e$ full width $\Delta \omega \approx 2(\sqrt{2} K v_{ox})$ is observed. We then

*Subscript $x$ will always refer to xenon, $h$ to helium, e.g. $S_{xx}(\mathbf{R}, \omega)$ is $S_{ij}(\mathbf{R}, \omega)$ where species $i$ and $j$ are both xenon.
study the variation of the scattered light spectrum as helium is added to the xenon. As helium pressure is increased the mean free path $\ell_{\text{XH}}$ for collisions of the xenon with helium decreases until, at sufficiently high helium pressure, the condition $\ell_{\text{XH}} << 1/K$ is reached. In this limit the xenon atoms diffuse over a length $1/K$ and their scattered light spectrum is Lorentzian of FWHH = $2DK^2$, where D is the mutual diffusion coefficient in the mixture. We have studied this evolution of the spectrum of the light scattered by the xenon from the Gaussian kinetic to the Lorentzian diffusion shape. To get an idea of the spectral change involved, at room temperature, scattering angle $\theta = 10.6^\circ$, the Gaussian $1/e$ full width $\Delta \omega$ is $\sqrt{2Kv_{\text{ox}}/\pi} = 112$ MHz. The Lorentzian FWHH at a helium pressure of 4.5 atm. is $DK^2/\pi \approx 12$ MHz so that a considerable spectral narrowing is observed. This is a direct manifestation of "collision narrowing" as discussed in sec. (II C 4).

The experiments were carried out in the helium-xenon mixture because of the large mass ratio and ratio of the total extinction of xenon to helium:

$$\frac{m_x}{m_h} \approx 32, \quad \frac{h_{t,x}}{h_{t,h}} \approx 378.$$ 

The large extinction ratio allows experimentation under the condition that the xenon number fraction, $x_x$, be small ($x_x << 1$) at the helium pressures where the xenon is in the hydrodynamic regime ($\ell_{\text{XH}} < 1/K$). When this condition is fulfilled the spectral density $S_{xx}(K, \omega)$ contains only information pertinent to collision narrowing. The large mass ratio renders the most probable velocity of a helium atom large compared to that of a xenon atom ($v_{\text{oh}} \sim 6v_{\text{ox}}$) so that the spectral contributions of the helium have a broader frequency distribution than those of the xenon. This condition, along with the large extinction ratio of xenon to helium allows the extraction of $S_{xx}(K, \omega)$ from the scattered light spectrum.
The motivation for the study of the helium-xenon mixture was the possibility of using collision narrowing to determine the applicability of approximate models of the xenon-helium collision. This was indicated in sec. (II C 4). There calculations were made of collision narrowing of the "self" spectrum in a pure gas using the hard collision and Fokker-Planck models. These models are directly applicable to the calculation of $S_{xx}(x, y)$, i.e. $S_{xx}(x, y) = S_D(x, y_D)$ where the parameter $y$ for $S_{xx}$ is determined by the diffusion coefficient for xenon in helium. The comparison of the hard collision and Fokker-Planck (soft collision) spectra in fig. (2.7) shows that the nature of the xenon-helium collision can be probed by measuring $S_{xx}(x, y)$. Of special interest in the helium-xenon mixture is the testing of the applicability of the Fokker-Planck model since the collisions of xenon with helium are soft to the xenon. Previous measurements of collision narrowing have been confined to one component systems where "hard" collisions are the rule.

We conclude the chapter with a discussion of sound propagation in a binary gas mixture.

B. Spectrum of the Scattered Light

In this section we seek to relate the spectrum of light scattered by a dilute binary monatomic gas mixture to the density correlation functions of the system. The calculation of the spectrum of the scattered light can be carried out in much the same manner as that employed in sec (II B) for a monatomic gas, that is by expressing the total scattered field as a sum of contributions from the various illuminated scatterers. A simpler procedure, the one which we shall follow, is to start with eq. (2.121), relating the scattered light spectrum to the correlation function for index of refraction fluctuations. Although we have derived eq. (2.121) for the monatomic gas, it may be shown to be valid for any system with a fluctuating index of refraction $\varepsilon(\vec{r}, t)$, as is indicated by the fact that none of the monatomic gas parameters appear in this equation. Our starting point is
In a two component gas mixture the index of refraction fluctuation may be expressed in terms of the number density fluctuations $\delta n_i(r, t)$ of the components as follows

$$\delta \varepsilon(r, \omega) = \frac{1}{2\pi} \left[ \frac{(k_0^2)^2 \sin \varphi}{4\pi \varepsilon_0} \right] S_{\delta \varepsilon}(k, \omega). \quad (3.1)$$

The correlation function for dielectric constant fluctuations then becomes

$$\langle \delta \varepsilon(r, \omega) \delta \varepsilon(0,0) \rangle = \left( \frac{\partial \varepsilon}{\partial n_i} \right)^2 \langle \delta n_i(r, \omega) \delta n_i(0,0) \rangle + \left( \frac{\partial \varepsilon}{\partial n_j} \right)^2 \langle \delta n_j(r, \omega) \delta n_j(0,0) \rangle$$

$$+ \left( \frac{\partial \varepsilon}{\partial n_i} \frac{\partial \varepsilon}{\partial n_j} \right) \left\{ \langle \delta n_i(r, \omega) \delta n_j(0,0) \rangle + \langle \delta n_j(r, \omega) \delta n_i(0,0) \rangle \right\}. \quad (3.3)$$

The derivatives $\left( \frac{\partial \varepsilon}{\partial n_i} \right)$ may be obtained in terms of the molecular polarizabilities $\alpha_i$ from the Clausius-Mossotti relation for the mixture (see eq. (2.93))

$$\frac{n^2 - 1}{n^2 + 2} = \frac{\alpha_i n_{10} + \alpha_j n_{20}}{3} \quad (3.4)$$

where $n_{10}$ is the average number density of the $i$th component. Since $n^2 + 2 = 3$ we find

$$\frac{\varepsilon}{\varepsilon_0} - 1 \equiv n^2 - 1 \leq \alpha_i n_{10} + \alpha_j n_{20}$$
\[ \frac{\partial \delta e}{\partial n_i} = \alpha_i \epsilon_o \]  

(3.5)

so that

\[ \langle \delta e(\vec{r}, t) \delta e(0, 0) \rangle = \epsilon_o^2 \left\{ \alpha_i^2 \langle \delta n_i(\vec{r}, t) \delta n_i(0, 0) \rangle + \alpha_j^2 \langle \delta n_j(\vec{r}, t) \delta n_j(0, 0) \rangle \right\} \]

\[ + \alpha_i \alpha_j \left[ \langle \delta n_i(\vec{r}, t) \delta n_j(0, 0) \rangle + \langle \delta n_j(\vec{r}, t) \delta n_i(0, 0) \rangle \right] \].

Using arguments analogous to those leading to equation (2.117), \( \langle \delta e(\vec{r}, t) \delta e(0, 0) \rangle \) may be expressed in terms of the conditional density distributions \( G_{ij}(\vec{r}, t) \) and \( \rho_{ij}(\vec{r}, t) \) defined by

\[ G_{ij}(\vec{r}, t) = \text{density of particles of kind } i \text{ at } (\vec{r}, t) \text{ given that a particle of kind } j \text{ was at } (0, 0), \]

\[ \rho_{ij}(\vec{r}, t) = \text{deviation of density of particles of kind } i \text{ at } (\vec{r}, t) \text{ from the average } n_{io}, \text{ given that a particle of kind } j \text{ was at } (0, 0). \]

We find that

\[ \rho_{ij}(\vec{r}, t) = G_{ij}(\vec{r}, t) - n_{io} \]  

(3.7)

\[ n_{jo} G_{ij}(\vec{r}, t) = \langle n_i(\vec{r}, t) n_j(0, 0) \rangle \]  

(3.8)

and

\[ n_{io} \rho_{ij}(\vec{r}, t) = \langle \delta n_i(\vec{r}, t) \delta n_j(0, 0) \rangle. \]  

(3.9)

With eq. (3.9) the correlation function \( \langle \delta e(\vec{r}, t) \delta e(0, 0) \rangle \) becomes
which, with eqs. (2.121) and (2.122), gives us the desired expression for \( h(\vec{K}, \omega) \) for a binary gas mixture in terms of the conditional fluctuation distributions of the system

\[
\langle \Delta \rho(\vec{r}, t) \Delta \rho(\vec{r}, 0) \rangle = \epsilon_0^2 \left\{ \alpha_1^2 n_{1o} \rho_{11}(\vec{r}, t) + \alpha_2^2 n_{2o} \rho_{22}(\vec{r}, t) + \alpha_1 \alpha_2 \left[ n_{1o} \rho_{12}(\vec{r}, t) + n_{2o} \rho_{21}(\vec{r}, t) \right] \right\} \tag{3.10}
\]

Letting \( S_{ij}(\vec{K}, \omega) \) denote the \( \vec{K}, \omega \) Fourier transform of \( \rho_{ij}(\vec{r}, t) \) in analogy with eq. (2.44) and \( x_i = n_{1o}/n \) where \( n \) is the total average number density, eq. (3.11) may be rewritten

\[
h(\vec{K}, \omega) = \frac{1}{2\pi} \left[ \frac{(k_0 \nu)^2 \sin \phi}{4\pi} \right]^2 \int d^3 \vec{r} \int dt e^{i(k^2 \vec{r} - \omega t)} \left\{ \alpha_1^2 n_{1o} \rho_{11}(\vec{r}, t) + \alpha_2^2 n_{2o} \rho_{22}(\vec{r}, t) + \alpha_1 \alpha_2 \left[ n_{1o} \rho_{12}(\vec{r}, t) + n_{2o} \rho_{21}(\vec{r}, t) \right] \right\} \tag{3.11}
\]

The extinction per unit solid angle \( h(\vec{K}) \), defined by eq. (2.54) is given by

\[
h(\vec{K}) = \left[ \frac{(k_0 \nu)^2 \sin \phi}{4\pi} \right]^2 \left( \alpha_1^2 n_{1o} + \alpha_2^2 n_{2o} \right) \tag{3.13}
\]

where we have neglected the small terms arising from net correlations (imperfect gas behavior) as discussed following eq. (2.98).
C. Hydrodynamic Limit

1. The Hydrodynamic Spectrum

The spectrum of light scattered by a binary gas monatomic mixture in the long wave length, low frequency limit may be calculated using the hydrodynamic equations for the system. This calculation has been carried out by Mountain and Deutch (2) for a binary fluid mixture and will now be applied to a binary gas mixture. We shall obtain the energy angle extinction \( h(\vec{k}, \omega) \) from eq. (2.121) by calculating the spectrum \( S_{\delta \varepsilon}(\vec{k}, \omega) \) of the index of refraction fluctuations of the medium which is given by

\[
S_{\delta \varepsilon}(\vec{k}, \omega) = \int \int d\vec{r} dt \ \epsilon^{i(\vec{k} \cdot \vec{r} - \omega t)} \langle \delta \varepsilon(\vec{r}, t) \delta \varepsilon(0, 0) \rangle. \tag{2.122}
\]

The fluctuations \( \delta \varepsilon(\vec{r}, t) \) in the dielectric constant can be related to fluctuations in a suitable set of thermodynamic variables, the space-time behavior of which is determined by the linearized hydrodynamic equations. The linearized hydrodynamic equations are appropriate since only small deviations from equilibrium are being considered. For a binary fluid mixture these equations are the continuity equation:

\[
\frac{\partial \rho}{\partial t} + \rho \nabla \cdot \vec{u} = 0, \tag{3.14}
\]

the longitudinal part of the Navier-Stokes equation

\[
\rho \left( \frac{\partial \vec{u}}{\partial t} \right) = -\nabla p + \eta \left( \nabla^2 \vec{u} + \frac{1}{3} \nabla(\nabla \cdot \vec{u}) \right), \tag{3.15}
\]

the diffusion equation

\[
\frac{\partial \varepsilon}{\partial t} = D \left[ \nabla^2 \varepsilon + \left( \frac{k_T}{\rho_o} \right) \nabla^2 T + \left( \frac{k_B}{\rho_o} \right) \nabla^2 \rho \right], \tag{3.16}
\]
and the energy transport equation:

\[ \rho \cdot C_p \frac{\partial T}{\partial t} - \rho \cdot \kappa \left( \frac{\partial \mu}{\partial \rho} \right) \cdot \frac{\partial c}{\partial t} + \rho \cdot \beta_T \cdot \frac{\partial \rho}{\partial t} = \kappa \nabla^2 T, \]  

where zero subscripts denote equilibrium values and we shall use the following definitions and notation:

- \( m_i \) = mass of a particle of kind \( i \)
- \( n_i \) = number density of kind \( i \)
- \( n = n_1 + n_2 \)
- \( x_i = \text{number fraction of kind } i = n_i/n \)
- \( p = \text{pressure} = nk_BT \)
- \( \rho = \text{mass density} = n_1m_1 + n_2m_2 \)
- \( c = \text{mass fraction of component } 2 = n_2m_2/\rho \)
- \( \rho \vec{u} = \text{mass flux} = \rho_1\vec{u}_1 + \rho_2\vec{u}_2 \)
- \( C_v = \text{heat capacity of the mixture at constant volume} \)
- \( C_p = \gamma C_v = 5C_v/3 \)  
  \( \gamma \) = isentropic exponent
- \( \mu_i = \text{chemical potential of component } i = k_BT \ln(n_i k_BT) \)
- \( \mu = \text{chemical potential conjugate to } c = \mu_2/m_2 - \mu_1/m_1 \)
- \( \beta_T = \text{thermal expansion coefficient} \)
- \( \kappa_s, \kappa_T = \text{adiabatic, isothermal compressibility} \)
- \( \eta = \text{shear viscosity of mixture} \)
- \( \chi = \text{thermal conductivity of mixture} \)
- \( D = \text{mutual diffusion coefficient of mixture} \)
- \( k_p = \text{barodiffusion coefficient} = [(p_0/\rho_0^2)(\partial \rho/\partial \rho c)_{p,T}]/(\partial \mu/\partial \rho c)_{p,T} \)
- \( k_T = \text{thermal diffusion coefficient} = \alpha_T (1 - c) \text{ where } \alpha_T \text{ is independent of } c. \)
These equations for the binary mixture may be compared with those for the single component fluid (eqs. (2.227 -9)). To specify the state of the binary mixture an additional independent equation (the diffusion equation) is required. The diffusion equation, eq. (3.16), shows that in general both pressure and temperature gradients drive fluctuations in the concentration. These equations include all hydrodynamic effects appropriate to a two component system.

The solution of eqs. (3.14-7) for the scattered spectrum proceeds in much the same way as the solution for the single component fluid. We must first relate the index of refraction of the medium to a suitable set of three thermodynamic state variables. Mountain and Deutch have chosen the statistically independent set \((p, \varphi, c)\) where

\[
\varphi = T - \frac{T_0 \beta_T}{\rho C_p} \rho, \quad \delta \varphi = \delta T - \frac{T_0 \beta_T}{\rho C_p} \delta \rho.
\]

The probability \(P\) of establishing a fluctuation over a volume \(v\), with changes of \((\Delta p, \Delta \varphi, \Delta c)\) in average values of \(p, \varphi, c\) from their respective equilibrium values is given by

\[
P \propto \exp\left[-\frac{(k)}{2k_B T} v \Delta p^2 - \frac{(C_p \rho)}{2k_B T^2} v \Delta \varphi^2 - \frac{(\rho \beta_T)}{2k_B T} v \Delta c^2\right]
\]

so that there are no correlations in fluctuations of the average values of these quantities \((\langle \Delta p \Delta \varphi \rangle = \langle \Delta p \Delta c \rangle = \langle \Delta \varphi \Delta c \rangle = 0\)). The set of state variables \((p, \varphi, c)\) is arrived at by noting that for the set \((p, T, c)\) we have \(\langle \Delta p \Delta c \rangle = \langle \Delta T \Delta c \rangle = 0\) but that \(\langle \Delta p \Delta T \rangle \neq 0\). The variable \(\varphi\) is the linear combination of \(p\) and \(T\) such that \(\langle \Delta p \Delta \varphi \rangle = 0\). Physically \(\delta \varphi = (C_D / T) \delta s_c\) where \(\delta s_c\) is the change in entropy at constant concentration.

Fluctuations, \(\delta \varepsilon(r^2, t)\), in the dielectric constant will be given by

\[
\delta \varepsilon(r^2, t) = \left(\frac{\partial \varepsilon}{\partial p}\right) \rho \delta p(r^2, t) + \left(\frac{\partial \varepsilon}{\partial \varphi}\right) \rho \delta \varphi(r^2, t) + \left(\frac{\partial \varepsilon}{\partial c}\right) \rho \delta c(r^2, t).
\]
Using eq. (3.20), in analogy with eqs. (2.224) through (2.226), we find for $S_{\alpha\epsilon}(\mathbf{k},\omega)$:

$$
S_{\alpha\epsilon}(\mathbf{k},\omega) = \left(\frac{1}{V}\right) 2 \text{Re} \left[ \left(\frac{2\epsilon}{\epsilon^p}\right)^2 \left\langle p(\mathbf{k},s) p(-\mathbf{k}) \right\rangle + \left(\frac{\epsilon}{\epsilon^p}\right)^2 \left\langle \phi(\mathbf{k},s) \phi(-\mathbf{k}) \right\rangle \right] + \left(\frac{2\epsilon}{\epsilon^c}\right)^2 \left\langle c(\mathbf{k},s) c(-\mathbf{k}) \right\rangle + \left(\frac{\epsilon}{\epsilon^c}\right)^2 \left\langle \phi(\mathbf{k},s) \phi(-\mathbf{k}) \right\rangle + \left\langle \phi(\mathbf{k},s) \phi(-\mathbf{k}) \right\rangle
\]$$

$$
+ \left(\frac{2\epsilon}{\epsilon^c}\right)^2 \left\langle c(\mathbf{k},s) c(-\mathbf{k}) \right\rangle + \left(\frac{\epsilon}{\epsilon^c}\right)^2 \left\langle \phi(\mathbf{k},s) \phi(-\mathbf{k}) \right\rangle + \left\langle \phi(\mathbf{k},s) \phi(-\mathbf{k}) \right\rangle
\]$$

Solution of the Laplace-Fourier transformed hydrodynamic equations gives the dispersion relation for the system and the transformed variables $p(\mathbf{k},s)$, $\phi(\mathbf{k},s)$, and $c(\mathbf{k},s)$ in terms of the initial values $p(\mathbf{k})$, $\phi(\mathbf{k})$, and $c(\mathbf{k})$. Mountain and Deutch have obtained the lowest order non trivial factorization of the characteristic determinant $D(s)$ of the system. They show $D(s)$ to be:

$$
D(s) \equiv (s + \Gamma_+)(s + \Gamma_-)(s - i\kappa_0 + \Gamma_{\beta})(s + i\kappa_0 + \Gamma_{\beta})
$$

where

$$
\Gamma_+ = \frac{1}{2} \left[ D_T K^2 + \sigma K^2 \right] + \frac{1}{2} \left[ (D_T K^2 + \sigma K^2)^2 - 4 D_T D K^4 \right]^{1/2},
$$

$$
\Gamma_{\beta} = \kappa^2 \left\{ \frac{4 M}{3 m} + D_T (\chi - 1) + \frac{D_{co}^2}{\rho^2} \left( \frac{\partial \rho}{\partial c} \right)_T - \frac{\rho^2 \kappa D}{\rho} + \frac{k_T}{C_p} \left( \frac{\partial \rho}{\partial c} \right)_T \right\},
$$

$$
D_T = \frac{\nu}{\rho C_p},
$$

$$
\sigma = D (1 - q) \quad \text{where} \quad q = \frac{k_T^2}{C_p} \left( \frac{\partial \mu}{\partial c} \right)_T.
$$
The dispersion relation $D(s) = 0$ shows that the system has four modes, and in the approximation of eq. (3.22) the resulting spectrum will contain four Lorentzian components. There will be a pair of Lorentzian lines split from the incident frequency by $\pm Kc$ and with a HWHH of $\Gamma_B$. Note that $\Gamma_B$ contains not only the usual contributions from $\eta$ and $\kappa$ but also a contribution from diffusion. This arises in a binary mixture because the pressure and temperature gradients in a sound wave result in the irreversible processes of thermal diffusion and barodiffusion. In addition to these propagating modes there are two non-propagating modes which yield a pair of unshifted lines of HWHH equal to $\Gamma_\pm$. These latter components arise only from the coupled energy transport and diffusion in the mixture as may be seen by solving the energy transport and diffusion equations (eqs. (3.16) and (3.17)) with pressure constrained to be constant ($p = v^2p = 0$). In this case one obtains the dispersion relation

$$s^2 - \left[ D_T + \rho \right] k^2 s + D_T D k^4 = 0 \quad (3.27)$$

which has the roots $s = \Gamma_\pm$. The resulting line widths have the simple diffusion width ($DK^2$) and entropy relaxation width ($DTK^2$) only when the coupling between energy transport and diffusion is small ($q \ll 1$) or when diffusion and energy transport relaxation times are widely separated (e.g. $D \ll DT$). We may show that the former is the case for a binary gas mixture by evaluating the coupling coefficient $q = \left( k_T^2 / TC_p \right) (\delta \mu / \delta c)$, making use of the definitions in eqs. (3.18) as required. Since $p = nk_BT$, constant $p$ and $T$ implies constant $n$ and we have

$$\left( \frac{\partial \mu}{\partial c} \right)_{p,T} = \frac{\partial}{\partial c} \left\{ \frac{k_BT \ln(n_2 k_BT)}{m_2} - \frac{k_BT \ln(n_1 k_BT)}{m_1} \right\} \quad (3.28)$$

or

$$= \frac{\rho k_BT}{m_1m_2n_in_i} \left( \frac{\partial n_i}{\partial c} \right)_n \quad (3.29)$$
Using

\[ \frac{\partial n_1}{\partial c} = \frac{\rho^2}{nm_1m_2} \]  

we find

\[ \frac{\partial \mu}{\partial c} \bigg|_{p,T} = \frac{k_B T \rho}{nm_1m_2 c(1-c)} \]  

and finally for \( q \) from eq. (3.22):

\[ q = \frac{[\alpha_T c(1-c)]^2}{k_B T \rho} \left( \frac{c}{nm_1m_2 c(1-c)} \right) = \frac{2}{5} x_1 x_2 \alpha_T^2. \]

The thermal diffusion factor \( \alpha_T \), is generally small for binary gas mixtures, being largest for mixtures of disparate masses, such as He-Xe, for which the experimental value of \( \alpha_T = 0.43 \) has been determined. Since \( x_1 x_2 = x_1 (1-x_1) < 0.25 \) we have \( q < 0.019 \). For \( q \ll 1 \) the roots of eq. (3.27) become

\[ \Gamma_+ = D_T K^2 \left[ 1 - q \left( \frac{D}{D_T - D} \right) \right] \]  

\[ \Gamma_- = D K^2 \left[ 1 + q \left( \frac{D}{D_T + D} \right) \right] \]

so that for a He-Xe mixture \( (D_T \sim 5D) \) the coupling between mass and entropy diffusion is small enough for the approximation

\[ \Gamma_+ = D_T K^2 \]  

\[ \Gamma_- = D K^2 \]  

(3.34)

to be valid to better than 1%. The spectrum will thus contain two Lorentzian lines unshifted in frequency, one of width \( DK^2 \) from concentration fluctua-
tions and one of width $D_T K^2$ from entropy fluctuations.

The parameters $c_o$ and $\Gamma_B$ pertaining to the propagating modes may be expressed in terms of specific properties of the constituent gases by evaluating the various thermodynamic derivatives which they contain. We have for $c_o$:

$$c_o = \left( \frac{1}{\rho K^2} \right)^{1/2} = \left( \frac{\gamma}{\rho K^2} \right)^{1/2} = \left( \frac{\gamma}{\rho} \right)^{1/2}$$

(3.35)

so that $c_o$, the adiabatic sound velocity is

$$c_o = \left( \frac{5k_B T}{3 \bar{m}} \right)^{1/2}$$

(3.36)

where

$$\bar{m} = m_1 \nu_1 + m_2 \nu_2.$$  

(3.37)

The Brillouin HWHH $\Gamma_B$ given in eq. (3.24) requires the evaluation of $k_p$, given in eq. (3.18), $(\partial \rho/\partial T)_{p, c}$ and $(\partial \rho/\partial T)_{p, c'}$, for which we find:

$$\left( \frac{\partial \rho}{\partial T} \right)_{p, c} = -\frac{\rho}{T}$$

(3.38)

$$\left( \frac{\partial \rho}{\partial c} \right)_{p, T} = \frac{\rho^2 (m_2 - m_1)}{n m_1 m_2}$$

(3.39)

$$k_p = \frac{\rho}{\rho^2} \left( \frac{\partial \rho}{\partial c} \right)_{p, T} = -\frac{(m_2 - m_1) c(1-c) n}{\rho}$$

(3.40)

Using eqs. (3.31), (3.38) and (3.40) in eq. (3.24) for $\Gamma_B$ we find:

$$\Gamma_B = \frac{1}{2} \left\{ \frac{4n}{3m_n} + D_T (\gamma - 1) \right\} K^2 + DK^2 \left( \frac{5\gamma}{3} \right) \left[ \frac{m_2 - m_1}{\bar{m}} + \frac{2\alpha}{5} \right]^2,$$

(3.41)
The relative amplitudes of the various contributions to the spectrum are determined by the solutions for the transformed fluctuations $\rho(K, s)$, $\phi(K, s)$ and $c(K, s)$ in terms of the initial values $\rho(K)$, $\phi(K)$, and $c(K)$. These solutions have been obtained by Mountain and Deutch who find

$$
\rho(K, s) = \frac{\rho(K)}{2} \left[ (s + iKc_o + \Gamma_o)^{-1} + (s - iKc_o + \Gamma_o)^{-1} \right] \tag{3.42}
$$

$$
\phi(K, s) = \frac{\phi(K)}{2} \left[ \left( \frac{\Gamma_p - D}{\Gamma_p - \Gamma_o} \right) (s + \Gamma_o)^{-1} + \left( \frac{\Gamma_p - D}{\Gamma_p - \Gamma_o} \right) (s - \Gamma_o)^{-1} \right] \tag{3.43}
$$

$$
+ \frac{\phi(K)}{2} \left[ \left( \frac{DK^2k_T}{C_p(\Gamma_p - \Gamma_o)} \right) \left\{ (s + \Gamma_o)^{-1} - (s - \Gamma_o)^{-1} \right\} \right]
$$

$$
c(K, s) = \frac{c(K)}{2} \left[ \left( \frac{\Gamma_p - D}{\Gamma_p - \Gamma_o} \right) (s + \Gamma_o)^{-1} + \left( \frac{\Gamma_p - D}{\Gamma_p - \Gamma_o} \right) (s - \Gamma_o)^{-1} \right] \tag{3.44}
$$

$$
+ \frac{\phi(K)}{2} \left[ \left( \frac{DK^2k_T}{C_p} \right) \left\{ (s + \Gamma_o)^{-1} - (s - \Gamma_o)^{-1} \right\} \right].
$$

In the case where the coupling between mass and entropy diffusion is small and eqs. (3.34) may be used, eqs. (3.42, 3 and 4) reduce to

$$
\rho(K, s) = \frac{\rho(K)}{2} \left[ (s + iKc_o + \Gamma_o)^{-1} + (s - iKc_o + \Gamma_o)^{-1} \right] \tag{3.45}
$$

$$
\phi(K, s) = \frac{\phi(K)}{2} \left[ (s + D - \Gamma^2)^{-1} \right] \tag{3.46}
$$
\[
c(R, s) = c(R) \left[ (s + Dk^2)^{-1} \right].
\]  \hspace{1cm} (3.47)

Thus under the approximation of eq. (3.22) the state variables \( p, \varphi \), and \( c \) are the normal coordinates of the system, the space-time behavior of each depending only on its own initial value.

We are now in a position to obtain the spectrum \( S_{\delta \epsilon}(\vec{k}, \omega) \) from eq. (3.21). Insertion of \( p(\vec{k}, s) \), \( \varphi(\vec{k}, s) \), and \( c(\vec{k}, s) \) from eqs. (3.45), (46) and (47) into eq. (3.21) will yield \( S_{\delta \epsilon}(\vec{k}, \omega) \) in terms of the ensemble averages:

\[
\langle p(\vec{k}) p(-\vec{k}) \rangle, \langle \varphi(\vec{k}) \varphi(-\vec{k}) \rangle, \langle c(\vec{k}) c(-\vec{k}) \rangle, \langle p(\vec{k}) \varphi(-\vec{k}) \rangle, \langle p(\vec{k}) c(-\vec{k}) \rangle, \ldots
\]

It is convenient to discuss these averages before writing out \( S_{\delta \epsilon}(\vec{k}, \omega) \) since many of them can be shown to be zero. Specifically, if \( x \) and \( y \) represent any two of the three variables \( p, \varphi, c \), then the statistical independence of \( x \) and \( y \) leads to \( \langle \Delta x \Delta y \rangle = 0 \) where \( \Delta x \) and \( \Delta y \) represent uniform fluctuations of \( \Delta x \) and \( \Delta y \) measured in the same volume element at a given time. Since fluctuations in the thermodynamic state variables in different volume elements at a given time are always statistically independent we have immediately

\[
\langle s_x(\vec{r}', \xi) s_y(\vec{r}, \xi) \rangle = 0
\]  \hspace{1cm} (3.48)

for all \( \vec{r}' \) and \( \vec{r} \). Defining \( x(\vec{K}) \) and \( y(\vec{K}) \) in analogy with eq. (2.225), eq. (3.48) leads to

\[
\langle x(\vec{r}) y(-\vec{r}) \rangle = \langle y(\vec{r}) x(-\vec{r}) \rangle = 0
\]  \hspace{1cm} (3.49)
if $x$ and $y$ are statistically independent. Thus all of the cross terms such as $\langle p(x)p(-x) \rangle$ etc. drop out leaving only $\langle p(x)p(-x) \rangle$, $\langle p(x)p(-x) \rangle$, and $\langle c(x)c(-x) \rangle$ to be evaluated. Considering the pressure $p$ first we have for $\langle p(x)p(-x) \rangle$

$$\langle p(x)p(-x) \rangle = \langle |p(x)|^2 \rangle = \int \int d^3 r d^3 r' e^{i(x-x')} \langle p(\vec{r},t) p(\vec{r}',t) \rangle.$$ 

The spatial correlation function, $\langle \delta p(\vec{r},t)\delta p(\vec{r}',t) \rangle$, indicates the extent to which a fluctuation in pressure at a point $\vec{r}$ at time $t$ influences the pressure at a point $\vec{r}'$ at time $t$. In general such influence extends only over distances $|\vec{r} - \vec{r}'|$ of the order of the pair correlation range. It follows that for a gas, the spatial correlation function $\langle \delta p(\vec{r},t)\delta p(\vec{r}',t) \rangle$ is short ranged, falling to zero for $|\vec{r} - \vec{r}'| > a$ where $a$ is the molecular diameter. The same is generally true for $\langle \delta c(\vec{r},t)\delta c(\vec{r}',t) \rangle$ and $\langle \delta c(\vec{r},t)\delta c(\vec{r}',t) \rangle$. The short ranged nature of the spatial correlations allows us to approximate $\exp[iK \cdot (\vec{r} - \vec{r}')]$ in eq. (3.50) by 1 since for the values of $K$ used in our experiments ($K< 2 \times 10^5 \text{ cm}^{-1}$) we have $K|\vec{r} - \vec{r}'| << 1$ wherever the spatial correlation functions are non-zero. We then have

$$\langle p(x)p(-x) \rangle = \int \int d^3 r d^3 r' \langle \delta p(\vec{r},t) \delta p(\vec{r}',t) \rangle. \quad (3.51)$$

Since the range of correlation for the pressure is very small we may assume $\langle \delta p(\vec{r},t)\delta p(\vec{r}',t) \rangle = 0$ for $\vec{r} \neq \vec{r}'$ and we have

$$\langle p(x)p(-x) \rangle = \langle \int d^3 r \delta p^2(\vec{r},t) \rangle. \quad (3.52)$$

To evaluate this ensemble average we return to eq. (3.19) where we have written the probability of establishing a uniform pressure fluctuation of $\Delta p$ over a volume $v$. Dividing $V$ into volume elements $v_i$ it follows from (3.14) that the probability, $\mathcal{P}$, of establishing over the volume, $V$, a pressure fluctuation $\delta p(\vec{r},t)$ with $\delta p(\vec{r},t) = \delta p_1$ in $v_i$ is
\[ \mathcal{O}(\delta p(\mathbf{r}, t)) \propto \exp \left\{ - \left( \frac{K_s}{2k_B T} \right) \int_{\mathcal{V}} \mathcal{V}_i (\delta p_i)^2 \right\} \]

\[ = \exp \left\{ - \left( \frac{K_s}{2k_B T} \right) \int_{\mathcal{V}} \delta p^2 (\mathbf{r}, t) \right\}. \quad (3.53) \]

The ensemble average \( \langle f_\mathcal{V} d^3 r \delta p^2 (\mathbf{r}, t) \rangle \) may then be evaluated from eq. (3.53) and we find from eq. (3.52)

\[ \frac{1}{V} \langle p(\mathbf{r}) p(-\mathbf{r}) \rangle = \frac{k_B T}{K_s}. \quad (3.54) \]

Similar arguments for the state variables \( \varphi \) and \( c \) yield

\[ \frac{1}{V} \langle \varphi(\mathbf{r}) \varphi(-\mathbf{r}) \rangle = \frac{k_B T^2}{\rho C_p}. \quad (3.55) \]

and

\[ \frac{1}{V} \langle c(\mathbf{r}) c(-\mathbf{r}) \rangle = \frac{k_B T}{\rho \left( \frac{\partial h}{\partial c} \right)_p T}. \quad (3.56) \]

For the specific case of a binary gas mixture we find

\[ \frac{1}{V} \langle p(\mathbf{r}) p(-\mathbf{r}) \rangle = \gamma n (k_B T)^2 \quad (3.57) \]

\[ \frac{1}{V} \langle \varphi(\mathbf{r}) \varphi(-\mathbf{r}) \rangle = \left( \frac{\gamma - 1}{\gamma} \right) \frac{T^2}{n} \quad (3.58) \]

\[ \frac{1}{V} \langle c(\mathbf{r}) c(-\mathbf{r}) \rangle = \frac{n m_1 m_2 c(1-c)}{\rho^2}. \quad (3.59) \]
To obtain $S_{\delta \varepsilon} (K, w)$ from eq. (3.21) we shall also need the derivatives $(\partial \varepsilon / \partial P)_{p, c}$, $(\partial \varepsilon / \partial \phi)_{p, c}$ and $(\partial \varepsilon / \partial c)_{p, \phi}$. These may be evaluated using the following thermodynamic relations:

\[
\frac{(\partial \varepsilon)}{(\partial c)_{p, \phi}} = \left( \frac{\partial \varepsilon}{\partial c} \right)_{p, T} \tag{3.60}
\]

\[
\frac{(\partial \varepsilon)}{(\partial \phi)_{p, c}} = \left( \frac{\partial \varepsilon}{\partial T} \right)_{p, c} \tag{3.61}
\]

\[
\frac{(\partial \varepsilon)}{(\partial P)_{\phi, c}} = \left( \frac{\partial \varepsilon}{\partial T} \right)_{p, c} = \left( \frac{\partial \varepsilon}{\partial P} \right)_{p, c} + \frac{T \alpha_T}{\rho C_p} \left( \frac{\partial \varepsilon}{\partial T} \right)_{p, c} \tag{3.62}
\]

and eqs. (3.2) and (3.5) which relate changes $\delta \varepsilon$ of $\varepsilon$ to changes $\delta n_1$, $\delta n_2$ of the constituent number densities:

\[
\delta \varepsilon = \varepsilon_0 \left[ \alpha_1 \delta n_1 + \alpha_2 \delta n_2 \right]. \tag{3.63}
\]

As an example we have for $(\partial \varepsilon / \partial c)_{p, \phi}$

\[
\frac{(\partial \varepsilon)}{(\partial c)_{p, \phi}} = \left( \frac{\partial \varepsilon}{\partial c} \right)_{p, T} = \left( \frac{\partial \varepsilon}{\partial c} \right)_h
\]

\[
= \varepsilon_0 \left\{ \alpha_1 \left( \frac{\partial n_1}{\partial c} \right)_h + \alpha_2 \left( \frac{\partial n_2}{\partial c} \right)_h \right\}
\]

\[
= \varepsilon_0 \left\{ \frac{\rho^2}{n m_1 m_2} \left( \alpha_2 - \alpha_1 \right) \right\}. \tag{3.64}
\]
Similarly:

\[
\left( \frac{\partial \varepsilon}{\partial \phi} \right)_{\rho_c} = \varepsilon \left\{ -\frac{n}{T} (\alpha_1 \nu_1 + \alpha_2 \nu_2) \right\} \tag{3.65}
\]

and

\[
\left( \frac{\partial \varepsilon}{\partial \rho} \right)_{\phi_c} = \varepsilon \left\{ \frac{1}{k_B T} - \frac{\alpha T h}{\rho c_p} \right\} (\alpha_1 \nu_1 + \alpha_2 \nu_2). \tag{3.66}
\]

We shall now proceed to evaluate \( S_{\delta \varepsilon} (\mathbf{K}, \omega) \). Inserting eqs. (3.45-7) into eq. (3.21) and dropping the cross terms according to eq. (3.49) we find for \( S_{\delta \varepsilon} (\mathbf{K}, \omega) \):

\[
S_{\delta \varepsilon} (R, \omega) = \left( \frac{\partial \varepsilon}{\partial \phi} \right)^2_{\rho_c} \frac{\langle \rho(\mathbf{R}) \rho(\mathbf{R}) \rangle}{V} \left\{ \frac{\Pi_0}{\Pi_0^2 + (\omega + \nu)^2} + \frac{\Pi_0}{\Pi_0^2 + (\omega - \nu)^2} \right\} + \\
+ \left( \frac{\partial \varepsilon}{\partial \phi} \right)^2_{\rho_c} \frac{\langle \phi(\mathbf{R}) \phi(-\mathbf{R}) \rangle}{V} \left\{ \frac{2 D_T K^2}{\omega^2 + (D_T K^2)^2} \right\} + \\
+ \left( \frac{\partial \varepsilon}{\partial \phi} \right)_{\rho_c, \phi} \frac{\langle c(\mathbf{R}) c(-\mathbf{R}) \rangle}{V} \left\{ \frac{2 D K^2}{\omega^2 + (D K^2)^2} \right\}.
\]

\]

\[
\tag{3.67}
\]

Using eqs. (3.64-6) and (3.57-9) this becomes
\[
\frac{1}{\varepsilon_0^2} \sum_{k} s_{k}(\omega) = n(\alpha_1, \omega) \left[ \frac{1}{\gamma} \left\{ \frac{\Gamma}{\Gamma^2 + (\omega + \kappa \omega_0)^2} + \frac{\Gamma}{\Gamma^2 + (\omega - \kappa \omega_0)^2} \right\} \right] \\
+ n(\alpha_1, \omega) \left[ (1 - \frac{1}{\gamma}) \left\{ \frac{2D_T k^2}{\omega^2 + (D_T k^2)^2} \right\} \right] \\
+ n(\alpha_1, \omega) \left( \alpha_2 - \alpha_1 \right)^2 \left[ \frac{2D_k^2}{\omega^2 + (D_k k^2)^2} \right],
\]

\[ (3.68) \]

where

\[ A(K, \omega) = \left( 1 - \frac{1}{\gamma} \right) \frac{2D_T k^2}{\omega^2 + (D_T k^2)^2} + \frac{1}{\gamma} \left[ \frac{\Gamma}{\Gamma^2 + (\omega + \kappa \omega_0)^2} + \frac{\Gamma}{\Gamma^2 + (\omega - \kappa \omega_0)^2} \right] \]

\[ (3.70) \]

\[ B(K, \omega) = \frac{2D_k^2}{\omega^2 + (D_k k^2)^2}. \]

\[ (3.71) \]

From eq. (2.121) we obtain the energy angle extinction:

\[
\eta(k, \omega) = \frac{1}{2\pi} \left[ \frac{(k_0)^2}{4\pi} \right]^2 \eta \left[ (\alpha_1 \alpha_1 + \alpha_2 \alpha_2) A(K, \omega) + \alpha_2 (\alpha_2 - \alpha_1) B(K, \omega) \right].
\]

\[ (3.72) \]

Thus the scattered light spectrum for binary gas mixture in the hydrodynamic limit and in the approximation of eq. (3.22) consists a density fluctuation part, \( A(K, \omega) \), similar to that obtained for a one component fluid (see eq. (2.250)), arising from pressure and entropy fluctuations, and, in addition, a concentration fluctuation part, \( B(K, \omega) \), a single Lorentzian of HWHH DK.
The spectrum $S_{\delta \varepsilon} (\vec{k}, \omega)$ for a binary gas mixture reduces to that for a one component fluid ($S_{\delta \varepsilon} (\vec{k}, \omega) = n_0 \alpha^2 A (\vec{k}, \omega)$) from eqs. (2.250) and (2.222) under the conditions that $\alpha_1 = \alpha_2 = \alpha$ or that $x_1 = 0, 1$. The extinction per unit solid angle $h(\vec{k})$ using eqs. (2.54) and (3.72) is, in the hydrodynamic limit

$$h(\vec{k}) = \int_{-\infty}^{\infty} d\omega \, h_0 (\vec{k}, \omega) = \left[ \frac{(k_0 \omega)^2}{4\pi} \right] \left( n_0 \alpha^2 + n_2 \alpha_2^2 \right)$$

(3.73)

an expression which is generally valid for a dilute binary mixture as was shown in eq. (3.13) from the consideration of the correlation functions. Eqs. (3.72) and (3.73) allow us to derive expressions for $h_d (\vec{k})/h(\vec{k})$ and $h_c (\vec{k})/h(\vec{k})$, the respective ratios of the extinction for density and concentration fluctuations to the net extinction $h(\vec{k})$. We have from eq. (3.72)

$$h_d (\vec{k}) \sim n_1 \alpha_1 (x_1 + \alpha_2 x_2)^2$$

(3.74)

so that

$$r_d \equiv \frac{h_d (\vec{k})}{h (\vec{k})} = \frac{(x_1 + \alpha_2 x_2)^2}{\alpha_1 \alpha_2 x_1 + \alpha_2^2 x_2}$$

(3.75)

$$r_c \equiv \frac{h_c (\vec{k})}{h (\vec{k})} = \frac{(\alpha_2 - \alpha_1)^2 x_1 x_2}{\alpha_1 \alpha_2 x_1 + \alpha_2^2 x_2}$$

Removing frequency independent factors the scattered light spectrum may be written

$$S(\vec{k}_1 \omega) = r_d A(\vec{k}_1 \omega) + r_c B(\vec{k}_1 \omega).$$

(3.76)
The ratios \( r_d \) and \( r_c \) depend only on the ratio \( \alpha_1/\alpha_2 \) of the polarizabilities and the number fraction \( x_1 \). We have plotted, in fig. (3.1), \( r_d(x_1) \) and \( r_c(x_1) \) for a He-Xe mixture. For this mixture, from Table (2.2) and eq. (2.94), we find \( \alpha_1/\alpha_2 = 19.45 \), with subscript 1 corresponding to xenon.

In summary, the scattered light spectrum of a dilute binary gas mixture in the hydrodynamic limit is a sum of Lorentzian lines arising from entropy fluctuations (thermal line), pressure fluctuations (Brillouin lines), and concentration fluctuations (diffusion line). Six quantities are required to specify the spectral shape: the linewidths \( D_TK^2, \Gamma_B \), and \( Dk^2 \) of the thermal, Brillouin, and diffusion lines, respectively; \( K_c \), the Brillouin splitting; \( \gamma - 1 \), the Landau-Placzek ratio relating the intensity in the thermal and Brillouin lines, and finally \( r_c \), relating the intensity in the diffusion line to that in the thermal and Brillouin lines. To give an idea of the relative magnitudes involved we present values of these quantities for the gas mixture studied-dilute xenon in helium, under the typical conditions of interest here: \( T = 22^\circ \text{C} \), scattering angle \( \theta = 10.60^\circ \), total pressure \( p = 3520 \text{ mmHg (4.5 atm.)} \), \( p_x = 22 \text{ mmHg (} x = 0.0064) \):

\[
\begin{align*}
D_TK^2/\pi & = 41 \text{ MHz} \\
Dk^2/\pi & = 12.6 \text{ MHz} \\
\Gamma_B/\pi & = 80 \text{ MHz} \\
K_c/2\pi & = 268 \text{ MHz} \\
\gamma - 1 & = 2/3 \\
r_c & = 0.64
\end{align*}
\]

The linewidths in eqs. (3.77) are the FWHH in frequency and were calculated using the measured transport coefficients for the mixture in eqs. (3.25) and (3.41). The linewidths all vary inversely as the total pressure. The Brillouin splitting was obtained from eq. (3.36). Since the average thermal energy of an atom in a gas depends only on the temperature and is independent of the composition of the gas, the heat capacities per particle, \( c_p \) and \( c_v \), and the ratio \( c_p/c_v = \gamma \) are those of any monatomic
Figure 3.1: Fraction of the total scattered power in concentration and density fluctuation spectra for a helium-xenon mixture.
gas, i.e. \( \gamma = 5/3 \). The ratio \( r_c \) was calculated from eq. (3.75) with \( a_x/a_h = 19.45 \). The Brillouin width and splitting will be discussed further in sec. (III E). A spectrum taken under the conditions just employed is shown in fig. (5.5).

2. Hydrodynamic Limit of \( S_{ij}(\vec{K}, \omega) \)

We have obtained in eq. (3.12) a general expression for the extinction \( h(\vec{K}, \omega) \) for a binary gas mixture in terms of the \( S_{ij}(\vec{K}, \omega) \), the space-time Fourier transforms of the conditional fluctuation distributions of the system:

\[
h(\vec{K}, \omega) = \frac{1}{2\pi} \left[ \frac{(k_0^2 \sin \phi)}{4\pi} \right] \ln \left\{ \alpha_1^2 \chi_1 S_{11}(\vec{K}, \omega) + \alpha_2 \chi_2 S_{22}(\vec{K}, \omega) \right. \\
+ \alpha_1 \alpha_2 \left[ \chi_2 S_{12}(\vec{K}, \omega) + \chi_1 S_{21}(\vec{K}, \omega) \right] \}.
\]

We have, in addition, in eq. (3.72), obtained the hydrodynamic limit of \( h(\vec{K}, \omega) \) for a binary gas mixture in terms of the density fluctuation spectrum \( A(K, \omega) \) and diffusion spectrum \( B(K, \omega) \):

\[
h(\vec{K}, \omega) = \frac{1}{2\pi} \left[ \frac{(k_0^2 \sin \phi)}{4\pi} \right] \ln \left\{ (\alpha_1 \chi_1 + \alpha_2 \chi_2)^2 A(K, \omega) \right. \\
+ \chi_1 \chi_2 (\alpha_1^2 - \alpha_2^2) B(K, \omega) \}.
\]

It is of interest here to compare \( h(\vec{K}, \omega) \) from eq. (3.12) with that from eq. (3.72) in order to determine the hydrodynamic limit for the spectral functions \( S_{ij}(\vec{K}, \omega) \). Equating terms with similar polarizability factors \( (\alpha_1^2, \alpha_2^2, \alpha_1 \alpha_2) \) one finds from eqs. (3.72) and (3.12) the following hydrodynamic forms for \( S_{ij}(\vec{K}, \omega) \):
$S_{11}(k_1, \omega) = \chi_1 A(k_1, \omega) + \chi_2 B(k_1, \omega)$

$S_{22}(k_1, \omega) = \chi_2 A(k_1, \omega) + \chi_1 B(k_1, \omega)$

$S_{21}(k_1, \omega) = \chi_2 [A(k_1, \omega) - B(k_1, \omega)]$

$S_{12}(k_1, \omega) = \chi_1 [A(k_1, \omega) - B(k_1, \omega)]$.

From these equations we obtain further:

$S_{11}(k_1, \omega) + S_{21}(k_1, \omega) = A(k_1, \omega)$

$S_{12}(k_1, \omega) + S_{22}(k_1, \omega) = A(k_1, \omega)$

$S_{22}(k_1, \omega) - S_{21}(k_1, \omega) = B(k_1, \omega)$

$S_{11}(k_1, \omega) - S_{12}(k_1, \omega) = B(k_1, \omega)$.

The sum $S_{11} + S_{21}$ in eq. (3.79) is the space-time Fourier transform of the sum $\rho_{11}(\vec{r}, t) + \rho_{22}(\vec{r}, t)$ which in turn is the fluctuation in the total particle density $n_1(\vec{r}, t) + n_2(\vec{r}, t)$, given that a particle of kind 1 was at $(0, 0)$. Eqs. (3.79 a, b) therefore show that the response of the total density at $(\vec{r}, t)$ to the placement of either kind of particle at $(0, 0)$, in the hydrodynamic limit, is a density fluctuation response having the spectrum given in eq. (3.70). That is, eqs. (3.79 a, b) show that the response of the total density in a binary mixture to the placement of a particle at $(0, 0)$ has the same
form as the density response of a one component fluid to the placement of a particle at \((0, 0)\).

On the other hand, eq. (3.79) shows that the difference in the density of component \# 2 at \((\vec{r}, t)\) with a particle of component \# 2 at \((0, 0)\) from the density of component \# 2 at \((\vec{r}, t)\) with a particle of component \# 1 at \((0, 0)\) has a pure diffusion response.

We shall be particularly interested in the situation where component \# 1 is in very small concentration, that is \(x_1 \ll 1, x_2 \approx 1\). In this case eq. (3.78a, b) become

\[
S_{11}(K, \omega) \approx B(K, \omega) \\
S_{22}(K, \omega) \approx A(K, \omega).
\]  

Eq. (3.80 a) shows that with \(x_1\) small a particle of kind 1 placed at \((0, 0)\) will have a diffusion type space-time distribution in the hydrodynamic limit. Thus the very dilute component \# 1 diffuses in component \# 2. Eq. (3.80b) shows on the other hand that component \# 2 carries the density fluctuation as one would expect when component \# 1 is dilute.

3. Applicability of Hydrodynamics to a Binary Gas Mixture

We have noted in the beginning of sec. (III C) that the equations (eqs. (3.15) - (3.17)) employed in the hydrodynamic calculation of the spectrum are valid only in the long wavelength, low frequency limit. It is of use here to define long wavelength and low frequency more precisely. The hydrodynamic equations (eqs. 3.15, 6, 7) are appropriate to the description of a disturbance of wave vector \(K\) and frequency \(\omega\) in a binary gas mixture under the following conditions: (i) The length \(1/K\) must be large compared to the velocity correlation length \(\tau_i\) for both species of the mixture \((\tau_i < 1/K, \ i = 1, 2)\); (ii) The frequency \(\omega\) must be small compared to the relaxation frequencies of the system.

*The length \(\tau_i\) is the distance in the gas over which a particle can travel before collisions greatly change its velocity. See sec. (III D2).
This latter condition has been considered in detail by Goldman and Sirovich. (5) These authors, starting from the coupled kinetic equations for the mixture (eqs. (3.83)) and using a method similar to the Chapman-Enskog procedure, have derived a set of hydrodynamic equations which more accurately describe high frequency phenomena in a gas mixture than do the eqs. (3.15, 6, 7) which we have employed in sec. (III C1). The equations of Goldman and Sirovich reduce to those used in sec. (III C1) in the long wavelength, low frequency limit. Goldman and Sirovich show that three relaxation frequencies characterize the return to equilibrium in a gas mixture: (i) \( w_M \) - the Maxwellization frequency: This is the stress relaxation frequency, i.e., the frequency at which the viscosity relaxes; (ii) \( w_u \) - the relaxation frequency for the relative velocity of the two components. Imagine prescribing at \( t = 0 \) a spatially uniform gas with an initial relative velocity \( \vec{u}_0 \) between components 1 and 2. The relative velocity \( \vec{u} \) dies away like \( \vec{u} = \vec{u}_0 \exp(-w_ut) \), where

\[
\omega_u = \frac{k_B T \rho}{m_1 m_2 n D};
\]

(iii) \( w_T \) - relaxation frequency for temperature equilibration of the two species. Imagine preparing at \( t = 0 \) a spatially uniform mixture with zero relative velocity but with species 1 at \( T_1^0 \) and species 2 at \( T_2^0 \). Then \( T_1 - T_2 \) will behave like \( T_1 - T_2 = (T_1^0 - T_2^0) \exp(-w_T t) \) where

\[
\omega_T = \frac{2nm_1m_2 w_u}{\rho(m_1 + m_2)}.
\]

Unlike the one component system, where the relaxation frequencies \( w_{11} \) for heat conduction and \( w_{02} \) for stress are nearly the same \( (w_{11} = 2/3 w_{02}) \), the relaxation frequencies \( w_M \), \( w_u \) and \( w_T \) in a binary mixture can be widely different.

A good example of this is the helium-xenon mixture, with xenon dilute \( (x_X < .03) \). In this system since the helium largely supports any stresses the Maxwellization frequency \( w_M \) is the stress relaxation frequency \( w_{02} \) of the helium. At a helium pressure of \( p_h = 1 \text{ atm} \), the
the calculated stress relaxation frequency from eq. (2.216) is \( \omega_{02}/2\pi = p/2\pi \eta \approx 810 \text{ MHz} \). Eq. (3.81) shows that \( \omega_u = k_B T/m_x D \) in the limit of low xenon concentration. Since from eq. (2.346) the velocity correlation time \( \tau_c \) of a diffusing particle is \( \tau_c = mD/k_B T \) we have that in the limit of low xenon concentration \( \omega_u \) is the inverse velocity correlation time for the xenon motion. At \( p_h = 1 \text{ atm.} \) we find \( \omega_u \approx k_B T/m_x D \approx 55 \text{ MHz} \).

Since the magnitude of the velocity of a xenon atom in the mixture with \( u = u_o \) at \( t=0 \) dies away as \( u = u_o \exp(-\omega_u t) \), its temperature, which depends on \( u^2 \), dies away as \( T = T_o \exp(-2\omega_u t) \) so we should expect \( \omega_T = 2\omega_u \). Eq. (3.82) shows this to be so and we find \( \omega_T = 110 \text{ MHz} \) at \( p_h = 1 \text{ atm.} \) The relaxation frequencies for velocity and temperature equilibration of xenon in a helium-xenon mixture are thus much smaller than that of stress relaxation. The relaxation times \( \omega_M, \omega_u, \) and \( \omega_T \) are all proportional to the helium pressure when the xenon is dilute.

We may now consider the application of conditions (i) and (ii) to the specific case discussed in eqs. (3.77), i.e. \( p_h = 4.5 \text{ atm, } x_x = 0.064 \) and \( \Theta = 10.0^\circ \). Under these conditions \( \omega_h \approx 1/8K, \omega_x \approx 1/5K, \omega_M = 3700 \text{ MHz}, \omega_u = 225 \text{ MHz} \) and \( \omega_T = 450 \text{ MHz} \). We see that condition (i) is reasonably well satisfied for \( \omega_h \) and \( \omega_x \). Condition (ii) is satisfied for the diffusion and thermal conduction components of the spectra so that the hydrodynamic equations employed here should describe these processes well. The Brillouin splitting (268 MHz), however, is larger than \( \omega_u \) and close to \( \omega_T \), making dubious the application of our hydrodynamic equations to describe sound propagation. The large value of \( \omega_M \), relative to the Brillouin splitting, however, indicates that the sound propagation spectrum should have a hydrodynamic form but with the velocity and temperature relaxations altering the splitting and width from the values predicted by the equations of the low frequency limit. These relaxations might be expected to contribute additional damped modes (Mountain modes) to the density fluctuations as do thermal and structural relaxation processes in liquids, thereby producing additional spectral components around \( \omega = 0 \).
D. The Helium-Xenon Mixture

1. Introduction

We have shown in eq. (3.11) that the spectrum of light scattered by a dilute binary mixture of monatomic gases is determined by the conditional density fluctuation distributions \( \rho_{ij}(\vec{r}, t) \). We shall now discuss the relationship of \( \rho_{ij}(\vec{r}, t) \) and \( S_{ij}(\vec{K}, \omega) \) to the kinetic theory of the gas mixture. In general the calculation of \( \rho_{ij}(\vec{r}, t) \) requires the solution of the coupled kinetic equations for the \( \mu \) space distributions \( f_{\mu}(\vec{r}, \vec{v}, t) \):\(^{(7)}\)

\[
\left( \frac{\partial}{\partial t} + \vec{v} \cdot \nabla \right) f_{\mu}(\vec{r}, \vec{v}, t) = \left( \frac{\partial f_{\mu}}{\partial t} \right)_{\text{coll}} + \left( \frac{\partial f_{\mu}}{\partial t} \right)_{\text{prod}}, \quad i = 1, 2. \tag{3.83}
\]

The collision operators determining the time evolution of \( f_{1}(\vec{r}, \vec{v}, t) \) account for both i-i collisions and i-j collisions. The equations couple since \( (\partial f_{i}/\partial t)_{\text{coll}} \) depends on \( f_{1}(\vec{r}, \vec{v}, t) \). The distribution \( \rho_{ij}(\vec{r}, t) \) is obtained as a velocity integral of \( f_{1}(\vec{r}, \vec{v}, t) \) with the initial placement of a particle of kind j at the origin in a way analogous to that outlined for the one component gas. General solutions of the eqs. (3.83) for \( \rho_{ij}(\vec{r}, t) \) (or better, \( S_{ij}(\vec{K}, \omega) \)) are presently available only in the extreme kinetic limit, obtained by setting the collision operators to zero, and in the hydrodynamic limit. One finds in the kinetic limit for \( S_{ii}(\vec{K}, \omega) \), the Gaussian spectrum expected if component i were alone, and, since in the kinetic limit there are no i-j collisions, one finds \( \rho_{ij} = S_{ij} = 0 \). In the hydrodynamic limit the Chapman-Enskog procedure can be applied to obtain the hydrodynamic equations for the mixture (eqs. (3.15 - 7)) which, as we have shown in sec. (III C 1), may be solved for the spectral functions \( S_{ij}(\vec{K}, \omega) \).

We shall be concerned here with circumstances in a binary gas mixture under which certain non-hydrodynamic behavior can be described more simply than by eqs. (3.83). Specifically we shall discuss the mixture of a light gas (helium) with a heavy gas (xenon) in the limit of low concentration of the heavy gas. We shall show that the kinetic equation
describing the evolution of $\rho_{x_x}(\vec{r}, t)^*$ for dilute xenon in a helium-xenon mixture can be simply formulated and solved for the spectral function $S_{xx}(\vec{k}, w)$. We shall show also that, because of the large extinction of xenon relative to helium ($\alpha_x^2/\alpha_h^2 = 378$), $S_{xx}(\vec{k}, w)$ can be extracted from the scattered light spectrum of a helium-xenon mixture.

2. Correlation Lengths and Times

We begin the discussion of the helium-xenon mixture by writing expressions for the velocity correlation time $\tau_x$ and length $l_x$ for xenon atoms and $\tau_h$, $l_h$ for helium atoms in the mixture. The velocity correlation time or collision time $\tau_i$ is the time required for a particle of kind i to lose by collision a given component of velocity (the time required for thermalization) and is defined by

$$\langle \vec{v}_i(t) \cdot \vec{v}_i(t+\tau) \rangle = \langle v_i^2 \rangle e^{-\tau/\tau_i}. \quad (3.84)$$

The associated correlation length or mean free path $l_i$ is given by

$$l_i = \sqrt{2} v_{oi} \tau_i \quad (3.85)$$

where $\sqrt{2} v_{oi} = \sqrt{2k_B T/m_i}$ is the most probable speed of species i. The correlation lengths $l_x$ and $l_i$ are given by

$$l_x^{-1} = l_x^{-1} + l_x^{-1} \quad (3.86)$$

$$l_h^{-1} = l_h^{-1} + l_h^{-1}$$

where $l_{ij}$ is the correlation length for particles of kind i colliding only with the particles of kind j in the mixture. The corresponding correlation $\rho_{ii}(\vec{r}, t)$, where component i corresponds to xenon.
We may determine $\ell_{ij}$ from $d_{ij}$, the mean distance traveled by a particle of kind $i$ between collisions with particles of kind $j$. For the helium-xenon mixture (8)

$$\ell_{ij} \equiv d_{ij} = \left\{ \frac{1}{\pi a_i^2 n_j} \right\}$$  \hspace{1cm} (3.88)

$$\ell_{xh} \equiv d_{xh} \cdot N = \left\{ \frac{1}{\pi a_{xh}^2 n_h} \frac{m_h}{m_x} \right\} \cdot N$$  \hspace{1cm} (3.89)

$$\ell_{hh} \equiv d_{hh} = \left\{ \frac{1}{\pi a_h^2 n_h} \right\}$$  \hspace{1cm} (3.90)

$$\ell_{hx} \equiv d_{hx} = \left\{ \frac{1}{\pi a_{hx}^2 n_x} \right\}$$  \hspace{1cm} (3.91)

Here respectively $m_i$, $n_i$ and $a_i$ are the molecular mass, number density and molecular diameter of component $i$ and $a_{ij} = a_j = (a_i + a_j)/2$. The correlation lengths $\ell_{ij}$ are nearly equal to $d_{ij}$ for $x - x$, $h - h$, and $h - x$ collisions since for these encounters thermalization occurs in one collision. In the case of xenon colliding with helium ($x - h$), however, the xenon atom, because of its relatively large mass must undergo many $(N)$ collisions with heliurns before being thermalized, thus $\ell_{xh} = d_{xh} \cdot N$. For the xenon-helium ratio ($m_x/m_h = 32.9$), one finds (8) $N \approx 12$.

We shall need in a later discussion the ratio $\ell_x/\ell_h$ of xenon correlation length to helium correlation length for a helium-xenon mixture in which the xenon is very dilute, i.e. $n_x << n_h$. In this limit collisions of a given particle occur predominately with helium atoms so that
\[ l_{xh} \ll l_{xx} \text{ and } l_{hh} \ll l_{hx}. \text{ From eqs. (3.86) we then find} \]

\[
\frac{l_x}{l_{hh}} \equiv l_{xh} \quad (3.92)
\]

\[
\frac{l_h}{l_{hh}} \equiv l_{hh}. \quad (3.92)
\]

The desired ratio then will be from eqs. (3.89) and (3.90)

\[
\frac{l_x}{l_h} \equiv \frac{l_{xh}}{l_{hh}} = \frac{a_h^2}{a_{xh}^2} \sqrt{\frac{2m_h}{m_x}} \cdot N. \quad (3.93)
\]

From the helium and xenon molecular diameters one finds \( a_h^2, a_{xh}^2, \) and \( a_x^2 \) to be in the ratio\(^9\)

\[
a_h^2 : a_{xh}^2 : a_x^2 \leftrightarrow 1 : 1.4 : 2.3 \quad (3.94)
\]

We then find from eq. (3.93)

\[
\frac{l_x}{l_h} \equiv 2. \quad (3.95)
\]

3. Properties of \( \rho_{xx}(\mathbf{r}, t) \) and \( S_{xx}(\mathbf{K}, \omega) \)

We now consider the variation of the conditional distribution function \( \rho_{xx}(\mathbf{r}, t) \) and spectrum \( S_{xx}(\mathbf{K}, \omega) \) for a helium-xenon mixture of constant xenon partial pressure as the helium partial pressure is varied. We shall discuss the variation for values of the xenon pressure and the scattering vector, \( \mathbf{K} \), such that in the absence of helium:

(i) \( l_{xx} \gg 1/K \), (ii) \( l_{xx} \geq 1/K \), (iii) \( l_{xx} \ll 1/K \).

(i) \( l_{xx} \gg 1/K \) In the absence of helium (\( p_h = 0 \)) the xenon mean free path is \( l_x = l_{xx} \) and the scattered light spectrum is \( S_{xx}(\mathbf{K}, \omega) \). When \( l_{xx} \gg 1/K \) the light scattering process samples the temporal evolution of \( \rho_{xx}(\mathbf{r}, t) \) for times short compared to the collision time \( \tau_x \) as discussed in sec. (IIB2c). That is, \( \rho_{xx}(\mathbf{r}, t) \) is sampled at times when the xenon atom
(say \#1) originally at (0, 0) is still in free flight, not having collided with any of the other particles. Contributions to the scattered light spectrum, \( S_{xx}(K, \omega) \) come from only the self part which has the Gaussian kinetic limit of eq. (2.89).

As helium is added, \( \ell_x \), because of x-h collisions, decreases from \( \ell_{xx} \) according to eqs (3.86) and (3.89). In the limit of high helium pressure x-h collisions determine the xenon correlation length and we have \( \ell_x \approx \ell_{xh} \). Since \( \ell_{xh} \sim 1/n_h \) we can adjust the helium density high enough so that \( \ell_{xh} \) becomes very small (\( \ell_{xh} \ll 1/K \)). In this limit a xenon atom undergoes many x-h collisions in a length \( 1/K \). When \( \ell_{xh} \ll 1/K \) the spectrum \( S_{xx}(K, \omega) \) samples \( \rho_{xx}(\vec{r}, t) \) for times long compared to the x-h correlation time, \( \tau_{xh} \), given in eq. (3.87). Over times long compared to \( \tau_{xh} \), the xenon particle \#1 has undergone many x-h collisions and is in diffusion among the helium atoms. In this limit the self distribution, \( P_s(\vec{r}, t) \), of xenon \#1 has the diffusion form of Table (2.1), with a spatial spread of \( \sqrt{4D_t} \), where \( D \) is the mutual diffusion constant for the mixture. The corresponding self spectrum has the form of \( S_D(K, \omega) \) in eq. (2.299). To obtain \( \rho_{xx}(\vec{r}, t) \) and \( S_{xx}(K, \omega) \) for \( t > \tau_{xh} \), however, both self and other contributions to \( \rho_{xx}(\vec{r}, t) \) are required. We must thus determine how the density of the remaining xenon atoms is influenced by the diffusion of xenon \#1. To this end we note that, since adjusting the mean free paths so that \( \ell_{xh} \) is small (\( \ell_{xh} \ll 1/K \)) will require \( n_x \ll n_h \), the discussion pertaining to eq. (3.95) will apply and \( \ell_x \sim \ell_h \ll 1/K \). The mean free paths for both xenon and helium will be small compared to \( 1/K \) so that the hydrodynamic forms for \( S_{ij}(K, \omega) \) may be employed. These are from eqs. (3.78)

\[
S_{xx}(K, \omega) = B(K, \omega) + x_x (A(K, \omega) - B(K, \omega)) \quad (a) \quad (3.96)
\]

\[
S_{hl}(K, \omega) = A(K, \omega) - B(K, \omega) \quad (b) \quad (3.97)
\]

where, since \( n_x \ll n_h \), we have used \( x_x \ll 1, x_h \approx 1 \). The dominant contribution to \( S_{xx}(K, \omega) \) in eq. (3.96) is the self contribution, \( B(K, \omega) \), from particle \#1 which we have described just above. The term \( x_x (A - B) \) arises from the remaining xenon atoms in the mixture. Eqs. (3.96, 7) indicate
that the response of the total density to particle # 1 is given by $A(K,\omega) - B(K,\omega)$, much the same as in a one component gas. Xenon # 1 pushes a hole ($-B(K,\omega)$) which leads to a collective density fluctuation ($A(K,\omega)$). The xenon atoms, composing a fraction $x_x$ of the total density, carry a fraction $x_x(A - B)$ of the density response $A - B$. The point we wish to make here is that in the hydrodynamic limit for $x_x << 1$, the self contribution dominates $S_{xx}(K,\omega)$ so that in calculating $S_{xx}(K,\omega)$ we may neglect the density disturbance in the remaining particles. The distribution $\rho_{xx}(\vec{r},t)$ in the limit of high helium pressure may be approximated by $P_{sx}(\vec{r},t)$, the self distribution of xenon # 1, moving in a sea of particles at equilibrium. Furthermore, under the stipulated condition $\epsilon_{xx} >> 1/K$, the approximation of $\rho_{xx}(\vec{r},t)$ by $P_{sx}(\vec{r},t)$ is valid at arbitrary helium pressure if we place the additional condition that the xenon number fraction be small ($x_x << 1$), when helium pressure is reduced to the pressure $p_h'$ at which $\epsilon_{xh} \sim 1/K$. Under these circumstances for helium pressures $p_h > p_h'$, xenon concentration is small so that xenon participation in collective behavior is small. On the other hand, for $p_h < p_h'$, we have $\epsilon_{xh} > 1/K$ and we sample the system for times short compared to $\tau_{xh}'$ when collective motion has not yet been excited by xenon # 1 and we need worry about only the self distribution.

To summarize, then, under the conditions that $\epsilon_{xx} >> 1/K$ and $x_x << 1$, when $\epsilon_{xh} \sim 1/K$, the conditional distribution $\rho_{xx}(\vec{r},t)$ of the xenon atoms may be approximated by the self distribution $P_{sx}(\vec{r},t)$ of a xenon atom moving in a background of helium atoms at equilibrium, for arbitrary helium pressure.

The coupled kinetic equations for the helium-xenon mixture are:

\[
\left( \frac{\partial}{\partial t} + \vec{v} \cdot \nabla \right) f_x(\vec{r},\vec{v},t) = \left( \frac{\partial f_x}{\partial t} \right)_x + \left( \frac{\partial f_x}{\partial t} \right)_h \quad (a)
\]

\[
\left( \frac{\partial}{\partial t} + \vec{v} \cdot \nabla \right) f_h(\vec{r},\vec{v},t) = \left( \frac{\partial f_h}{\partial t} \right)_x + \left( \frac{\partial f_h}{\partial t} \right)_h \quad (b)
\]

(3.98)
The distribution $\rho_{xx}(r, t)$ may be calculated from these equations using the above-mentioned approximation by a) setting the helium distribution to its equilibrium value, b) setting $(\frac{\partial f_x}{\partial t})_{\text{coll}} = 0$ since we neglect $x - x$ collisions; c) approximating $(\frac{\partial f_x}{\partial t})_{\text{h}}$ by a model appropriate to the xenon-helium collision. The calculation of $\rho_{xx}(r, t)$ and $S_{xx}(K, \omega)$ from the remaining kinetic equation for $f_x(r, \vec{v}, t)$ is identical to the calculation of $P_K(r, t)$ for a one component fluid as described in sec. (II C 4). We would expect the Fokker-Planck model to be more appropriate to the approximation of $(\frac{\partial f_x}{\partial t})_{\text{coll}}$ than the hard collision model because of the large number ($\approx 12$) of $x - h$ collisions required to thermalize the xenon.

In the present case of xenon moving in helium the velocity correlation time $\tau_{\text{xh}}$ takes the place of $\tau_c$ in the Fokker-Planck equation (eq. (2.324)) and is determined experimentally by the mutual diffusion coefficient $D$ of the mixture and eq. (2.301)

$$\tau_{\text{xh}} = \frac{D}{\nu_{\text{ox}}^2}. \quad (3.99)$$

We define for the present case, in analogy to eq. (2.328), a uniformity parameter $\gamma_{\text{nc}}$ for xenon-helium collisions (nc because xenon-helium collisions are Non-Conserving of xenon momentum and energy). We find for $\gamma_{\text{nc}}$

$$\gamma_{\text{nc}} = \frac{1}{\sqrt{2} K \nu_{\text{ox}} \tau_{\text{xh}}} = \frac{\nu_{\text{ox}}}{\sqrt{2} K D}. \quad (3.100)$$

For a binary gas mixture $D \sim (\text{total pressure})^{-1}$ so that when $x_x <\ll 1$ we have $D \sim 1/p_h$ and for a fixed scattering angle and temperature

$$\gamma_{\text{nc}} \propto p_h. \quad (3.101)$$

*Under these assumptions $f_x(r, \vec{v}, t)$ is the $\mu$-space distribution of xenon atom #1.
Therefore in the limit of high helium pressure ($n_{\text{He}} \to \infty$) the spectrum $S_{xx}(K, \omega)$ approaches the Lorentzian of HWHH $DK^2$ given in eqs. (2.299) and (2.300), and as $p_0 \to 0$ we have $n_{\text{He}} \to 0$ and the kinetic Gaussian form for $S_{xx}(K, \omega)$ of eqs. (2.297) and (2.298). The spectral evolution of $S_{xx}(K, \omega)$ vs. $n_{\text{He}}$ is given in fig. (2.6).

(ii) ($L_{xx} \gtrsim 1/K$) In this range of $L_{xx}$ we sample the system at the time that, in the absence of helium, xenon \#1 makes its first collision with another xenon atom. This situation differs from case (i) in that, in the absence of helium, excitation of the collective modes of the xenon will have started during the sampled time interval. Therefore, for low helium pressures, i.e. for $L_{xh} \gtrsim L_{xx}$, we must account for x-x collisions in the calculation of $\rho_{xx}(\vec{r}, t)$. This is accomplished by retaining the x-x collision operator, $(\partial f_x/\partial t)_x^{\text{coll}}$, in the kinetic equation (eq. (3.98a)) for $f_x(\vec{r}, \vec{v}, t)$. In case (i) we were able to approximate the helium distribution, $f_h(\vec{r}, \vec{v}, t)$ by its equilibrium value, which is convenient because it decouples the equations. If we again require $x_x \ll 1$ when $p_h = p_h'$, this approximation will still be valid in the present case for helium pressures $p_h > p_h'$, i.e. for $L_{xh} < 1/K$ for the same reasons given in case (i): the xenon will constitute only a small fraction of the density. For $p_h < p_h'$ the validity of the approximation of $f_h(\vec{r}, \vec{v}, t)$ by its equilibrium distribution depends on the extent to which any deviation of $f_h(\vec{r}, \vec{v}, t)$ from its equilibrium value will modify the distribution of the xenon particles 2 to $N_x$. For $p_h < p_h'$ we have $L_{xh} > 1/K$ and since $L_{xx} \gtrsim 1/K$ we sample $\rho_{xx}$ at a time when xenon \#1 has made less than one x-h or x-x collision respectively. Since during less than one x-h collision time the modification of the helium distribution due to xenon \#1 will be small, and since there will be less than one collision time for the resulting modification of $f_h(\vec{r}, \vec{v}, t)$ to influence the xenon atoms 2 to $N_x$, it would seem in this case reasonable to again assume that $f_h(\vec{r}, \vec{v}, t)$ has its equilibrium value. The assumption will certainly break down for xenon pressure such that $L_{xx} < 1/K$ and collective motion in the xenon is excited by xenon \#1. Such collective motion will modify the helium distribution and the coupled kinetic equations will be required. For $L_{xx} > 1/K$, 

...
however, in the above approximation, we have the simple equation for \( f_x(r, \vec{v}, t) \)

\[
\left( \frac{\partial}{\partial E} + \vec{V} \cdot \vec{V} \right) f_x(r, \vec{v}, t) = \left( \frac{\partial f_x}{\partial t} \right)_x + \left( \frac{\partial f_x}{\partial t} \right)_h.
\]

(3.102)

In summary, this equation makes the following approximations: a) treats all \( x \times x \) collisions exactly; b) treats exactly the interaction of xenon atom \# 1 with the helium atoms; c) neglects the interaction of the remaining xenon atoms with the helium. In sec. (4) we will solve eq. (3.102) for the spectrum \( S_{xx}(K, \omega) \) with the exact collision operator for \( x \times x \) collisions and an approximate model (Fokker-Planck) for the \( x \times h \) collision operator.

(iii) \( (\ell_{xx} \ll 1/K) \) We now discuss the case when \( \ell_{xx} \ll 1/K \) and both \( x \times x \) and \( x \times h \) collisions play a part in determining the temporal evolution of \( \rho_{xx}(r, t) \). In the limit of high helium pressure the xenon correlation length, \( \ell_x \), is controlled by \( x \times h \) collisions \( (\ell_x \sim \ell_{xh}) \) and the situation is exactly the same as for cases (i) and (ii), that is \( \rho_{xx}(r, t) \) is approximately the xenon self distribution for a diffusing particle. In the absence of helium since \( \ell_{xx} \ll 1/K \) the spectrum \( S_{xx} \) has the form of the hydrodynamic spectrum for pure xenon. As helium pressure is increased, then, \( S_{xx} \) evolves from the three component hydrodynamic spectrum of pure xenon to the single component diffusion spectrum when \( \ell_{xh} \ll \ell_{xx} \). Since \( \ell_{xx} \ll 1/K \) implies that \( \ell_x, \ell_h \ll 1/K \), the variation of \( S_{xx}(K, \omega) \) with \( p_h \) can in this case be obtained from hydrodynamics. The hydrodynamic form of \( S_{xx}(K, \omega) \) in eq. (3.96a) shows that for \( p_h \) low (\( x \sim 1 \)) we have \( S_{xx} \approx A(K, \omega) \) whereas for \( p_h \rightarrow \infty \) we find \( S_{xx} \approx B(K, \omega) \).

4. Calculation of \( S_{xx}(K, \omega) \)

We now outline the calculation of \( S_{xx}(K, \omega) \) for the helium-xenon mixture using the approximate kinetic equation (eq. (3.102)) which was formulated to describe \( f_x(r, \vec{v}, t) \) under the conditions of cases (i) and (ii), these being \( \ell_{xx} \ll 1/K \) and \( x_x \ll 1 \) when \( \ell_{xh} \sim 1/K \). The equation to be
solved is

\[
\left( \frac{\partial}{\partial t} + \mathbf{v} \cdot \nabla \right) f_x(\mathbf{r}, \mathbf{v}, t) = \left( \frac{\partial f_x}{\partial t} \right)_x + \left( \frac{\partial f_x}{\partial t} \right)_h, \tag{3.102}
\]

subject to the initial condition of an extra thermalized xenon atom at \( \mathbf{r} = 0 \) at \( t = 0 \) since we desire to calculate \( S_{xx}(K, \omega) \):

\[
f_x(\mathbf{r}, \mathbf{v}, 0) = \left( n_{oX} + \delta(x) \right) f_{oX}(\mathbf{v}). \tag{3.103}
\]

Solutions of this equation for \( S_{xx}(K, \omega) \) have been obtained by replacing the collision operators \( (\partial f_x/\partial t)_x^{\text{coll}} \) and \( (\partial f_x/\partial t)_h^{\text{coll}} \) by approximate tractable models. The kinetic model for Maxwell molecules (see sec. (II C 2c)) was used to approximate the x - x collision operator, since this approximation was found to be suitable in describing the effects of x - x collisions in pure xenon. The x - h collision operator was approximated by the Fokker-Planck model (see sec. (II C 4c)) for two reasons: (i) The Fokker-Planck approximation should be applicable in the limit that a heavy particle (xenon) moves in a sea of very light (helium) particles; (ii) The velocity functions \( \psi_i(\varepsilon) \) which are eigenfunctions of the x - x collision operator, are also eigenfunctions of the Fokker-Planck operator \( A^i \), given in eq. (2.327). This latter fact makes the solution of eq. (3.102) very similar to the solution of the Boltzmann equation in pure xenon in the kinetic model approximation.

The solution of eq. (3.102) proceeds as did that of the Boltzmann equation (see sec (II C 1b)) and the Fokker-Planck equation (see sec. (II C 4c)) with the introduction of the dimensionless transformed distribution \( a(K, \tilde{\varepsilon}, x) \) dimensionless velocity, \( \tilde{\varepsilon} \), frequency, \( x \), and Maxwellian, \( \phi(\varepsilon) \), given in eqs. (2.157), (2.153), (2.156) and (2.160) respectively. With these substitutions and eqs. (2.158), (2.184), and (2.326) we find for eq. (3.102):

\[
i(\nu - \mathbf{K}, \mathbf{\tilde{v}}) a(\mathbf{r}, \mathbf{\tilde{v}}, \nu) = \frac{i}{2\pi} - \frac{\nu_1}{\lambda_{il}} J(\mu) + \frac{\nu n_1}{2} \mathcal{A}_s(\mu). \tag{3.104}
\]
Here \( y_c \sim 1/K_{xx} \) is the uniformity parameter for \( x - x \) collisions (Conserving the xenon energy and momentum) and is determined by eq. (2.217) and the xenon partial pressure. The parameter \( y_{nc} \) is the uniformity parameter for \( x - h \) collisions (Non-Conserving xenon energy and momentum) and is given by eqs. (2.328) and (2.301) and the mutual diffusion constant \( D \) of the mixture:

\[
y_{nc} = \frac{v_{0x}}{\sqrt{2K}D}.
\]  

(3.105)

The relative magnitudes of \( y_c \) and \( y_{nc} \) determine which collision operator in eq. (3.104) dominates. Proceeding along the lines of the kinetic model we expand \( a(K, \xi, x) \) in the orthonormal velocity eigenfunctions \( \psi_i(\xi) \) of the collision operator \( J \) as in eqs. (2.167 - 172). Since we are dealing with Maxwell molecules the eigenvalue matrix \( \lambda_{ij} \) is diagonal. The velocity functions \( \psi_i(\xi) \) are also eigenfunctions of the Fokker-Planck operator \( A_s \) of the eq. (2.327). In terms of the \( r, l, m^* \) indexing of the \( \psi_i \):

\[
A_s \psi_{r,l,m}(\xi) = -(2r + l) \psi_{r,l,m}(\xi)
\]

(3.106)

which we shall denote by

\[
A_s \psi_i(\xi) = \xi_i \psi_i(\xi).
\]  

(3.107)

We now make a kinetic model approximation of the effect of \( A_s \), exactly analogous to that made for \( J \) in eqs. (2.178 - 181):

\[
A_s(a(\kappa, \xi, x)) = \sum_{j=1}^{N} (\xi_j + \xi_i) a_j(\kappa, x) \psi_j(\xi) - \xi_i a(\kappa, \xi, x)
\]  

(3.108)

*sec. (II C 2 a)
We have replaced here all eigenvalues $\xi_i$ for $i > N$ by a single constant $-\xi$. Inserting into eq. (3.108) the expansion of eq. (2.167) for $a(K, \vec{c}, x)$ and the kinetic model approximations of eq. (2.181) for $J$ and eq. (3.108) for $\Lambda_s$ we find

$$
\left[ i(\nu - \xi_0) - \frac{\lambda_N}{\tilde{\lambda}_1} + \frac{\nu \lambda_N}{2} \right] \sum_{j} \alpha_j(\nu, \nu, \nu) \psi_j(\xi) \\
= \frac{1}{2\nu} - \frac{\lambda_N}{\tilde{\lambda}_1} \sum_{j=1}^{N} \psi_j(\nu, \nu, \nu) \psi_j(\xi),
$$

(3.109)

where

$$\beta_j = \frac{\lambda_j}{\tilde{\lambda}} + 1 \quad (3.110)$$

$$\delta_j = \frac{\nu \lambda_j}{\tilde{\lambda}} + 1 \quad (3.111)$$

Eq. (3.108) reduces to eq. (2.182) in the limit $\nu \rightarrow 0$. We find from eq. (3.109), in analogy to eq. (2.185)

$$a_n(\nu, \nu, \nu) = \frac{1}{2\nu} \sum_{j=1}^{N} \psi_j(\nu, \nu, \nu) \psi_j(\xi) \sum_{j=1}^{N} \alpha_j(\nu, \nu, \nu) \psi_j(\xi)$$

(3.112)

where

$$\gamma_{ij} = \left( \frac{\psi_i}{i(\nu - \xi_0) - \frac{\lambda_N}{\tilde{\lambda}_1} + \frac{\nu \lambda_N}{2} \psi_j} \right) \quad (3.113)$$

and

$$\alpha_j = \frac{\lambda_N}{\tilde{\lambda}_1} \beta_j + \frac{\nu \lambda_N}{2} \delta_j \quad (3.114)$$
Eqs. (3.112) are of exactly the same form as eqs. (2.185) so that the computer programs used to solve eqs. (2.185) needed only slight modification to solve eqs. (3.112). We again choose \( \lambda = \lambda_{N+1} \) and similarly \( \zeta = \zeta_{N+1} \).

The solution of eq. (3.112) for \( S(x,y_C,y_{nc}) \) was carried out for the values of \( y_C \) and \( y_{nc} \) pertinent to our experiment: \( y_C = 0.184 \), \( 0 \leq y_{nc} \leq 1.6 \), for order \( N = 15 \), at which convergence was obtained. The variation of these spectra with \( y_{nc} \) is very similar to that of the pure Fokker-Planck model (\( y_C = 0 \)), shown in fig. (2.6). The deviation produced by the nonzero \( y_C \) is greatest, as would be expected, for \( y_{nc} \leq y_C \). For \( y_{nc} = 0 \), the spectrum \( S(x,y_C,0) \) has the form of the spectrum \( S(x,y_C) \) for a one component Maxwell gas in the kinetic model. For \( y_{nc} > 1.6 \), the spectra with \( y_C = 0.184 \) are negligibly different from those with \( y_C = 0 \) (pure Fokker-Planck).

5. Determination of \( S_{xx}(K,\omega) \)

We now discuss the determination of \( S_{xx}(K,\omega) \) for the following specific conditions in the helium-xenon mixture: \( T = 22^\circ \text{C} \), \( \varrho = 10.6^\circ \), \( p_x = 16.8 \text{ mmHg} \), \( p_h = 0 \to 4.5 \text{ atm} \). Under these conditions, in the absence of helium, the xenon mean free path \( \ell_x \) is large compared to \( 1/K (\ell_x \sim 5/K) \). The uniformity parameter \( y_x \) for \( x-x \) collisions is, from Table (5.1), \( y_x = 0.184 \) for \( p_x = 16.8 \text{ mmHg} \). At this value of \( y_x \), as will be discussed in sec. (V A), measurements of \( S_{xx}(K,\omega) \) in pure xenon indicate that although \( S_{xx}(K,\omega) \) is nearly Gaussian, deviations from the Gaussian kinetic limit (\( y_x = 0 \)) are clearly noticeable. This is indicated by fig. (5.3). At low values of helium pressure, therefore, \( x-x \) collisions must be accounted for. In addition, under the above conditions, we find \( p'_{h} = 1 \text{ atm} \), i.e. \( \ell_{xh} \sim 1/K \) when \( p_h = 1 \text{ atm} \). We thus have a xenon number fraction of \( x_x \sim 0.02 \) when \( p_h = p'_h \) and the condition that \( x_x << 1 \) when \( p_h = p'_h \) is satisfied. The remarks of case (ii) in sec. (III D 3) therefore apply here.

We consider first the extraction of \( S_{xx}(K,\omega) \) from the scattered light spectrum \( S(K,\omega) \) at the highest helium pressure studied: \( p_h = 4.5 \text{ atm} \). At this helium pressure we have \( \ell_x \sim 0.2/K \) and \( \ell_h \sim 0.1/K \) so that the
spectrum is hydrodynamic, being the sum of the density fluctuation spectrum $A(K, \omega)$ and concentration fluctuation spectrum $B(K, \omega)$, as was stated in eq. (3.76):

$$S(k, \omega) = \rho_d A(k, \omega) + \rho_c B(k, \omega).$$  \hspace{1cm} (3.76)

Fig. (5.5) shows a typical spectrum from a helium-xenon mixture under these conditions ($p_h = 4.50$ atm).

The basic step in obtaining $S_{xx}(K, \omega)$ is to remove from the spectrum the density fluctuation contribution $\rho_d A(K, \omega)$. This leaves the concentration fluctuation portion, $\rho_c B(K, \omega)$, which is nearly equal to $S_{xx}(K, \omega)$ as we shall show shortly. The large central peak in figure (5.5) is the sum of the thermal line and $\rho_c B(K, \omega)$ which cannot be easily distinguished. The Brillouin lines, however, do provide a handle for determining the thermal line. Because the Brillouin lines are separated from the rest of the spectrum, the density fluctuation spectrum can be identified by fitting the Brillouin peaks to Lorentzians to determine their height, width, and area. Only the region of the spectrum in the vicinity of the Brillouin peaks is employed for the fitting. Even so, because of the possible presence of the tails of the thermal and diffusion lines in the vicinity of the Brillouin peaks, the determination of the Brillouin height and width is only approximate. With the approximate area of the Brillouin peaks, the Landau-Placzek ratio, and the measured thermal conductivity of the mixture, the Lorentzian thermal line can be calculated and added to the Brillouin lines to give the density fluctuation spectrum $A(K, \omega)$. Subtracting this from the total spectrum gives the diffusion contribution $B(K, \omega)$. With the thermal and diffusion lines determined, any contribution of their tails in the vicinity of the Brillouin peaks can be estimated and subtracted out. The whole process is then repeated until self consistent results are obtained.

To be able to determine $B(K, \omega)$ in this way requires that the three Lorentzian approximation to the density fluctuation spectrum $A(K, \omega)$ be sufficiently accurate. In practice this requirement is not severe because the thermal line accounts for a relatively small portion of the area of the central peak ($\sim 20\%$ at $p_h = 4.5$ atm., decreasing to $\sim 14\%$ at $p_h = 2.25$ atm.,
and ~7% at \( p_h = 1 \text{ atm.} \)). Because it is primarily the helium that carries
the density fluctuation the appropriateness of the three Lorentzian
approximation to describe the density fluctuation spectrum can be estimat-
ed from the ratio of the helium-helium collision length to \( 1/K \). For pure
helium at \( p_h = 4.5 \text{ atm.} \) we have from Table (5.1), \( y_h = 7.4 \) so that the
helium is hydrodynamic. At this value of \( y_h \) the three Lorentzian
approximation can be used. In fact the helium motion is sufficiently hydro-
dynamic so that the three Lorentzian approximation can be used throughout
the range of helium pressure where the density fluctuation spectrum need
be known: \( 0.78 \text{ atm} < p_h < 4.5 \text{ atm.} \) \( (1.3 < y_h < 7.4) \). At the lower pressures
in this range the next higher order hydrodynamic approximation, the
Kadanoff-Martin form (see eq. (2.247)) was also employed to describe
\( A(K, \omega) \). This form leaves the thermal line unchanged and adds asymmetric
terms to the Brillouin components. As Table (2.5) shows it is able to
approximate rather well the kinetic model spectra, even for \( y \) values as
small as 0.77. The Kadanoff-Martin approximation for \( A(K, \omega) \), when
subtracted from the total spectrum yielded essentially the same result
for \( B(K, \omega) \) as the three Lorentzian form for helium pressures in the above
range. For helium pressure below \( 0.78 \text{ atm.} \), the density fluctuation con-
tribution to the spectrum is small enough and broad enough compared to
the diffusion contribution to be approximated by a constant.

Once we are able to remove from the total spectrum \( S(K, \omega) \), the
density fluctuation contribution, \( r_d A(K, \omega) \), we must ask how \( S_{xx}(K, \omega) \) is
related to what is left. We again start in the hydrodynamic regime. We
have listed in Table (3.1) the coefficients of the contributions of the spectral
densities \( S_{xx}(K, \omega) \), \( S_{xh}(K, \omega) \), \( S_{hx}(K, \omega) \), and \( S_{hh}(K, \omega) \) to the total scattered
intensity, to \( B(K, \omega) \) and to \( A(K, \omega) \). The coefficients (removed of common
constants) are obtained from sec. (III C 2) and are listed: (a) for the general
case; (b) for \( x_x < 1 \), \( x_h \sim 1 \); and (c) for \( x_x < 1 \), \( x_h \sim 1 \), where
we have indicated the relative magnitudes of the various terms by setting
\( \alpha_x = 19.45 \), \( \alpha_h = 1 \). Table (3.1) shows that in the hydrodynamic limit,
\( S_{xx}(K, \omega) \) contributes to both \( A(K, \omega) \) and \( B(K, \omega) \). However, as was dis-
cussed in sec. (III D 3), when \( x_x < 1 \), the contribution to \( A(K, \omega) \) is a very
small part of \( S_{xx}(S_{xx} \simeq B + x_x A) \) and arises from the interaction of xenon
atoms 2 to N with the helium. Since we are interested in finding that part
Table 3.1: Coefficient of $S_{ij}(K, \omega)$ in Total Scattered Intensity and in the Density and Concentration Fluctuation Spectra in the Hydrodynamic Limit.

<table>
<thead>
<tr>
<th>$S_{ij}(K, \omega)$</th>
<th>$S_{xx}(K, \omega)$</th>
<th>$S_{xh}(K, \omega)$</th>
<th>$S_{hx}(K, \omega)$</th>
<th>$S_{hh}(K, \omega)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coefficients of Contribution of $S_{ij}$ to $\sigma$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(a) $h(K)$</td>
<td>$n(\sigma_x^2 \sigma_x)$</td>
<td>0</td>
<td>0</td>
<td>$n(\sigma_h^2 \sigma_x)$</td>
</tr>
<tr>
<td>$B(K, \omega)$</td>
<td>$n(\sigma_x^2 \sigma_x \sigma_h)$</td>
<td>$-n(\sigma_x \sigma_x \sigma_h)$</td>
<td>$-n(\sigma_x \sigma_x \sigma_h)$</td>
<td>$n(\sigma_h^2 \sigma_x \sigma_h)$</td>
</tr>
<tr>
<td>$A(K, \omega)$</td>
<td>$n(\sigma_x^2 \sigma_x^2)$</td>
<td>$n(\sigma_x \sigma_x \sigma_x)$</td>
<td>$n(\sigma_x \sigma_x \sigma_x)$</td>
<td>$n(\sigma_h^2 \sigma_x \sigma_h)$</td>
</tr>
<tr>
<td>(b) $x_x &lt;&lt; 1$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$x_h = 1$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$h(K)$</td>
<td>$\sigma_x^2 \sigma_x$</td>
<td>0</td>
<td>0</td>
<td>$\sigma_h^2 \sigma_h$</td>
</tr>
<tr>
<td>$B(K, \omega)$</td>
<td>$\sigma_x^2 \sigma_x$</td>
<td>$-\sigma_x \sigma_x \sigma_x$</td>
<td>$-\sigma_x \sigma_x \sigma_x$</td>
<td>$\sigma_h^2 \sigma_x$</td>
</tr>
<tr>
<td>$A(K, \omega)$</td>
<td>$\sigma_x^2 \sigma_x \sigma_x$</td>
<td>$\sigma_x \sigma_x \sigma_x$</td>
<td>$\sigma_x \sigma_x \sigma_x$</td>
<td>$\sigma_h^2 \sigma_h$</td>
</tr>
<tr>
<td>(c) $x_x &lt;&lt; 1$, $x_h = 1$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\alpha_x^2 = 378$, $\alpha_h^2 = 1$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$h(K)$</td>
<td>378 $\sigma_x$</td>
<td>0</td>
<td>0</td>
<td>$\sigma_h$</td>
</tr>
<tr>
<td>$B(K, \omega)$</td>
<td>378 $\sigma_x$</td>
<td>$-19.5 \sigma_x$</td>
<td>$-19.5 \sigma_x$</td>
<td>$\sigma_x$</td>
</tr>
<tr>
<td>$A(K, \omega)$</td>
<td>378 $\sigma_x \sigma_x$</td>
<td>$19.5 \sigma_x$</td>
<td>$19.5 \sigma_x$</td>
<td>$\sigma_x$</td>
</tr>
</tbody>
</table>
of $S_{xx}$ arising from xenon-xenon collisions and xenon # 1 - helium collisions only, the part of $S_{xx}$ given by $A(K, \omega)$ need not be determined and may be subtracted out along with the other contributions of the form $A(K, \omega)$. The part of $S_{xx}$ arising from the diffusive motion of xenon # 1 in the hydrodynamic limit has the form of $B(K, \omega)$ and contains a fraction $x_h$ (nearly all) of the light contributed by the xenon. Table (3.1) shows in addition that the hydrodynamic limit all of the spectra $S_{ij}(K, \omega)$ contribute to the coefficient of $B(K, \omega)$, in relative amounts which depend only on the ratio $\alpha_x/\alpha_h$. However, because $\alpha_x/\alpha_h$ is so large the contribution of $S_{xx}$ dominates, being a factor of 10 larger in area than the contribution of $S_{xh}$ and $S_{hx}$ combined. Therefore, in the hydrodynamic limit, the spectrum, $S(K, \omega) - r_d A(K, \omega)$, which remains after the subtraction of $r_d A(K, \omega)$ is dominated by that part of $S_{xx}$ which we wish to determine. The presence of $S_{xh}$ and $S_{hx}$ along with $S_{xx}$ in the spectrum $S(K, \omega) - r_d A(K, \omega)$ is of no consequence in the hydrodynamic limit since all of these spectra contribute to $S - r_d A$ a term of the form $B(K, \omega)$. As the helium pressure is lowered and the kinetic regime for xenon motion is approached, $S_{xx}, S_{xh}$ and $S_{hx}$ will in general still all contribute to $S(K, \omega) - r_d A(K, \omega)$ but their contribution will change in shape and area. In the limit of zero helium pressure, the density fluctuation contribution to $S(K, \omega)$ disappears ($r_d \rightarrow 0$) as do $S_{xh}$ and $S_{hx}$. The contribution of $S_{xx}$ maintains the same total area (equal to all of the intensity scattered by the xenon) but evolves to the near Gaussian spectrum of the pure xenon under the stated conditions ($y_x = 0.184$). We note therefore that the areas of the contributions $S_{xh}(K, \omega)$ and $S_{hx}(K, \omega)$ to $S(K, \omega) - r_d A(K, \omega)$ decrease with helium pressure. This is an important point because the shapes of $S_{xh}$ and $S_{hx}$ cannot be easily calculated for arbitrary helium pressure and in measuring $S(K, \omega) - r_d A(K, \omega)$ to obtain $S_{xx}(K, \omega)$ we include the contributions of $S_{xh}$ and $S_{hx}$. To get accurately the shape of $S_{xx}(K, \omega)$ therefore, it is necessary that either $S_{xh}$ and $S_{hx}$ contain only a very small fraction of the area of $S_{xx}$ or that they have nearly the same shape. The latter is the case in the hydrodynamic limit (high helium pressure) where, although $S_{xh}$ plus $S_{hx}$ has 10% of the area of $S_{xx}$ they contribute the same shape, $B(K, \omega)$, to $S(K, \omega) - r_d A(K, \omega)$. On the other hand in the kinetic limit (low helium pressure) $S_{xh}$ and $S_{hx}$ have such small area that their shape by all reasonable estimates does not matter.
An idea of the importance of the presence of $S_{xh}$ and $S_{hx}$ in the determination of $S_{xx}$ can be had by measuring the area of the contributions of $S_{xh}$ and $S_{hx}$ to $S(K, \omega) - r_d A(K, \omega)$. This information can be obtained from measurements of the ratio, $r_d$, of the area of the density fluctuation contribution $A(K, \omega)$ to the total spectrum $S(K, \omega)$. Under hydrodynamic conditions this ratio should be given by eqs. (3.75). We note from Table (3.1) that the effect of the cross terms $S_{xh}$ and $S_{hx}$ in the hydrodynamic limit is to decrease the area (intensity) of the $B(K, \omega)$ term and increase that of the $A(K, \omega)$ term by the same amount. A decrease in the area of the cross terms as the kinetic regime is approached thus should produce a decrease in the ratio, $r_d$, of the area of $A(K, \omega)$ to the total area of the spectrum from that predicted by the hydrodynamic equations. A small decrease in the area ratio $r_d$ will also be caused in the kinetic regime by the disappearance of the contribution of $S_{xx}$ to $A(K, \omega)$. A decrease in $r_d$ is, in fact, observed and analysis shows that the area of $S_{xh}$ plus $S_{hx}$ decreases to $\sim 5\%$ of that of $S_{xx}(K, \omega)$ at a helium pressure of $p_h = 0.78$ atm.

The spectral densities $S_{xh}(K, \omega)$ and $S_{hx}(K, \omega)$ are the Fourier transforms of the conditional distributions $p_{xh}(\vec{r}, t)$ and $p_{hx}(\vec{r}, t)$ of the density fluctuation of one species at $(\vec{r}, t)$ given a particle of the other species at $(0, 0)$. Estimates of the shapes of $S_{xh}$ and $S_{hx}$ can be made from the kinetic model calculation since $p_{xh}$ and $p_{hx}$ are, similar in form to the "other" distribution $(NP_0(\vec{r}, t))$ for the one component gas. The approximate shapes of $S_{xh}$ and $S_{hx}$ along with the measurements of the area of the $S_{xh} + S_{hx}$ contribution allow one to estimate the effect of $S_{xh}$ and $S_{hx}$ in the measurement of $S_{xx}(K, \omega)$. These estimates show that the possible error introduced in obtaining $S_{xx}(K, \omega)$ from $S(K, \omega) - r_d A(K, \omega)$, due to the presence of $S_{xh}$ and $S_{hx}$, is small and probably not detectable with the signal to noise available in these experiments. This point will be further discussed in sec. (V B 3) where measurements of $S_{xx}(K, \omega)$ are presented.

In closing we point out that the possibility of the extraction of $S_{xx}(K, \omega)$ from the scattered light spectrum of a helium xenon mixture rests on the large mass ratio $(m_x/m_h \approx 32)$ and extinction ratio $(\sigma_x^2/\sigma_h^2 = 378)$ of xenon to helium. The large mass ratio results in the spectrum of light...
arising from the xenon being generally narrower in frequency spread than that arising from the helium which allows easier subtraction of the unwanted parts of the spectrum. The large extinction ratio renders $S_{xx}(K, \omega)$ a predominant contribution to the spectrum and allows operation at a very small xenon concentration, a requirement for our approximate calculation of $S_{xx}(K, \omega)$.

E. Sound Propagation in Binary Gas Mixtures

We have obtained in sec. (III C 1) the dispersion relation for the collective modes of a binary gas mixture in the long wavelength low frequency limit. We pointed out in sec. (III C 3) that this dispersion relation will not be correct at frequencies now comparable to the relaxation frequencies $\omega_u$ for the velocity difference and $\omega_T$ for the temperature difference of the two components. We now discuss a calculation of the dispersion relation of Goldman(11), (12) which takes these relaxations into account.

Goldman and Sirovich,(5) starting from the coupled kinetic equations (eq. (3.83) and following a Chapman-Enskog type of procedure, have obtained a set of hydrodynamic equations which are more generally valid than those employed above in sec. (III C 1) in the calculation of the dispersion relation, (eqs. 3.14 - 7). The hydrodynamic equations used in sec. (III C 1) describe the mixture in terms of four variables which we may choose to be $n_1$, $n_2$, $\bar{u}$, and $T$, i.e. the component densities, and the overall velocity and temperature. Goldman and Sirovich obtain a set of hydrodynamic equations in the six variables $n_1$, $n_2$, $\bar{u}_1$, $\bar{u}_2$, $T_1$, and $T_2$, i.e. they place no constraints on the velocity difference $\bar{u}_2 - \bar{u}_1$, or temperature difference, $T_2 - T_1$. They account for the finite time required for gradients in the temperatures and densities to set up their corresponding currents. As an example of this we may consider the generalization of the diffusion equation (eq. (3.16)). Defining $\vec{j}(\vec{r}, t)$ to be the conjugate current to the concentration $c(\vec{r}, t)$ we find from eqs. (3.18)

$$\vec{j}(\vec{r}, t) = c_0(1 - c_0) \left\{ \bar{u}_2(\vec{r}, t) - \bar{u}_1(\vec{r}, t) \right\}$$
where \( c_0 \) is the equilibrium value of concentration, \( c_0 = \rho_{20}/\rho_0 \). Equation (3.16) is obtained by combining the conservation equation

\[
\frac{\partial c(r^2, t)}{\partial t} + \nabla \cdot j(r^2, t) = 0
\]  
(3.116)

with the transport equation

\[
j(r^2, t) = -D \left\{ \nabla c(r^2, t) + \frac{k_T}{T} \nabla T(r^2, t) + \frac{k_p}{P} \nabla p(r^2, t) \right\}
\]  
(3.117)

Note that in eq. (3.17) the current \( j \) responds instantaneously to the application of gradients in \( c, T, \) or \( p \). The essential generalization which results from the Goldman-Sirovich theory is to replace eq. (3.17) by

\[
j(r^2, t) = \frac{1}{\omega_u} \frac{\partial j(r^2, t)}{\partial t} - D \left[ \nabla c(r^2, t) + \frac{k_T}{T} \nabla T(r^2, t) + \frac{k_p}{P} \nabla p(r^2, t) \right]
\]  
(3.118)

wherein the current \( j \) responds to gradients only after a relaxation time \( \tau_u = 1/\omega_u \) has elapsed, where \( \omega_u \) was given in eq. (3.81). For dilute xenon in helium as was pointed out in sec. (III C 3) the relaxation time \( \tau_u \) is just the time required to have its velocity markedly changed by collisions with helium atoms. A similar generalization is introduced into the energy transport equation (eq. 3.17).

The calculation of the dispersion relation using the theory of Goldman and Sirovich has been carried out by Goldman. The characteristic determinant \( D(s) \) in this case is a sixth order polynomial in \( s \), indicating that there are six independent collective modes. We have obtained the dispersion relations of the Goldman calculation by numerically solving for the six roots of \( D(s) \). These calculations show that the following approximate factorization of \( D(s) \) is appropriate:

\[
D(s) = (s + i\kappa')^2(s + \kappa^2)(s + \omega_u)(s + \omega_T)(s - i\kappa + \eta^2)(s + i\kappa - \eta^2) \]  
(3.119)
which may be compared with eq. (3.22), remembering from eqs. (3.34) that $\Gamma_+ = D_T K^2$ and $\Gamma_- = D k^2$. This characteristic equation shows the presence of damped modes corresponding to velocity ($\omega_u$) and temperature ($\omega_T$) relaxations, in addition to those of mass diffusion ($D k^2$) and thermal diffusion ($D_T K^2$). The relaxation frequencies $\omega_u$ and $\omega_T$ are given in eqs. (3.81) and (3.82) respectively. There are also the propagating modes but with a velocity $c'_o$ and attenuation $\Gamma'_B$ which differ from the low frequency values of $c'_o$ and $\Gamma_B$ given in eqs. (3.36) and (3.41) respectively as $\omega/\omega_u = Kc'_o/\omega_u$ and $\omega/\omega_T = Kc'_o/\omega_T$ become appreciable. This is illustrated in fig. (3.2) for the helium-xenon mixture.

The helium-xenon mixture is an appropriate choice for study of the velocity and temperature relaxations since in this mixture, as was discussed in sec. (III C 3), the relaxation frequencies for these processes are small compared to the Maxwellization frequency $\omega_M$, the relaxation frequency for thermal conductivity and viscosity. The effects of the velocity and temperature relaxation can thus be studied independently of those of Maxwellization. In fig. (3.2) we show for a mixture of dilute xenon in helium the acoustic damping coefficient $\Gamma'_B$ and Brillouin splitting $Kc'_o$ under our experimental conditions ($\varnothing = 10.6^\circ$, $\lambda = 6328 \AA$, $T = 22^\circ C$). Since $\Gamma'_B$, the attenuation in the low frequency limit is inversely proportional to the total pressure $p$ we have plotted $\Gamma'_B p$. The curves are plotted for various values of $p$. The relaxation frequencies $\omega_u$ and $\omega_T$ are proportional to $p$ so that $\omega/\omega_u$ and $\omega/\omega_T$ decrease and the low frequency regime is approached with increasing $p$. At $p = 50$ atm. $\omega/\omega_u$ and $\omega/\omega_T$ are small ($\omega/\omega_u = 2\omega/\omega_T \sim .07$) and $c'_o$ and $\Gamma'_B$ have their low frequency values. In this limit the total attenuation $\Gamma'_B$ (see eq. (3.41)) is a sum of the "classical" attenuation arising from viscosity and thermal conductivity (indicated by the dashed line) and the diffusion contribution. The classical attenuation has been calculated for various values of xenon concentration using the measured thermal conductivity and viscosity for the helium-xenon mixture. (13) Note that in the helium-xenon mixture the diffusion contribution is rather large, doubling $\Gamma_B$ at a xenon number fraction of only .004. The velocity $c'_o$ decreases according to eq. (3.36) with increasing xenon concentration as $m$, the average mass per particle in the mixture, increases. As the total pres-
Figure 3.2: Brillouin splitting, $K_{C_0}$ and HWHH $\Gamma'$ for a helium-xenon dilute gas mixture, calculated from the theory of Goldman and Sirovich.
sure is decreased the effects of the relaxation of the velocity and temperature on $c'_o$ and $\Gamma'_B$ become apparent. We have indicated $c'_o$ and $\Gamma'_B$ for $p = 4.53$ atm ($\omega/\omega_u \approx 0.7$) and $p = 1.69$ atm. ($\omega/\omega_u \approx 2.4$). At the lowest pressure ($p = 1.69$ atm) the Maxwellization frequency is still high enough ($\omega/\omega_M \approx 5$) so that the classical attenuation will have only begun to relax. Almost all of the change of $c'_o$ and $\Gamma'_B$ as $p$ decreases from 50 to 1.69 atm. is thus attributable to the velocity and temperature relaxations. As may be seen the effect of the relaxations is to reduce the influence of the xenon on the attenuation and velocity. This is to be expected if we recall that $\tau_u$, the velocity relaxation frequency for a mixture of dilute xenon in helium is just the inverse velocity correlation time for the xenon, i.e., it takes a time $\tau_u$ for the motion of a xenon atom to influence or be influenced by its environment.
References: Chapter 3


7. Reference 4 - Chapter 8.

8. Reference 4 - Chapter 5.


11. E. Goldman, J. Acoust. Soc. Am. 44, 708 (1968). There are several algebraic errors in the characteristic equation presented in this paper (eqs. 23, 4). They are corrected by replacing in eqs. (24), $b_{2 2}$ by $\gamma b_{2 2}$ and $b_{4 2}$ by $\imath b_{4 2}$.


CHAPTER IV: EXPERIMENTAL TECHNIQUE AND APPARATUS

A. Introduction

We begin this section with a discussion of the choice of experimental conditions for the spectral analysis of the light scattered by gases and gas mixtures. Experiments were performed on xenon gas as the primary scatterer at a scattering angle \( \Theta = 10.6^\circ \). Xenon was chosen because it has the largest scattering cross section of any readily available monatomic gas and the small scattering angle was chosen for three reasons:

1.) As the scattering angle nears the forward (\( \Theta = 0^\circ \)) or backward (\( \Theta \approx 180^\circ \)) direction, the illuminated volume from which one can collect scattered light into a spectrometer increases, enhancing the resulting signal to noise ratio; 2.) The frequency spectrum of the scattered light is relatively narrow in the forward direction (\( \sim 100 \text{MHz} \) wide for xenon) enabling one to use a spherical Fabry-Perot (FPS) interferometer to do frequency analysis. The instrumental transmission characteristics of an FPS are much more stable than those of a flat Fabry-Perot, obviating the need for frequent measurement of the instrumental profile. In addition, the spherical Fabry-Perot interferometer, suitable for use in the forward direction (free spectral range \( \sim 600 \text{MHz} \)) has about ten times the light collection ability of the flat Fabry-Perot interferometer required in the backward direction (free spectral range \( \sim 6 \text{GHz} \)).

These advantages are somewhat offset by the requirements placed by the narrower spectrum on the spectral width and frequency stability of the light source, but these problems have been solved. 3.) For xenon gas and \( \Theta = 10.6^\circ \) the kinetic-hydrodynamic transition occurs over the pressure range 10 mmHg (\( y \sim 0.1 \)) to 500 mmHg (\( y \sim 5.4 \)). For these pressures the imperfect gas corrections to the spectra are small and the Boltzmann

*This fact cancels the gain of a factor of 10 in scattered power obtained by going to the backward direction. One obtains this factor because the total scattered intensity is proportional to the pressure and in the backward direction the kinetic-hydrodynamic transition occurs at pressures 10 times greater than at \( \Theta = 10.6^\circ \).
equation applicable to the study of density fluctuations.

A block diagram of the experimental apparatus is shown in fig. (4.1). The light source is a He-Ne laser producing 10-15 mw of optical power in a single TEM\textsubscript{00} mode. Light from the laser is spatially filtered by a pinhole and focused into the scattering cell containing the gas under study. The incident beam passes out of the scattering cell through holes in the conical lens and mirror. A conical lens refracts light scattered at some particular angle into a parallel beam which is directed by a mirror to the spectrometer, a spherical Fabry-Perot interferometer that acts as a tunable optical filter. The transmission frequencies of the FPS are swept across the scattered light spectrum either by piezoelectric or density scanning, and the transmitted light detected by an ITT FW 130 photomultiplier (PMT) and photon counting electronics. The resulting record is the spectrum of the scattered light convolved with the profile of a single transmission peak of the FPS, repeated periodically along the chart as adjacent FPS resonances pass through the scattered light spectrum. The repetition period on the chart serves to calibrate its frequency axis, the period length corresponding to a frequency interval equal to the free spectral range of the FPS.

Errors in the measured spectra arise primarily from shot noise which will be discussed in sec. (IV E), and frequency drifts. Suppose that the incident optical frequency drifts in an unknown way an amount Δf relative to the measuring FPS resonance during the time necessary to sweep through an FPS free spectral range \( f_r \). This drift will result in a non-uniform spacing of the adjacent spectra on the chart and thus produce an ambiguity in determining the frequency dispersion (frequency vs. distance on the chart). If a free spectral range is swept out in a time \( \Delta T \), then the ratio of drift rate \( f_d = \Delta f / \Delta T \) to sweep rate \( f_s = f_r / \Delta T \) limits the accuracy of the spectra, the fractional error in dispersion being just the ratio \( f_d / f_s \):

\[
\text{Fractional Error in Frequency Calibration} \sim f_d / f_s.
\]
Figure 4.1: Experimental apparatus.
It is desirable to reduce the effects of error due to drift to a level below that arising from shot noise, thus effectively eliminating them. For these experiments the typical r.m.s. error due to shot noise in the determination of a given point of a spectrum is 1%. An FPS of free spectral 577 MHz had to be swept at a rate of one free spectral range per hour ($f_s \sim 600$ MHz/hr.) to obtain this signal to noise, requiring drift rates of less than 6 MHz/hr. to attain better than a 1% determination of the frequency axis. Relative drift rates of less than 3 MHz/hr. were attained by stabilization of the frequencies both of the light source and FPS resonances.

We now proceed to discuss various parts of the experimental apparatus in greater detail.

B. The Light Source

1. Introduction

The light source used for these experiments was a He-Ne gas laser producing $\sim 15$ mw of optical power in a single longitudinal cavity mode. It employs a single moding scheme proposed by A.G. Fox and first used by P.W. Smith (Fox-Smith scheme)\(^{(1)}\). Before the Fox-Smith method single mode operation of He-Ne lasers was obtained by making the laser resonator very short ($L \sim 15$ cm), thereby increasing the spacing $\delta f$ in frequency between allowed modes of oscillation ($\delta f = c/2L$) so that at a given time only one mode could be in a frequency regime where the gain was sufficient to sustain oscillation. This type of laser was used to good advantage in this laboratory in previous studies of the scattered spectrum from liquids\(^{(2)}\) and gases.\(^{(3)}\) However, since the optical gain of the discharge tube decreases with decreasing length, the short cavity He-Ne lasers are limited to relatively low output power, producing at most $\sim 2$ mw. Fox, and subsequently many others\(^{(4)}\), have devised methods whereby a long laser cavity may be made to operate in a single mode. These methods also involve discrimination against unwanted frequencies by enhancing cavity losses at all but one mode, but do not suffer from the power limitation of the short cavity. We shall now proceed to describe the Fox-Smith scheme and to present details of the particular laser used.
for the experiment.

2. Fox-Smith Scheme

Fox proposed that one of the mirrors of the laser cavity be replaced by a three mirror multiple pass interferometer (Fox-Smith interferometer) shown in fig. (4.2), that acts as a frequency dependent reflector. The power reflectivity as a function of frequency for such an arrangement has been calculated and may be shown to be closely related to that of a Fabry-Perot interferometer (FPI). In fact, the power reflectivity $R_{FSI}$ of the Fox-Smith interferometer (FSI) has the same functional dependence on frequency as the power transmissivity $T_{FPI}$ of a FPI, as shown in figure (4.3). Here $\rho_3 = \rho_4 = 1$, since in practice these mirrors are chosen to be maximum attainable reflectivity ($\rho_3, \rho_4 \approx 0.999$). The FSI is an ideal mode selector since its reflectivity, $R$, peaks close to 1 at its resonant frequencies ($R_{\text{max}}$ is not exactly 1 if losses at the mirrors are taken into account) and can be made to fall rapidly as the frequency is changed. Single mode operation of the laser is attained by placing the resonant frequency of some mode of the system at a reflectivity peak of the FSI as indicated in fig. (4.4). This mode will oscillate most strongly since cavity losses are minimum at the reflectivity peak. The spacing $\Delta f_{23}$ between reflectivity peaks must be made large enough so that only one such peak lies in the frequency interval where the active medium of the cavity has gain. Oscillation will then be confined to frequencies near this single reflectivity peak. To assure that only one mode near this peak will oscillate cavity parameters must be chosen in such a way that the reflectivity at frequencies of modes adjacent to the one at the reflectivity peak will be too low to permit the oscillation of these modes. The relevant parameters are $\Delta f_{23}$, the spacing between reflectivity peaks

$$\Delta f_{23} = \frac{c}{2(L_2 + L_3)} \quad ,$$

(4.1)
Figure 4.2: Laser cavity arrangement for employment of the Fox-Smith scheme.
Figure 4.3: Comparison of the ratios of transmitted power and reflected power to incident power for the FPI and FSI.
\[ \delta f_H, \text{ the halfwidth at half reflectivity of a reflectivity peak,} \]
\[ \delta f_H = \frac{\Delta f_{23}}{\pi} \sin^{-1} \left\{ \frac{1 - \rho_2^2}{2\rho_2} \right\}, \tag{4.2} \]

and the spacing, \( \Delta f_r \), between adjacent resonant frequencies of the system. In the case where the \( M_1 - M_2 \) cavity is long compared to the FSI (in fig. (4.2): \( L_1 + L_2 \gg L_2 + L_3 \)), \( \Delta f_r \) is given by

\[ \Delta f_r \approx \Delta f_{12} = \frac{c}{2(L_1 + L_2)}. \tag{4.3} \]

The spacing \( \Delta f_{23} \) between reflectivity peaks must be chosen large enough so that only one reflectivity peak fits under the gain curve but small enough so that the reflectivity peak width \( \delta f_H \) is sufficiently narrow compared to the resonant mode spacing \( \Delta f_r \) to allow effective discrimination at moderate values of \( \rho_2 \). It is desirable to keep \( \rho_2 \) as small as possible since, due to losses at the mirrors, the maximum reflectivity of the FSI decreases with increasing \( \rho_2 \). Figure (4.4) shows the gain profile, FSI reflectivity, and resonant frequencies of the laser used in these experiments, for which \( \Delta f_{12} = 120\text{MHz} \), \( \Delta f_{23} = 1000\text{MHz} \), and \( \rho_2 = 0.6 \).

Smith\(^{(5)}\) has shown that the use of the FSI leads to a particularly simple frequency and amplitude stabilization scheme. Referring to figs. (4.2 & 5) let us consider variation of the power outputs \( P_1 \) and \( P_2 \) with \( L_1 \). As \( L_1 \) is changed the resonant frequencies of the overall cavity formed by \( M_1, M_2, M_3 \) and \( M_4 \) change according to

\[ \Delta f = -\frac{c}{\lambda} \left( \frac{\Delta L_1}{L_1 + L_2} \right). \tag{4.4} \]

where \( \Delta f \) is the frequency shift of a given resonance. Thus for a \( \lambda/2 \) change of \( L_1 \), resonant frequencies are shifted through their spacing. As \( L_1 \) is changed and resonant frequencies pass through the reflectivity peak, their strength of oscillation will take the form shown in fig. (4.5a).
Figure 4.4: Gain profile, FSI reflectivity, and resonant frequencies for the He-Ne laser used in these experiments.
Cavity power $P_c$ vs. $L_1$ has been plotted. Suppose that for $L_1 = L_0$ some mode is centered on the reflectivity peak so that cavity power is maximized. As $L_1$ is increased the mode moves away from the peak, reducing cavity power until, as shown in fig. (4.5c), $T_{FSI}$ (the transmission of the FSI) has increased to $T'$, the largest FSI transmission for which oscillation can be sustained, at which point oscillation ceases. As $L_1$ increases further another mode approaches the reflectivity peak and oscillation resumes, $P_c$ peaking at $L_1 = L_0 + \lambda/2$, at which point this next mode is at the reflectivity peak. The output powers $P_1$ and $P_2$ may be obtained from $P_c$ from the equations:

$$P_1 = (1 - \rho_1^2)P_c$$  \hspace{1cm} (4.5)

$$P_2 = T_{FSI}P_c = (1 - R_{FSI})P_c$$  \hspace{1cm} (4.6)

where $T_{FSI}$ given in fig. (4.5c). Note that whereas $P_1$ is simply proportional to $P_c$, $P_2$ contains $T_{FSI}$ which is minimum at the reflectivity peak as shown in fig. (4.5c). An idea of the relative magnitudes of $P_c$, $P_1$ and $P_2$ can be obtained from the peak values of each of these quantities for the laser used in the present experimental work:

$P_c^{max} \approx 700$ mw; $P_1^{max} \approx 7$ mw; $P_2^{max} \approx 15$ mw. The solid curve of fig. (4.5d) is that expected if $T_{FSI}$ has a minimum of zero. In actuality because of losses at the mirrors, $T_{FSI} \approx 1\%$ at its minimum so that $P_2$ does not fall to zero at this point but takes the dotted curve of fig. (4.5(d)).

These considerations lead to the following method for stabilizing the laser. The power $P_2$ is taken to be the working output and the laser is operated near point $L'(fig. \ 4.5 \ (b))$ where $P_2$ is maximum. Since $P_1$ changes rapidly with length around $L'$, $P_1$ can be servoed to some constant value $P_1'$, shown in fig. (4.5b), by sensing $P_1 - P_1'$. Such a loop will lock the frequency of the laser relative to the position of the reflectivity peak which depends on $L_2 + L_3$. The overall frequency stability then will depend on: (i) The optical path length $L_2 + L_3$; (ii) Changes in mirror alignment and discharge tube excitation current that affect the functional dependence of $P_1$ on $L_1$. 
Figure 4.5: Optical power at various locations vs. $L_1$. Spacing between adjacent peaks is $\Delta f_{12}$ in frequency and $\lambda/2$ in $L_1$. 
It may be noted finally that to obtain an error signal with this scheme it is not necessary to modulate the laser cavity length, eliminating the effective broadening of the laser line width that such modulation produces.

3. The Laser

A diagram of the He-Ne laser used in these experiments is shown in fig. (4.6). A Spectra-Physics type 116 discharge tube was used, primarily because of its high gain (15% single pass). The tube dimensions (length = 112cm, bore diameter = 2.75mm) were the starting parameters in determining the cavity dimensions. The space between $M_1$ and the end of the discharge tube was enclosed and filled with methane gas to suppress the strong lasing transition at $3.39\mu$. The FSI was mounted in an invar block with the beam splitter $M_2$ inserted at the Brewster's angle to minimize reflection from its back face. Angular adjustments were provided for $M_1$ and $M_4$ which were mounted on piezoelectric PZT cylinders. Cavity dimensions $L_1 + L_2$ and the radii of curvature $R_1$ and $R_3$ of mirrors $M_1$ and $M_3$ were chosen to optimize the coupling of the $M_1 - M_3$ cavity to the active medium, with the constraint that $M_3$ be flat. This latter constraint was imposed to facilitate the choice of the radius of curvature of mirror $M_4$ which should match the wavefront radius of curvature in the $M_1 - M_3$ cavity at a distance $L_2 + L_3$ from $M_3$ (the effective position of $M_4$). The chosen $M_1 - M_3$ cavity configuration was confocal, since this geometry provides a nearly uniform mode diameter, with a mean mode diameter of $1/\sqrt{5}$ times the bore diameter, the recommended ratio for optimum coupling. The FSI cavity length, $L_2 + L_3$, was chosen to make the spacing between FSI reflectivity peaks, $\Delta f_{23}$, large enough to assure that only one reflectivity peak could fit under the gain curve at a time as fig. (4.4) shows ($\Delta f_{23} = 1000\text{MHz}$). The radius $R$ was then set to $R_4 = 10\text{m}$, the effective wavefront radius at a distance $L_2 + L_3$ ($L_2 + L_3 = 15\text{cm}$) from $M_3$ in the $M_1 - M_3$ cavity. The final parameter, $\rho_2$, determines the width of the reflectivity peaks and is chosen so that the frequency interval over which the system will oscillate (where the FSI transmissivity is less than the gain of the active medium)
Figure 4.6: Diagram of laser and associated servo loops.
is smaller than the spacing $\Delta f_{12}$ of the resonant frequencies ($\Delta f_{12} = 120\text{MHz}$).

The final cavity parameters were:

\[
\begin{align*}
R_1 &= 2.5\text{m} \\
R_2 &= \infty \\
R_3 &= \infty \\
R_4 &= 10\text{m} \\
\rho_1^2 &= 0.998 \\
\rho_2^2 &= 0.6 \\
\rho_3^2 &= 0.998 \\
\rho_4^2 &= 0.998 \\
L_1 + L_2 &= 125\text{cm} \\
L_2 + L_3 &= 15\text{cm}
\end{align*}
\]

The components of the laser were mounted on a 3"x6"x8' piece of aluminum jig plate resting on a heavy wooden table. To isolate the laser from building vibrations the table was supported by three pads of horizontal inflated inner tubes, the resulting system having resonant frequencies of 2Hz and 1Hz for vertical and horizontal motion respectively. In spite of these steps, fluctuations in $L_1$ ($\sim 400\text{Å}$ peak to peak with frequencies in the range 0-30Hz) caused serious optical frequency fluctuations ($\sim 15\text{MHz}$ peak to peak) and amplitude fluctuations (20% peak to peak) of the laser output necessitating some sort of frequency stabilization. Long term thermal drifts in $L_1$ also contributed to the frequency drift of the unstabilized laser.

Three servo loops were employed to stabilize the frequency and amplitude of the laser output. They are as follows:

a) Fast loop--This is the servo loop described in section (2) which uses the variation of $P_1$ with $L_1$ to lock the laser frequency to the FSI and is
shown in fig. (4,6). In this loop the difference between a stable reference voltage and the output of silicon solar cell illuminated by $P_1$ is amplified by a broad band DC amplifier filtered, and applied to the PZT element on mirror $M_1$. The resulting change of $L_1$ is of such polarity that it will reduce the initial voltage difference. This loop has a closed loop gain of 20 at d.c. and reduces fluctuations in $P_1$ to ~1% of its average value. At $f_c$, the mechanical resonance frequency of the PZTA-M$_1$ system, the phase of the displacement of $M_1$, relative to the phase of an oscillatory voltage applied to PZTA, changes by $\pi$ radians. This will cause the servo loop to be unstable unless the loop gain is reduced below 1 near $f_c$. The RC filter in the feedback path served to roll off the closed loop gain, the time constant $R'C'$ being adjusted for stable operation of the loop. The time constant $R'C'$ was typically ~0.015 sec. An estimate of the short term frequency excursion produced by a 1% residual fluctuation in $P_1$ may be obtained from fig. (4.5(b)) if we take the slope $dP_1(L_1)/dL_1$ at the operating point to be $P(X/4)$. Then

$$\Delta f = \frac{df}{dL_1} \cdot \frac{dL_1}{dp_1} \delta p_1 = \frac{120 \text{MHZ}}{\lambda/2} \cdot \frac{\lambda/4}{p_1} \delta p_1 = 60 \text{MHZ} \cdot \frac{\delta p_1}{p_1},$$

(4.7)

$$\Delta f \sim 600 \text{KHz}.$$ (4.8)

The observed short term peak excursion was ~800KHz in good agreement with this estimate.*

b) Thermal Loop--Because it employs a piezoelectric crystal to vary $L_1$ the fast loop is rather limited in the total correction of $L_1$ that it can apply (~9000Å). The net change due to thermal expansion in the aluminum support exceeded this range in a few minutes. The thermal loop, shown in fig. (4.6), senses the slow drift in $L_1$ and corrects for it by regulating the average support temperature.

*Sec (IV B 4)
It operates as follows. A heater is wrapped around the aluminum support and maintains it at all times about 10°C above room temperature. During operation the heater current is slightly increased so that the support can be made either to expand or contract by switching the heater current on or off. The heater current is switched by a level crossing detector which senses the voltage \( V \) applied to mirror \( M_1 \). The polarity is adjusted in such a way that the state of the heater current will make \( V \) always return toward \( V_0 \), the switching point of the level crossing detector. If, for example, the support is expanding, \( V \) will cut off heater power as it crosses \( V_0 \) and vice versa. The fast loop then always operates around \( V_0 \) which is in the middle of its dynamic range.

c) Reference Loop--With the fast and thermal servos in operation the frequency stability of the laser depends primarily on the position of FSI resonance. This resonant frequency, due to thermal expansion of the invar FSI mount, changes with temperature at a rate of 750MHz/°C so to attain 2MHz/hr. stability its temperature must be regulated to \( \sim 0.002 ^\circ \text{C}/\text{hr} \), a difficult task because of the proximity of the FSI to the hot discharge tube. Instead, a temperature stabilized FPS interferometer* serves as a frequency standard and the laser frequency was locked to its transmission peak by a standard technique (9), described below. Laser quality mirrors (spherical and matched to \( \lambda/20 \)), coated to 99.5% reflectivity, were used for the reference FPS and the leakage from \( M_3 \) was focused at its midpoint so that this beam diameter at the FPS mirrors was only 1 mm. Over this diameter the surface figure in considerably better than \( \lambda/20 \). The reference FPS has a free spectral range of 500MHz (cavity length = 15cm), a measured finesse of 150 for a line width of 8.3MHz, and peak transmission of the incident beam of 10%. The mirrors are mounted in invar holders connected to the ends of a low expansion CERVIT(10) tube, and one of the mirrors is on a PZT cylinder. The FPS is supported on plexiglass rings in an evacuated brass can which is wrapped with tubing through which temperature controlled water flows.

The power in the beam transmitted by \( M_3 \) (\( \sim 400 \mu \text{w} \)) was sufficient to operate the reference loop and was passed through an optical isolator, made up of a \( \lambda/4 \) retardation plate and a polaroid filter, to

*Sec (IV D)
prevent light reflected by the FPS from interfering with the operation of the laser. The light was then focused at the center of the FPS and detected by solar cell B. The length of the FPS cavity was modulated at 400Hz by applying the voltage of a reference oscillator to the element PZT C. The phase of the resulting amplitude modulation of the transmitted light changes its sign relative to that of the reference oscillator when the laser frequency crosses the transmission peak of the FPS. A phase sensitive detector can provide a d.c. voltage proportional to the phase difference between the a.c. reference signal and the amplitude modulation, thus proportional to the frequency excursion of the laser from the FPS transmission peak. Its output, applied to the PZT element on M₄ with the proper polarity, changes L₂ + L₃ in such a way that it always returns the laser frequency to the transmission peak. The phase sensitive detector was a PAR, model JB-4, lock-in amplifier which also provided the 400Hz a.c. reference voltage.

As shown in figs. (4.6) and (4.7a), included in the feedback path of the reference loop is a low pass filter and an augmenting integrator amplifier. (11) The low pass filter is required to remove a.c. components from the lock-in output since these will oscillate M₄ and produce frequency modulation of the laser output. The time constant RC was 0.1 sec.

Without the augmenting integrator the reference loop is simply proportional, so that if initially the adjustable d.c. voltage on PZT B is set so that the laser frequency is centered on the FPS reference, at a later time the deviation of the laser frequency from the FPS resonance is simply the net frequency drift without feedback, divided by the d.c. loop gain. Thus to keep the servo operating with the laser frequency centered on the FPS resonance it is necessary to continually adjust the d.c. source in series with PZT B. This problem can be circumvented by introducing the augmenting integrator (AI) into the feedback path. Its effect can be understood in the frequency domain by considering the diagram of the reference loop in fig. (4.7a,b). The ratio of the unservoed frequency drift x(s) to the servoed frequency drift y(s) is the closed loop
Figure 4.7: 

a) Representation of the reference loop.
b) Transfer functions for reference loop feedback path in the frequency domain.
c) Magnitude of the closed loop gain.
gain $G(s)$ and is given by \(^{(12)}\)

\[
G(s) = \frac{\nu(s)}{\gamma(s)} = \frac{1}{1 + \frac{1}{1 + H(s)}} = \frac{1}{1 + H_1 H_2 H_3}
\]

(4.9)

where $H_1, H_2$ and $H_3$ are found in fig. (4.7b). Here $H_1$ is the transfer function for the AI, $H_2$ the transfer function for the low pass filter and $H_3 = \Lambda$ lumps all other constants of proportionality of the loop. One finds

\[
G(s) = \frac{\Lambda A'(\frac{R_2}{R_1} + s R_1 C_1) + (1 + s RC)(1 + s A' R_1 C_1)}{(1 + s RC)(1 + s A' R_1 C_1)}
\]

(4.10)

Fig. (4.7c) is a Bode plot of the magnitude of the closed loop gain $G(s)$ for the feedback path with and without the AI. As can be seen the AI increases $G(s)$ at frequencies below $f_0 = 1/2\pi R_1 C_1$ (typically $R_1 C_1 = 1$ sec.), enhancing the d.c. gain by a factor of $\Lambda$. For the operational amplifier used here (Philbrick K2-W) we have $\Lambda = 10^5$ so that the circuit provides an essentially infinite d.c. closed loop gain, reducing the lock-in output voltage necessary to cancel long term drift. \(^{(13)}\) The voltage required to cancel long term drift is stored across capacitor $C_1$ by the integrator. The laser frequency then fluctuates about the center of the FPS resonance and the lock-in output fluctuates about zero volts for any amount of accumulated drift, up to a maximum determined by the dynamic range of the operational amplifier in the AI,

We conclude our remarks about the servos by mentioning that the thermal loop functions relative to the fast loop in the same fashion as the AI functions relative to the reference loop, in that it controls the length of the aluminum beam in such a way as to allow the fast loop to operate in the middle of its dynamic range.

4. Laser Power and Frequency Stability

We complete the discussion of the laser with a few words about its amplitude and frequency stability. Frequency instabilities fall into two categories: short term fluctuation and long-term drifts. The short term fluctuations about the reference FPS transmission peak could be observed by displaying on an oscilloscope the voltage of the solar cell detec-
Figure 4.8: Laser power vs. time for a typical run.
tor B and observing the fluctuations in adjacent periods of the 800 Hz second harmonic of the FPS modulation frequency. Peak to peak excursions about the transmission peak were ~ 800 KHz in agreement with the estimate of eq. (4.8). Long term drifts of interest are those of the reference FPS resonant frequencies relative to those of the measuring FPS and are discussed in sec (IV D2).

The amplitude stability was limited only by the stability of mirror orientations. Output power constant to within 10% over a period of 6 hours was usually attained. A typical power vs. time plot is shown in fig. (4.8).

C. Optical Arrangement

1. Cell Geometry and Stray Light

In this section we discuss the scattering cell geometry and measures taken to reduce stray light. The elimination of stray light becomes a prime experimental consideration in the measurement of the spectra of dilute gases, because of their very small scattering cross section.

Referring to fig. (4.1) before entering the scattering cell, the incident laser beam is spatially filtered by a pinhole to remove the irregular halo about the beam from the laser caused by scatter at the laser cavity mirrors and reflections from the discharge tube bore. The spatial filter consisted of a focusing lens (focal length=2cm), a 50μm pinhole, and a collimating lens (focal length =2.8 cm), arranged as in fig. (4.1) with the pinhole in the superimposed focal planes of the two lenses. The pinhole is chosen to be slightly larger in diameter than the diffraction limited primary beam diameter at the focal plane. Thus the pinhole stops all light which is not focused to the diffraction limit, and the filter output is a diffraction limited beam. The diffraction limited beam diameter (1/e diameter of the Gaussian distribution) was calculated to be 32μ at the point of focus(14) and a pinhole of diameter 50μ was employed. A larger minimum beam diameter resulted in considerable diffraction by the pinhole. Generally about 10% of the incident power was rejected by the spatial filter.
Figure 4.9: Detailed scattering geometry employed for these experiments.
The scattering cell and collecting lens are shown in fig. (4.9). The left and right ends of the cell are formed by the focusing lens and the conical collecting lens respectively. A conical collection lens was used because of its superior light collection ability when the scattering angle is to be well defined, as is the case here ($\Delta\theta/\theta \sim 10^{-2}$). The laser beam is focused to a thin line along the axis of the cell in the scattering chamber. Referring to fig. (4.9) all of the light scattered from the cross hatched part of the incident beam in a small range of angles $\Delta\theta$ about the scattering angle $\theta$ is collected by the conical lens into quasi-parallel light with an angular spread of $\Delta\theta$. The collecting lens and the apertures of the spectrometer determine the distribution of scattering angles contributing to the measured spectra. Stray light scattered by the cell walls in the region noted so:******, will also enter the spectrometer. To reduce the amount of stray light in the scattering chamber the following steps were taken: (i) An axial hole was made in the conical lens into which a tube terminated by a Brewster angle window was epoxied. This enabled the incident beam to exit the cell without reflection back into the scattering chamber. (ii) Referring to fig. (4.10), light scattered from the final lens of the spatial filter and the focusing lens was prevented from entering the scattering chamber by stops A and B, which also served as references for coaxial alignment of the incident beam and the cell axis. Although it cannot enter the spectrometer directly since it does not appear to come from the cross hatched portion of the incident beam, the light scattered from the focusing lens and final spatial filter lens can rescatter from various surfaces of the collection optics into rays which will be collected by the spectrometer. As shown in fig. (4.10), stop B was chosen small enough so that this stray light, scattered from the incident beam by the focusing lens, was prevented from entering the conical lens, but large enough to prevent a serious diffraction of the incident beam. The effectiveness of these measures could be roughly checked by setting up the scattering cell but replacing the conical lens by a white sheet of paper with a small hole for the beam to pass through. With the room darkened this procedure displays clearly the effects of scattering and diffraction of the incident beam. The incident beam was found to be 0.5mm. in diameter and was surrounded by a faint halo roughly 2mm. in diameter. The beam and halo passed entirely into the exit tube which
Figure 4.10: Geometric shadow effect of stops A and B.
had an i.d. of 3 mm. No illumination of the paper was visible outside of this diameter. Typical dimensions were: beam diameter at stop A = 2 mm.; stop A diameter = 3 mm.; beam diameter at stop B = 0.5 mm.; stop B diameter = 1 mm. Stops C, D, and E prevent light diffracted through small angles by stop B from entering the spectrometer. All cell surfaces were flat black anodized.

With these steps, stray light was reduced to a point where it did not significantly contribute to experimental error for the experiments reported here. The contribution of stray light to the observed spectra under various conditions is shown in figs. (5, 1, 4 and 5). Quantitatively the contribution of the stray light to the total observed intensity was typically 0.05% of the contribution of Xe at STP.

We believe that the residual stray light collected by the spectrometer was due primarily to the rather poor condition of the conical lens surface enhancing the probability of the scattering of stray light into collected rays. Considerable reduction of the stray light contribution from the level observed here should be possible with the employment of micro-polished finishes on the spatial filter collimating lens, the primary focusing lens, the conical lens, and the collecting lens. A lower stray light level would be desirable in the study of gases with cross sections smaller than that of xenon.

2. The Experimentally Measured Spectrum

The measured spectrum, as determined by the optical power transmitted by the measuring interferometer, is not simply the desired density fluctuation spectrum $S_{\rho}(K, \omega)$ but rather $S_{\rho}(K, \omega)$ modified by three experimental conditions: a) the finite extent of the illuminated region; b) the finite acceptance solid angle of the measuring interferometer; and c) the finite width of the instrumental profile of the measuring interferometer. We shall now discuss these conditions and their effects on the measurement of $S_{\rho}(K, \omega)$.

The effect of the finite extent of the illuminated region was dis-
cussed in sec. (II B4) where it was shown in eq. (2.109) that the scattered light spectrum $S_E(\vec{k}, \omega)$ is a convolution of the density fluctuation spectrum $S_p(\vec{k}, \omega)$ and a normalized $\vec{k}$ space distribution, $\mathcal{B}(\Delta \vec{k})$, of incident wave vectors about $\vec{k}_0$. For our experiments the illuminated region is a pencil beam with a constant Gaussian intensity distribution given by $I(r) \propto \exp \left\{ - (r/a)^2 \right\}$ where $r$ measures radial distance from the beam axis, which we choose to be the z axis. The vector $\vec{k}_0$ then lies along the z axis. The distribution $\mathcal{B}(\Delta \vec{k})$, in this case, from eq. (2.105), is well approximated by

$$\mathcal{B}(\Delta \vec{k}) \propto \exp \left\{ - \frac{(\Delta k_a)^2}{2} \right\} \delta(\Delta k_z)$$

(4.12)

where $\Delta k$ measures radial distance in the $\Delta k_x \Delta k_y$ plane. This apparent distribution of incident $\vec{k}$ vectors about $\vec{k}_0$ is indicated in fig. (4.11a). The corresponding spread of scattering angles $Q(\Delta \Theta)$ about $\Theta_0$ is given by

$$Q(\Delta \Theta) = k_0 B(k_0 \Delta \Theta) \propto \exp \left\{ - \frac{(k_0 \Delta \Theta)^2}{2} \right\}$$

(4.13)

where, referring to fig. (4.11a), we have used $\Delta \Theta = \Delta k / k_0$. For our optics, $a \sim 0.02 \text{cm}$ and $k_0 \sim 10^5 \text{cm}^{-1}$ so that the distribution $Q(\Delta \Theta)$ falls to $1/e$ of its peak value at $\Delta \Theta = 10^{-3} \text{ rad}$.

In addition to this smearing, because the spectrometer requires finite scattered power, it must collect light from over a range of scattered directions and thus from a range of scattering angles. The range of scattering angles collected is expressable in terms of a probability distribution $P(\Theta)$, $P(\Theta) d \Theta$ being the fraction of the total power collected by the spectrometer, scattered from $\vec{k}_0$ through angles in the range $(\Theta, \Theta + d \Theta)$. The distribution $P(\Theta)$ is determined by the collection optics diagrammed in fig. (4.11b)). The spectrometer, a spherical Fabry-Perot interferometer, is represented by two circular apertures of diameter $d$, spaced by $R$. One focal point of the collecting lens is at the conical
Figure 4.11:  
a) Effective distribution of incident wave vectors.  
b) Collection geometry.  
c) \( P(\Theta) \) for our experimental configuration.  
d) The collection probability distribution \( P(\Theta) \), and the distribution of incident angles \( Q(\Theta) \).
lens and the other at the center of the FPS. Since scattered light arises only from the axis of the conical lens, all scattered light rays lie in planes containing this axis so that the collection problem is two rather than three dimensional. Radii \( r_1 \) and \( r_2 \) are the minimum and maximum usable radii of the conical lens. All light transmitted by the FPS is focused to the active PMT photosurface. We have plotted in fig. (4.11c) the distribution \( P(\Theta) \) determined by the collection optics and show in fig. (4.11d) this distribution for the experimental parameters employed here: \( d = 0.5 \) cm, \( R = 13 \) cm, \( f = 60 \) cm, \( r_1 = 0.5 \) cm and \( r_2 = 1.5 \) cm. Fig. (4.11d) also shows the distribution \( Q(\Theta) \) of incident angles.

The spectrum \( S_i(\omega) \) measured by the interferometer with the simultaneous smearing of scattering angle due to \( P(\Theta) \) and \( Q(\Theta) \) will be given by

\[
S_i(\omega) = \{Q(\Theta) \otimes P(\Theta)\} \otimes S_E(k(\Theta), \omega),
\]

where \( \otimes \) denotes convolution.

The interferometer convolves this spectrum with its instrumental profile \( I(\omega) \) so that the final experimental spectrum \( S_e(\omega) \) is given by

\[
S_e(\omega) = I(\omega) \otimes S_i(\omega).
\]

The convolution \( Q(\Theta) \otimes P(\Theta) \) has been performed numerically for our experimental parameters and contains 90% of its area within \( \Theta < 0.004 \) rad so that \( \Theta \) is spread over a range \( \Delta \Theta \approx 0.008 \) rad.

The most serious effect of the smearing of \( \Theta \) is the smearing in the hydrodynamic regime of the Brillouin splitting \( \omega_0 = k_c \Theta \approx k_o c_o \Theta \), which produces a false broadening of the Brillouin components. At
the Brillouin lines are smeared over a frequency range

\[ \Delta \omega_0 = k_0 c_0 \Delta \theta = k_0 / k \left( k c_0 \right) \Delta \theta \approx 5 \omega_0 \Delta \theta \approx 0.04 \omega_0. \]

For xenon at 10.6°, \( \omega_0 \approx 60 \text{ MHz} \) so that \( \Delta \omega_0 \approx 2.4 \text{ MHz} \). The experimentally measured Brillouin line in the hydrodynamic regime is the convolution of \( I(\omega) \), the instrumental profile of the FPS, with the Lorentzian Brillouin line of the scattered light spectrum of width given by eq. (2.40). The FWHH of the Brillouin lines in the scattered light spectrum decreases with increasing pressure, having a minimum value of 6MHz at the highest xenon pressure studied, (500mmHg). The instrumental profile has a FWHH of 24MHz so that the FWHH of the experimentally observed Brillouin lines is at least 30MHz. Such a line is broad enough so that when the distribution in \( \omega_0 \) is convolved with it the resulting distortion is negligible. The smearing of \( \mathbb{R} \) due to the finite size of the illuminated region and finite range of collected scattering angles, then, need not be considered in the analysis of the data.

D. The Spherical Fabry-Perot (FPS) Interferometers

1. Operation of the FPS

The frequency distribution of the scattered light was analyzed in these experiments using a spherical Fabry-Perot interferometer as a tunable optical filter. The FPS is an optical resonant cavity formed by two high quality spherical mirrors, confocally arranged, as shown in fig. (4.12). For the confocal arrangement any incident ray which intersects the mirrors near the cavity axis retraces its initial path after every four passes between the mirrors, producing multiple interference in the transmitted light. For rays which pass through the mirrors near the cavity axis, the optical path length \( P \) over four passes is simply \( P = 4nR \) where \( R \) is the mirror radius (and separation) and \( n \) is the index of refraction of the medium between the mirrors. The resonant frequencies of the cavity are those for which there is perfect constructive interference of the exiting light, and therefore maximum transmitted intensity. This occurs for wavelengths \( \lambda_N \) given by

\[ \theta = 10.6° \]
Figure 4.12: Spherical Fabry-Perot geometry.
\[ \lambda_N = \frac{4nR}{N} \quad , \quad N = 1, 2, \ldots \] (4. 16)

and the corresponding resonant frequencies \( f_N \) are:

\[ f_N = \frac{cN}{4nR}. \] (4. 17)

The ratio \( T(f) \) of transmitted optical power to incident optical power as a function of frequency for the FPS is always of the form

\[ T'(f) = \sum_N L(f - f_N) \] (4. 18)

where, in practice, the function \( L(f) \) can be approximated by a Lorentzian centered at \( f = 0 \):

\[ L(f) = \frac{0.5}{1 + \left( \frac{f}{\Gamma/2} \right)^2} \] (4. 19)

with the full frequency width at half transmission, \( \Gamma \), being given by

\[ \Gamma = \frac{c}{4nR} \left( \frac{1 - R^2}{\pi R} \right) \] (4. 20)

where \( R \) is the power reflectivity of the mirror coatings. We have assumed here that the interferometer is being operated in a non "mode matched" configuration so that there is no interference between the two sets of exiting rays for a given incident ray. This leads to a peak transmissivity of 0.5 for the FPS as indicated in eq. (4. 19). Defining the free spectral range \( f_R \) as the spacing in frequency between adjacent resonances:

\[ f_R \equiv f_{N+1} - f_N = \frac{c}{4nR} \] (4. 21)
and the reflectivity finesse $F$

$$F \equiv \frac{\pi \mathcal{R}}{1 - \mathcal{R}^2}$$

eq. (4.20) may be written simply $\Gamma = f / F$. In practice one chooses $\mathcal{R} \cong 1$ so that $F >> 1$ and $\Gamma << f_r$, making the transmission frequency profile $T(f)$ of the FPS consist of a series of peaks, narrow in comparison to their spacing $f_R$.

The FPS is employed as an optical filter by sweeping its transmission peaks in frequency and measuring the transmitted optical power vs. frequency. With monochromatic incident light one would simply observe $T(f)$. If the incident light has a spectral power distribution $G(f)$, the transmitted optical power $P_t(f)$ will be proportional to

$$P_t(f) \propto G(f) \otimes T(f) = \sum_{N} G'(f - f_N)$$

(4.22)

where $G'(f) = G(f) \otimes L(f)$. The measured spectrum $P_t(f)$ then is the convolution of the instrumental profile $L(f)$ with the actual spectrum $G(f)$, repeated in frequency every $f_R$ Hz. It is generally desirable to have the distribution $G(f)$ narrow compared to $f_R$ so that the adjacent orders do not significantly overlap.

The transmission profile $L(f)$ in practice is determined not only by mirror reflectivity but also by mirror losses, mirror surface figure, spherical aberration, and mirror alignment.

Scatter and absorption losses upon reflection from high quality dielectric coatings generally amount to $\sim 0.03\%$ so that for a circuit of the FPS cavity there is $\sim 0.12\%$ loss ($\xi \sim 0.12\%$). This loss becomes important in determining the shape of $L(f)$ when $\xi$ becomes comparable to $1 - \mathcal{R}$, that is when absorption losses in the cavity are comparable to the coupling losses. This is generally the case only for extremely high reflectivities ($\mathcal{R} > 0.99$), but for the reflectivities employed here ($\mathcal{R} \sim 0.95$) absorption and scatter losses have a relatively small effect on $L(f)$, increasing the linewidth a few percent over the value given by eq. (4.20).
The Lorentzian form for $L(f)$ in eq. (4.19) is generally true with a single ray incident on the FPS. However, due to the last three of the above-mentioned effects (surface figure, aberration, and alignment), the path length for a circuit of the FPS cavity for a given ray, is not simply $4nR$ but depends on the precise orientation of the ray. This variation in path length makes the resonant frequencies $f_N$ in eq. (4.17) also depend on the ray in question. With a distribution of incident rays there is a distribution of resonant frequencies $f_N$ which smears out the Lorentzian $L(f - f_N)$ in eq. (4.18). If $P(f_N) df_N$ is the fraction of the incident power with resonant frequencies in the interval $(f_N, f_N + df_N)$ we may write for the observed profile $L_0(f - f_N)$

$$L_0(f - f_N) = L(f - f_N) \otimes P(f_N).$$

(4.23)

It is generally desirable to keep the distribution $P(f)$ narrow compared to $L(f)$.

In the case of perfectly aligned, perfectly matched and spherical mirrors, spherical aberration contributes to the ray orientation dependence of the deviation, $\Delta f$, of the resonant frequencies $f_N$ from $NC/4nR$. For rays passing through the mirrors within a radius, $a$, of the FPS axis the deviation $\Delta f$ is such that

$$\Delta f < f_N \left( \frac{a^4}{4R^4} \right).$$

(4.24)

To keep the spread $\Delta f$ small compared to the reflectivity width $\Gamma = f_R / F$, we find the condition

$$f_N \left( \frac{a^4}{4R^4} \right) < \frac{f_R}{F},$$

(4.25)
or

\[ a < a_o = R \left( \frac{\lambda}{RF} \right)^{1/4} \]  \hspace{1cm} (4.26)

Apertures of radius \( a \) can be chosen to ensure that this condition will be met, and these apertures will limit the light gathering ability of the interferometer.

The deviation of the mirror surfaces from being matched and spherical also contributes to \( \Delta f_N \) by producing a deviation, \( \Delta P \), in the path length \( P \approx 4nR \) for a circuit of the cavity that varies slowly with ray orientation. The resulting shift \( \Delta f_N \) in \( f_N \) will be

\[ \frac{\Delta f_N}{f_N} = \frac{\Delta P}{P} \]  \hspace{1cm} (4.27)

and the condition \( \Delta f_N \ll \Gamma \) leads to \( \Delta P \ll \lambda/nF \), implying that the width \( \delta P \) of the distribution of path lengths about \( 4nR \) should be small compared to \( \lambda/nF \). If a mirror deviates from being matched and spherical by a distance \( \Delta x \) over the area being used, the corresponding \( \Delta P \) will be \( \Delta P = 2\Delta x \) so that the width \( \delta x \) of the distribution in \( x \) is limited by \( \lambda/2nF \).

We may illustrate this limit by assuming a rectangular distribution of \( x \) of width \( \delta x = \gamma(\lambda/2nF) \), for which the resulting smearing of \( f_N \) increases the width of the instrumental profile by a factor of \( \sqrt{1 + \gamma^2} \). This gives a 30% increase in linewidth for a surface figure of \( \lambda/75 \) and reflectivity finesse of 30. Additional broadening of the distribution in \( P \) will arise from localized hills and valleys on the mirror surfaces which produce a path length variation which fluctuates randomly with ray orientation.

The great utility of the FPS arises primarily from the insensitivity of \( L(f) \) to the angular alignment of the mirrors. Angular misalignment of the mirrors of an FPS results only in a redefinition of the optical axis of the cavity. As a result the optical properties of the FPS are very stable so that once the FPS is assembled and aligned the instrumental profile will remain constant unless the instrument is given very rough handling.
The spherical Fabry-Perot interferometers used in this experiment were confocal resonators of spacing 10 cm. and 13 cm., having the following characteristics:

Table 4.1 Spherical Fabry-Perot Characteristics

<table>
<thead>
<tr>
<th>R (cm)</th>
<th>R</th>
<th>Free Spectral Range (MHz)</th>
<th>FWHH from R (MHz)</th>
<th>FWHH Observed (MHz)</th>
<th>Aperture Radius (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>9.962</td>
<td>95.8%</td>
<td>750.4</td>
<td>20</td>
<td>25.89</td>
<td>1.5</td>
</tr>
<tr>
<td>12.997</td>
<td>96.5%</td>
<td>576.5</td>
<td>12.8</td>
<td>24</td>
<td>2.5</td>
</tr>
</tbody>
</table>

(Mirrors are spherical to λ/75 and matched to λ/75 over a central radius of 2.5 mm) They are supplied by Optical Surfaces Ltd., Kenley, Surrey, U.K.

The mirror spacing is adjusted to be confocal by optimizing the finesse and peak transmission of the cavity. The free spectral range is then determined from eq. (4.21) and the mirror radii of curvature.

The values of FWHH of the instrumental profile calculated from the power reflectivity R and eq. (4.20) and those observed are indicated in Table 4.1. The aperture radius of the 750 MHz FPS was chosen so that \( a = 0.75a_0 \) so that from eq. (4.26) effects of spherical aberration should be small. The observed profile of the 750 MHz instrument was accurately Lorentzian with a FWHH about 6 MHz larger than that calculated from R. This excess width is attributable to mirror non-sphericity (4 MHz) and spherical aberration (2 MHz). The 577 MHz instrument had a FWHH of 12.8 MHz calculated from eq. (4.20) and an aperture radius of \( a = a_0 \). Assuming mirror non-sphericity of same order as observed for the the 750 MHz instrument, one would expect a FWHH of about 18 MHz. At \( a = a_0 \) the smearing of L(f) by spherical aberration causes an additional broadening of 30% of the reflectivity FWHH (12.8 MHz) bringing the expected width to 22 MHz, close to that which was observed. The instru-
mental profile of the 577 MHz instrument was observably non-Lorentzian, an effect due also to the smearing of $L(f)$ by spherical aberration.

The resonant frequencies of the FPS are swept by changing either the mirror spacing $L$, or the index of refraction of the intervening medium. The mirror spacing $L$ can be varied over a region of $\sim 10 \lambda$ about $L = R$ without observably influencing the shape of the transmission profile $L(f)$. The rate of change of the frequencies $f_N$ with spacing $L$ is given by

$$\frac{\Delta f_N}{\Delta L} = \frac{-f_N}{\lambda/4} \quad (4.28)$$

so that a free spectral range $f_R$ is swept through for a $\lambda/4$ change in mirror spacing. A linear sweep of $L$ may be conveniently obtained by mounting one of the mirrors on a piezoelectric element and applying a linearly increasing voltage.

Sweeping may also be accomplished by changing the density and thus the index of refraction, $n$, of the gas in the FPS cavity. Writing $n-1 = \alpha \rho$ where $\rho$ is the gas density and $\alpha$ a constant of proportionality we find

$$\frac{\Delta f_N}{\Delta \rho} = -\alpha f_N. \quad (4.29)$$

For a wavelength $\lambda = 6328 \AA$ we have $f_N \approx 4.75 \times 10^{15}$ Hz, and for air at STP we have $\alpha = 3 \times 10^{-4}$/ amagat so that for the conditions of this experiment

$$\frac{\Delta f_N}{\Delta \rho} = 14.25 \text{ GHz/amagat}. \quad (4.30)$$

Thus a free spectral range of 577 MHz is swept through with a density change of $\delta \rho = .00406$ am., or, at constant temperature, a pressure change of 3.08 mm Hg.
Figure 4.13: Spherical Fabry-Perot etalon
Temperature drifts in the various parts of the FPS and sweeping apparatus can cause unwanted drifts in the resonant frequencies of the FPS and, as described in sec. (IV A), ambiguity in determining the frequency calibration of the observed spectra. We now turn to discuss such drifts.

2. Frequency Scanning and Drifts

In use, the interferometer etalon, shown in fig. (4.13), is mounted in a sealed brass can which is wrapped with tubing through which temperature controlled water flows. Drifts in the resonant frequencies of the FPS arise from two sources: (i) Changes with temperature of the length of the invar etalon: For an uncompensated invar etalon the resonant frequencies of an FPS will drift with the temperature at a rate of $750 \text{ MHz/}^\circ\text{C}$. This rate can be reduced somewhat by introducing the proper compensating length of high expansion material (such as brass) into the cavity (see fig. (4.13)) to cancel the length change of the invar. Such compensation is effective only if all parts of the etalon remain in thermal equilibrium with each other as the temperature drifts. (ii) Changes with temperature of the gas density in the interferometer: This is a problem only if density scanning is employed. If the interferometer is piezoelectrically swept, its container can be made airtight and the density will be independent of temperature. For a density scanning system, however, the gas density in the interferometer can is a function of the temperature of all parts of the scanning system and it is not sufficient to temperature control only the interferometer container. 

In the model system shown in figure (4.14), $V_1$, the interferometer container is held at constant temperature and the temperature, $T_2$, of $V_2$, the scanning system, is changed. The coefficient $\Delta \rho_1 / \Delta T_2$ of gas density change in $V_1$ with $T_2$ may be obtained by requiring that the pressure be constant throughout the system and is

$$\frac{\Delta \rho_1}{\Delta T_2} = \frac{\rho}{T} \cdot \frac{V_2}{V_1 + V_2} ,$$  

(4.31)
where $\rho$ and $T$ are the average density and temperature. The corresponding rate of frequency drift will be

$$\frac{\Delta f}{\Delta T_2} = \frac{f_0}{T} (n-1) \frac{V_2}{V_1 + V_2}$$  \hspace{1cm} (4.32)$$

where $f_0$ is the average optical frequency, and $n$ the index of refraction of the gas at the density $\rho$. For $V_1 = V_2$, and air at 1 atm in the system one finds $\Delta f/\Delta T_2 = 250 \text{ MHz}/^\circ\text{C}$ so that $T_2$ must be held constant to
The density sweeper consisted of a piston driven at a constant rate into a cylinder connected by tubing to the interferometer container. The piston-cylinder assembly and brass interferometer container were wrapped with Tygon tubing through which temperature controlled water flowed, and further surrounded by styrofoam or fiberglass insulation. The tube connecting the sweeper and interferometer was also water jacketed and insulated. A Lauda K2-R regulator specified to hold water temperature at its output constant to $\sim0.01^\circ$C supplied the temperature controlled water to both the sweeper-interferometer and the FPS reference cavity for the laser. Although observed short term fluctuations in the water temperature were more like $\sim0.05^\circ$C, the thermal equilibration time constants for the various parts of the system were long enough so that long term drifts rates $\sim0.01^\circ$C/hr. were achieved. We shall return shortly to discuss the long term frequency stability of the system.

Both piezoelectric and density scanning were employed in this experiment. Piezoelectric sweeping is simple to set up and use, but the particular PZT element employed here had a rather nonlinear displacement vs. voltage curve producing $\sim5\%$ changes in spacing between adjacent spectra on the chart per free spectral range of sweep. This nonlinearity was repeatable, however, and could be accounted for in taking data from the chart.

Density scanning was achieved by connecting the interferometer container to a linearly changing volume. This method of sweeping is inherently nonlinear since $p \propto 1/V$ which limits its use to large spacing interferometers where only a small density change is required per free spectral range. This method of density sweeping is convenient because it is easy to change and reverse sweep speeds and is compact, an advantage when temperature control of the sweeping system is involved.

The effect of the $p \sim 1/V$ nonlinearity on the spacing of adjacent orders on a chart record may be understood by considering monochromatic light of frequency $f'$ incident on the FPS. Both the interferometer volume, $V$, and distance along the chart record, $s$, are swept linearly in time i.e.
s, V ‼ t so that s ≈ 1/ρ and thus

\[ s = \frac{\gamma}{\rho} \tag{4.33} \]

where \( \gamma \) is a constant of proportionality. Suppose that, at \( s_0 = \gamma/\rho_0 \), the density \( \rho_0 \) was such that a resonance frequency \( f_N \) of the FPS was equal to \( f' \), \( s_0 \) then being at the center of one of the transmission peaks on the chart. Suppose further that the density change per free spectral range (calculated from eq. (4.30)) is \( \delta \rho \) so that successive peaks on the chart occur at densities \( \rho_n = \rho_0 + n \delta \rho \) where \( n = 0 \pm 1, \pm 2 \ldots \). Then, using eq. (4.33) we have \( s_n = \gamma/\rho_n \) and

\[ s_n = \frac{\gamma}{\rho_0 + n\delta \rho} \tag{4.34} \]

For \( \rho_0 \approx 1 \) am we have \( \delta \rho \ll \rho_0 \) so that for small values of \( n(n<10) \) we may expand \( \rho_0 + n \delta \rho \) and delete higher order terms

\[ s_n \approx \frac{\gamma}{\rho_0} \left( 1 - \frac{n\delta \rho}{\rho_0} + \left( \frac{n\delta \rho}{\rho_0} \right)^2 \right) \tag{4.35} \]

The spacing between adjacent peaks \( \Delta s_n \) is given by

\[ \Delta s_n = s_n - s_{n+1} \]

and we find

\[ \Delta s_n = \frac{\gamma\delta \rho}{\rho_0} \left( 1 + \frac{2n\delta \rho}{\rho_0} \right) \tag{4.36} \]

Therefore, as long as \( n \) is such that \( n\rho/\rho_0 < 1 \), the spacing between adjacent spectra on the chart record increases linearly with the orders of the free spectral range. If we consider \( n \) in eq. (4.35) to be a continuous variable and interpret it to be the reduced frequency excursion of \( f_N(n = (f_N - f_N^0)/f_R) \), then eq. (4.35) continuously relates distance on the chart to transmission frequency.

Our experiments involving density scanning employed an FPS of free spectral range 577 MHz for which we found in sec. (1) that \( \delta \rho = .004 \) am.
Figure 4.15: Chart distance per free spectral range ($\Delta S_n$ vs. $n$) for a typical run. The nine free spectral ranges were swept out in 5 hours.
Assuming $p_0 = 1 \text{ in am}$, we have $2 \delta p / p_0 = 0.008 \ll 1$. In this case $\Delta s_n$ in eq. (4.36) is the frequency dispersion of the chart (chart distance per free spectral range) at a point on the chart halfway between peaks $n$ and $n + 1$. To obtain the dispersion at the peaks we may plot $\Delta s_n$ vs $n$ for the successive free spectral ranges on the trace and fit the plotted points with a smooth line. The chart dispersion at peak $n$ then will be the value of the fitted curve at a point halfway between points $n - 1$ and $n$, that is $n - 1/2$. Fig. (4.15) shows a plot of $\Delta s_n$ (distance per free spectral range) vs. $n$ for a typical trace, obtained using a FPS of free spectral range of 577 MHz. Eq. (4.36) indicates that such a plot should yield a straight line and this behavior was generally observed. Deviations from straight line behavior are due to drifts in the frequency of the laser relative to the resonant frequencies of the measuring FPS. Root mean square fluctuation of the measured spacings range of 577 MHz was $\sim 0.3\%$, indicating a random drift rate of $\sim 3$ MHz/hr between the laser and FPS frequencies. This value was confirmed through additional checks, made by parking the laser frequency on the side of the instrumental line and observing the drift of the transmitted intensity. Frequency drifts contribute $\sim 0.3\%$ error in the frequency calibration of the data.

3. Measurement of the Instrumental Profile

As mentioned above in this section, because of the spherical aberration in the FPS, its transmission profile is a function of the spatial distribution of the light which illuminates it. Instrumental profiles of the interferometers were obtained by scattering light from solutions of polystyrene balls in water, contained in a cell having the same geometry of the gas cell, to produce the same distribution of light in the FPS.

E. Light Detection Equipment

A photon counting system, shown in fig. (4.1) was used to detect the scattered light. The photomultiplier tube (PMT) employed was an ITT FW 130 with an effective cathode diameter of 0.1" and a dark count rate of 11/sec when the discrimination level of the single
channel analyzer was set to accept 90% of the pulses arising from photocathode electron emission. The standard pulses from the analyzer were amplified, passed through a three stage RC filter, and the resulting signal displayed on a strip chart recorder. As will be discussed in sec. (IV G), to correct the data for any effects of finite filter time constant, one must know the impulse response, h(t), of the amplifier-filter-recorder system. This impulse response was obtained by applying a short pulse to the amplifier input and observing the resulting recorder deflection.

The accuracy of the measured spectra is limited by shot noise, present because the optical power transmitted by the FPS is not measured directly but inferred from the number \( \dot{n} \) of pulses per second produced at the output of the single channel analyzer. The effects of shot noise on the measurement of spectra can be obtained from the spectral and temporal properties of the single channel analyzer output current and the recorder deflection. The output current of the single channel analyzer consists of the sum of a series of pulses, each of total charge Q and each being short in duration compared to the duration of h(t), the impulses response of the amplifier-filter-recorder system. With this condition the recorder deflection \( x(t) \) is the sum of a series of pulses each having the shape of the impulse response h(t). The average recorder deflection, \( \langle x \rangle \), is related to the average single channel analyzer output current, \( \langle i \rangle \), and average pulse rate, \( \langle \dot{n} \rangle \), by

\[
\langle x \rangle = \gamma \langle i \rangle = \gamma Q \langle \dot{n} \rangle,
\]

where \( \gamma \) is a proportionality constant. We assume for the impulse response \( h(t) \) that of an ideal single-pole low pass filter:

\[
h(t) = \begin{cases} 
0 & t < 0, \\
\frac{1}{\tau} e^{-t/\tau} & t \geq 0,
\end{cases}
\]

(4.38)
where $T$ is the filter time constant. With this assumption the spectral power density $S_x(\omega)$ of the recorder deflection may be shown to be

$$
S_x(\omega) = \gamma Q \langle \chi \rangle \left\{ 2\pi \delta(\omega)\langle \hat{n} \rangle + \frac{(\frac{1}{2}\Delta)^2}{\omega^2 + (\frac{1}{2}\Delta)^2} \right\}
$$

(4.39)

and consists of two parts: the signal part - a d.c. component proportional to $\langle \hat{n} \rangle$; and the noise part - a Lorentzian distribution with a HWHH of $1/T$. The signal to noise ratio $S/N$ is given by

$$
\frac{S}{N} = \left( \frac{P_S}{P_N} \right)^{1/2}
$$

(4.40)

where $P_S$ and $P_N$ are the total signal and noise power respectively and are obtained by integrating $S_x(\omega)$ over all $\omega$. We find for $S/N$:

$$
\frac{S}{N} = (2\langle \hat{n} \rangle T)^{1/2}
$$

(4.41)

so that the signal detectability depends only on the average count rate $\langle \hat{n} \rangle$ and the system time constant $T$. For the observation of a spectrum the average count rate $\langle \hat{n} \rangle$ varies slowly in time as the spectrum is swept out so that the signal to noise ratio will be a function of position on the chart.

In addition to determining the signal to noise ratio of the measured spectra, the amplifier-filter-recorder system also modifies to some extent the measured spectral shape at the recorder. Suppose that, as a spectrum is swept out, $S_e(t)$ is the single channel analyzer output current in the absence of shot noise. (21) The resulting recorder deflection, the measured spectrum, $S_m(t)$, will be given by the convolution of $S_e(t)$ and the impulse response function $h(t)$ of the system

$$
S_m(t) = \int_{-\infty}^{\infty} S_e(\tau) h(t-\tau) \, d\tau.
$$

(4.42)
As the time constant T of the impulse response of the system is increased the distortion of $S_e(t)$ produced by this convolution becomes more severe. The choice of T then is dictated by two criteria: signal to noise ratio and spectral distortion. We shall discuss this choice further in section (IV G).

**F. Gas Handling Apparatus**

The system diagrammed in fig. (4.17) was constructed to fill the cell and measure the resulting pressure. The plumbing was 3/8" copper refrigeration tubing with soft soldered and "Swagelock" fittings. All valves were of the rubber diaphragm vacuum variety (1/4" Speedivalves), except valve A which was a stainless steel stem valve (1/4" Whitey #OVM2A), used on the cell because of its compactness. Maximum permissible system pressure was 150 psi. Thermocouple (TC) gauges determined the quality of the vacuum attained previous to filling. The system could be pumped down to 2μHg by a duo-seal rotary pump. Three instruments were employed to measure the pressure: a low pressure dial gauge from 0 to 20 mmHg (Wallace & Tiernan type FA-141); a precision mercury manometer from 20 to 800 mmHg (Wallace & Tiernan type FA 187) and a 0 to 150 psi dial gauge (Wallace & Tiernan type FA 145). Accuracy of the measured pressure was: 1% in the vicinity of 10 mmHg, increasing to 0.1% at 800 mmHg, and ~0.5% for pressure greater than 800 mmHg.

In the experiments on mixtures, the following procedure was used to fill the cell: The component to be at the lower partial pressure is introduced into the entire system at the desired pressure $P_1$, valve A is closed, and the system reevacuated except for the cell. The system is then filled with the second component to a pressure $P_2 > P_1$. Valve A is then cracked and the second component allowed to slowly enter the cell, $P_2$ being increased so as to always maintain a flow into the cell. When the desired total pressure is reached, the system is sealed and valve A opened momentarily to allow pressure equilibration between the cell and the rest of the system so that the total pressure in the cell can then be measured. Immediately after filling, the antechamber of the scattering cell contains a higher
Figure 4.16: Cell filling apparatus.
concentration of component #1, so that measurements cannot be made until the concentrations have equilibrated by diffusion. The equilibration could be monitored by observing the intensity of the scattering of component #1, usually xenon, increase as it diffused into the scattering chamber. The cell was generally left for 24 Hrs after a filling to assure a uniform mixture and to allow dust to settle out. The research grade helium and xenon under study here were obtained from the Matheson Co. and were not further purified.

G. Data Analysis

1. Introduction

In this section we discuss the techniques used to analyze the data to be presented. As we have discussed in sec. (IV E) an experimentally determined spectrum is the convolution of the spectrum of the scattered field with the instrumental profile of the measuring interferometer. To compare the experimental spectra with those from an appropriate theory, it is necessary to convolve the theoretical spectra with the instrumental profile used to obtain the data. This convolution must be carried out numerically since, in general, neither the theoretical spectra or instrumental profile have the simple algebraic forms that would be amenable to analytic convolution. Numerical convolution of the theoretical spectra and instrumental profiles was performed using the fast Fourier transform (24) and will be discussed in the next section.

In sec. (3) we discuss the handling of the experimental spectra.

2. Numerical Convolution

The comparison of experimental and theoretical spectra requires the numerical convolution of the theoretical spectra with the proper instrumental profile. Numerical convolutions may be performed conveniently and rapidly by employing the discrete Fourier transform and calculating such transforms via the fast Fourier transform algorithm. (24) We shall now briefly describe the use of the discrete Fourier transform (DFT) in performing numerical convolution. Fig. (4.17) shows typical functions to
be convolved. Here \( T(x) \) represents the theory and \( I(x) \) the instrumental profile. The functions \( T(x) \) and \( I(x) \) of the reduced frequency parameter \( x \) are defined over an interval of length \( L \) and are assumed to be zero for \( x > L/2 \). To obtain the DFT of, for example, \( T(x) \), one samples \( T(x) \) at \( N \) equally spaced positions \( x_k \) spaced by \( \Delta x = L/N \) over the distance \( L \). These samples will be denoted by \( T_k \). The coefficients of the DFT of \( T_k \) are given by:

\[
J_j = \frac{1}{N} \sum_{k=0}^{N-1} T_k e^{-2\pi i \left( \frac{jk}{N} \right)} \quad j = 0, 1, \ldots, N-1, \tag{4.43}
\]

with the inverse relationship

\[
T_k = \frac{1}{N} \sum_{j=0}^{N-1} J_j e^{2\pi i \left( \frac{jk}{N} \right)} \quad k = 0, 1, \ldots, N-1, \tag{4.44}
\]

The fast Fourier transform is a recently discovered algorithm\(^{(24)}\) for performing the operations on \( T_k \) and \( J_j \) indicated in eqs. (4.43) and (4.44) that reduce greatly the number of required additions and multiplications from that of the straightforward method. The only requirement placed on the arrays \( T_k \) and \( J_j \) is that the total number of samples be a power of 2, i.e. \( N = 2^M \) with \( M \) an integer.

The utility of the DFT in performing convolutions arises from the relation of the DFT coefficients \( J_j \) to the integral Fourier transform, \( J(k) \) of \( T(x) \):

\[
J(k) = \int_{-\infty}^{\infty} dx \ e^{-ikx} T(x) \tag{4.45}
\]

or for short:

\[
J(k) \leftrightarrow T(x). \tag{4.46}
\]
Figure 4.17: a) Typical spectrum and instrumental profile to be convolved.  
b) Effective convolution performed using the DFT.
When \( T(x) \) is slowly varying over the sampling interval \( \Delta x \) this relationship may be shown to be

\[
J_j = \frac{N}{L} J\left(\frac{2\pi j}{L}\right)
\]  

(4.47)

so that if the \( T_k \) are samples of \( T(x) \) at intervals \( \Delta x \) then the \( J_j \) are samples of the Fourier transform \( J(k) \) of \( T(x) \) at intervals \( 2\pi/L \). It is required that \( T(x) \) vary slowly over \( \Delta x = L/N \) since the shortest wavelength in the discrete Fourier transform is \( \Delta x \) (when \( j = N - 1 \), \( k = 2\pi N/L = 2\pi/\Delta x \)).

We desire to perform the convolution of \( T(x) \) and \( I(x) \) given as follows

\[
D(\chi) = \int_{-\infty}^{\infty} T(x) I(\chi - y) \, dy.
\]

(4.48)

Taking Fourier transforms of both sides of the equation leads to the k-space relation

\[
\mathcal{D}(k) = J(k) \mathcal{J}(k)
\]

(4.49)

where we have defined \( \mathcal{D}(k) \) and \( \mathcal{J}(k) \) in analogy to eq. (4.46). The convolution \( D(x) \) is obtained, then, by multiplying the Fourier transforms of \( T(x) \) and \( I(x) \) and then Fourier inverting the product. The discrete analogy to eq. (4.48) starting with the arrays \( T_k \) of samples of the theory and \( I_k \) of samples of the instrumental profile, is given by

\[
D_k = \Delta \chi \sum_j T_j I_{k-j}
\]

(4.50)

The discrete convolution may be carried out by calculating the DFT arrays.
\( J_j \) and \( I_j \) of \( T_k \) and \( I_k \) respectively, forming the product \( D_j = J_j \cdot I_j \)
for \( j = 0, 1, \ldots, N - 1 \) and then inverting the array \( D_j \) to obtain the desired array \( D_k \).

Eq. (4.44) shows that the DFT arrays \( T_k \) and \( I_k \) are periodic in their indices, with period \( N \), i.e. \( T_k \equiv N = T_k \). As a result, the discrete convolution of \( T_k \) and \( I_k \) as performed via the DFT is equivalent to the convolution with \( I(x) \) of a function made up of a periodic repetition in \( x \) of \( T(x) \) with period \( L \). This is indicated in fig. (4.17b). It is, therefore, essential that the functions \( I(x) \) and \( T(x) \) to be convolved be confined to a small portion of the interval \( L \), so that at any given shift \( x' \), \( I(x + x') \) significantly overlaps only one replica of \( T(x) \).

The convolutions of theoretical spectra \( T(x) \) with the instrumental profile were performed with \( L = 6.4 (0 \leq |x| \leq 3.2) \) in the reduced frequency parameter \( x \). The number of samples \( N \) taken over \( L \) varied from \( N = 256 (\Delta x = 0.025) \) to \( N = 1024 (\Delta x = 0.00625) \), depending on the sharpness of the features of \( T(x) \). To assure that \( \Delta x \) was small enough sample spectra were convolved with \( I(x) \) using various values of \( \Delta x \). Various spacings \( L \) were also tested to determine the effects of overlap. The above selection of \( L \) and \( N \) assure convolutions accurate to better than 0.01%.

3. The Experimental Spectra

As described in sec. (IV E), in the photon counting system used for these experiments, the desired spectrum \( S_e(t) \) is proportional to the output pulse rate of the single channel analyzer, and thus to the average analyzer output current at a time \( t \). The average analyzer output current is determined by passing the current through an amplifier, low pass filter and onto a recorder, the resulting recorder deflection being \( S_m(t) \), the measured spectrum. The time constant \( T \) of the amplifier-filter-recorder system determines the signal to noise ratio, \( S/N \), of the measurement and \( S/N \) is given by eq. (4.41):

*or vice versa
\[ \frac{S}{N} = (2nT)^{1/2} \]  \hspace{1cm} (4.41)

where \( n \) is the pulse rate. It was also pointed out that the low pass filter distorts the measured spectrum. If \( S_e(t) \) is the variation of pulse rate with time during the recording of a spectrum then eq. (4.42) gives the measured spectrum \( S_m(t) \):

\[ S_m(t) = \int_{-\infty}^{\infty} d\tau \; S_e(\tau) h(t-\tau). \]  \hspace{1cm} (4.42)

The choice of time constant \( T \) is dictated by two criteria. According to eq. (4.41) it is desirable to choose \( T \) as large as possible to enhance signal-to-noise, but \( T \) must be kept small compared to the time it takes to sweep out a spectrum if the spectrum is not to be distorted by the convolution of eq. (4.42). The most frequently made choice of \( T \) is conservative one, that is \( T \) is chosen to be very small so that there will be no chance of distortion of the measured spectrum. This choice, however, is made at the expense of some signal to noise.

For these experiments \( T \) has been chosen large to optimize signal to noise. As a result a small amount of distortion of the measured spectrum is produced by the finite response time of the amplifier filter recorder system. The measured spectrum may be corrected for this distortion by solving eq. (4.42) for \( S_m(t) \) in terms of \( S_e(t) \). If the impulse response of the system is that given in eq. (4.38) we have for \( S_m(t) \)

\[ S_m(t) = \frac{1}{T} \int_{-\infty}^{T} d\tau \; S_e(\tau) e^{-\frac{(\tau - t)}{T}}. \]  \hspace{1cm} (4.51)

This equation may be exactly solved for \( S_e(t) \) and we find
Thus one may obtain the desired spectrum $S_e(t)$ from the measured spectrum $S_m(t)$ and its derivative $S_m'(t)$. Since the derivative $S_m'(t)$ is inherently more noisy than the measured spectrum $S_m(t)$, it is necessary that $T$ be small enough so that the correction term $T S_m'(t)$ be small ($\lesssim 5\%$) compared to $S_m(t)$. If this is the case the correction of the measured spectrum can be made without an additional contribution to the noise on it. With this technique one adjusts the filter time constant $T$ to its largest practicable value consistent with a small distortion of the spectrum. Fig. (4.18) shows the correction of a typical spectrum. The abcissa is given in terms of the reduced frequency parameter $x$. The solid points are data from a trace and the open circles the result of applying the correction of eq. (4.52) to this data. The solid curve represents the impulse response of the filter used to measure the spectrum.

To indicate the advantage in selecting $T$ as described above we have shown in fig. (4.19) spectra taken under identical conditions but with increasing time constants $T$. The time constant $T$ employed for each spectrum is indicated. The extent of spectral correction due to a finite $T$ may be indicated by the shift in the peak height of the spectrum when eq. (4.52) is employed. This correction is $\sim 0.01\%$, for the smallest $T$, $\sim 0.2\%$ for the middle $T$, and $\sim 1\%$ for the largest $T$. The comparison of fig. (4.19) shows clearly the reduction of shot noise attainable at the expense of only a small correction of the measured spectrum.

The employment of this correction requires the measurement from a data trace of both $S_m(t)$ and its derivative. Typically $S_m(t)$ was measured at about a hundred points along each experimental spectrum to form a data array $S_i$. There will also be the corresponding abcissa array $x_i$ of frequencies at which the $S_i$ were taken. To obtain the array of derivatives $S'_i$ at these points and to smooth the data, a continuous curve with a continuous first derivative was drawn through the data points using a computer. The

\[
S_e(t) = S_m(t) + TS_m'(t).
\] (4.52)
Figure 4.18: Correction of a measured spectrum for distortion due to the finite response time of the amplifier-filter-recorder system. This spectrum is from pure xenon gas at $y = 3.48$. 

- Corrected Spectrum, $S_e$
- Measured Spectrum, $S_m$

$p_{x_e} = 318 \text{ mmHg}$, $y = 3.48$

impulse response used to measure this spectrum,

$T = 0.06 \text{ units of } x$
Figure 4.19: Spectra obtained under identical conditions for various values of \( T \).
curve was determined by least squares by fitting successive sets of a small number, \( m \) (\( m = 5, 7 \)), of data values to a cubic polynomial. Each set of \( m \) successive points along the data was fit in this way.

The fitting technique was the method of Forsythe (26) in which a set of orthonormal polynomials is generated for a given abcissa array. The data value of point \( i \) was then replaced by the value of the polynomial fitted to that set of points situated symmetrically about point \( i \). The derivative of the polynomial may be obtained algebraically so that arrays of smooth data \( S_i \) and its derivative \( S_i' \) are provided.

It was sometimes required to interpolate data values of frequencies between those initially taken from a trace. Interpolation of the data was accomplished starting with the arrays \( S_i \) and \( S_i' \) of the smoothed data and its derivative. These arrays provide four boundary conditions \((S_i, S_i', S_{i+1}, S_{i+1}')\) for a function which interpolates the data between points \( i \) and \( i + 1 \). The data was interpolated between points \( i \) and \( i + 1 \) by requiring a cubic polynomial to assume the value and first derivative \( S_i \) and \( S_i' \) at \( x_i \) and \( S_{i+1} \) and \( S_{i+1}' \) at \( x_{i+1} \) respectively. The four boundary conditions at points \( i \) and \( i + 1 \) determine exactly the polynomial to be used between points \( i \) and \( i + 1 \). This curve provides a continuous curve with a continuous first derivative through the smoothed data points. This technique was also used to interpolate the theoretical spectra from the kinetic model to obtain a sufficient number of points for convolution. Calculation of the kinetic model spectra from the theory was very expensive ($5/point) so that interpolation was required in this case.

Experimental spectra were corrected for the filter response by employing eq. (4.52) as described above in this section. Eq. (4.52) is valid only when the impulse response is that given in eq. (4.38) for the simple low pass filter. This ideal impulse response and the actual impulse response of the amplifier-filter-recorder system are shown in fig. (4.19). The actual impulse response has a finite rise time because of the loading
Figure 4.20: Comparison of the ideal and actual impulse response of the amplifier-filter recorder system.

\[ h(t) \]

\[ \tau \text{ in units of } T \]

---

Ideal Impulse Response

---

Actual "" ""

\( T = \text{time constant} \)
of each stage in the filter by successive stages. The appropriateness of the use of eq. (4.52) in correcting the spectra for the effects of the convolution with the actual impulse response was checked by numerically convolving sample spectra with the actual impulse response and then deconvolving them using eq. (4.52). This procedure showed that eq. (4.52) provides accurate deconvolution of the spectra from the actual impulse response.
References: Chapter 4


6. An interface at the Brewster's angle has reflection losses of 0.01% - 0.001% and scatter losses of 0.03%, or total losses of \( \sim 0.04\% \). An interface employing a high quality A.R. coating has reflection losses of \( \sim 0.1\% \) and scatter losses of \( \sim 0.03\% \) for total losses of \( \sim 0.13\% \).

7. All of the piezoelectric cylinders used were PZT-5H ceramic and were obtained from Clevite Corp., Piezoelectric Division, Bedford, Ohio.


10. CER-VIT is a ceramic material having a low linear thermal expansion coefficient, manufactured by the Owens-Illinois Development Center, Box 1035B, Toledo, Ohio.


13. The use of a combination fast proportional and slow integral feedback loop was suggested by J. D. Litster and D. S. Cannell who have employed such feedback in temperature control servos.


16. The spherical Fabry-Perot was invented by P Connes: P. Connes, Revue d'Optique 35, 37 (1956). Thorough discussions of its properties are available in the following articles:

17. We are indebted to Prof. T. J. Greytak for the use of his piston-cylinder assembly.


19. We are indebted to Mr. Joseph Lunacek for the use of his photon counting equipment.


21. This would be possible if for example we could let $Q \rightarrow 0$, $\langle n \rangle \rightarrow \infty$ such that the product $Q \langle \hat{n} \rangle = \langle i \rangle$ was held constant.


23. Whitey valves are a product of the Whitey Research Tool Co., Emeryville, Calif. 94608.

25. A Fortran IV subroutine, using the algorithms in reference 24, has been written by Mr. Joseph Lunacek and was employed here to calculate DFT's and inverse DFT's.

A. One Component Monatomic Gas

1. Introduction

We have measured the spectrum of He-Ne laser light scattered at an angle of 10.6° by pure xenon gas at room temperature at sixteen pressures \( p \) in the range 10mmHg (0.022 atm) < \( p \) < 500mmHg (0.66 atm). For our wavelength, \( \lambda = 6328 \text{Å} \), the corresponding range of the uniformity parameter \( y \) will be 0.11 < \( y \) < 5.4. Over this range in \( y \) the entire kinetic-hydrodynamic transition is mapped out, the spectrum being nearly Gaussian for \( y = 0.1 \) and accurately hydrodynamic for \( y > 5 \).

Measurements have also been made in pure helium gas at a scattering angle of 10.6° and pressures of 2.046 atm. and 3.055 atm. corresponding to \( y = 3.47 \) and 5.18 respectively.

We shall now present and discuss the experimental results in pure xenon and pure helium gas.

2. Determination of \( x \) and \( y \)

The experimental spectra are measured as functions of two parameters: the reduced frequency \( x \), determined by eq. (2.156) from the frequency shift \( \omega \); and the uniformity parameter \( y \) given by eq. (2.47). We now discuss the evaluation of \( x \) and \( y \).

The reduced frequency \( x \) was used to plot both theory and data and was determined on the data from the frequency calibration (see sec. (IVD2)). The frequency interval \( \Delta f_x \) corresponding to a unit change of \( x \) is given in eq. (2.156):

\[
\Delta f_x = \frac{\omega x}{2\pi} = \sqrt{2} K v_o
\]

where \( v_o = k_B T/m \) and \( K \), the magnitude of the scattering vector, is given by eq. (2.6)
\[ \kappa = \frac{4\pi}{\lambda} \sin \left( \frac{\Theta}{2} \right). \]  

(2.6)

In practical units we find

\[ \Delta f_x = 2.578 \times 10^6 \left( \frac{T(K)}{\text{MW}} \right)^{\frac{1}{2}} \frac{\sin(\Theta/2)}{\lambda(\AA)} \text{MHz}, \]

(5.2)

where MW is the molecular weight of the gas molecules. The wavelength \( \lambda \) is that in the gas under study and may be accurately determined from the known He-Ne vacuum wavelength of 6329.9 Å and the index of refraction of the gas. The parameters \( x \) and \( y \) were calculated using the index of refraction of xenon at a pressure of 270 mmHg, the middle of the pressure range which was studied. The wavelength in xenon at 270 mmHg is \( \lambda = 6328.5 \) Å and differs from this value by less than 0.02% over the pressure range 0–542 mmHg. This dependence of \( \lambda \) on the index of refraction of the gas is negligible. The scattering angle \( \Theta \) is determined by the apex angle and index of refraction of the conical lens. The dependence of \( \Theta \) on the index of refraction of the gas is also negligible. Fractional uncertainty in \( \Theta \) is less than \( \pm 0.1\% \) \((\Delta \Theta/\Theta < \pm 0.1\% \)).

Error in the determination of \( x \) does arise from the frequency calibration and from the temperature variation of the cell. As discussed in sec. (IV D2) the frequency calibration, i.e. the factor relating chart distance to frequency was accurate to \( \pm 0.3\% \). The scaling factor \( \Delta f_x \) was calculated using \( T = 22^\circ \text{C} \). Cell temperature was that of the room and was \( 22 \pm 1^\circ \text{C} \). The net error in the determination of \( x \) was \( \pm 0.34\% \).

In terms of measurable experimental parameters \( y \) is given by eq. (2.217):

\[ y = \frac{\sqrt{2}}{3} \frac{m_n \nu_0}{\eta K} = \frac{\sqrt{2}}{3} \frac{p}{\eta K \nu_0}, \]

(5.3)

* The exact scattering angle was 10.58º.
where \( p \) is the pressure, \( m \) is the molecular mass, and \( \eta \) is the viscosity. In practical units \( \gamma \) is given by

\[
\gamma = 4.17 \times 10^{-2} \left\{ \left( \frac{MW}{T(\text{oK})} \right)^{1/2} \frac{p(\text{atm}) \lambda(\text{A})}{\eta(\mu\text{poise}) \sin(\theta/2)} \right\}
\]

The additional quantities needed to determine \( \gamma \) are the pressure, \( p \), and viscosity, \( \eta \). The accuracy of the pressure measurement was indicated in sec. (IV F). Table (5. 1) shows the measured viscosities of xenon and helium gas and the resulting values of \( \gamma \) at \( T = 22^\circ \text{C} \) and \( \theta = 10.6^\circ \).

Since \( \gamma \) changes slowly with temperature \( (\gamma \sim T^{-1/2}) \), the variation in \( T \) of \( \pm 1^\circ \text{C} \) contributes negligibly to the error in \( \gamma \). Error in the determination of \( \gamma \) contributed less then 0.15% error to the measurement of \( S_e(x, y) \).

<table>
<thead>
<tr>
<th>MW</th>
<th>Viscosity (( \mu ) poise) ( ^{(a)} )</th>
<th>( \gamma )</th>
<th>( \Delta f ) (MHz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Xe</td>
<td>131.3</td>
<td>228.85 ± 0.07%</td>
<td>8.326 [p(atm)]</td>
</tr>
<tr>
<td>He</td>
<td>4.0026</td>
<td>197.06 ± 0.06%</td>
<td>1.688 [p(atm)]</td>
</tr>
</tbody>
</table>

\( ^{(a)} \) J. Kestin & W. Leidenfrost Physica, 25, 1033 (1959). The AIP handbook, 2nd ed., presents the xenon data incorrectly, quoting the viscosity of 231.02 \( \mu \) poise at 20 \( ^\circ \text{C} \) instead of 25 \( ^\circ \text{C} \).

3. The Measured Spectra \( S_e(x, y) \) in Xenon Gas

The scattered light spectrum \( S_e(x, y) \) of xenon gas has been measured at sixteen values of \( y \) in the range \( 0.1 < y < 5.5 \) for \( |x| < 3.2 \). The typical traces are shown in fig. (5.1). The contribution of stray light to the spectrum is determined by evacuating the cell at the end of a run, and must be subtracted from each spectrum to be analyzed. Spectra are corrected for any distortion due to the finite filter response time accord-
Figure 5.1: Typical scattered light spectra observed in xenon gas at $T = 22^\circ C$, $\Theta = 10.6^\circ$.

```
\begin{figure}
\centering
\includegraphics[width=\textwidth]{scatter_light_spectra}
\caption{Typical scattered light spectra observed in xenon gas at $T = 22^\circ C$, $\Theta = 10.6^\circ$.}
\end{figure}
```
ing to the discussion in sec. (IV G3). Data points of the corrected spectra are obtained at intervals $\Delta x = 0.025$ of the reduced frequency parameter $x$. For comparison with theory, the experimental spectra are normalized using Simpson's rule to unit area relative to the reduced frequency parameter $x$ over the range $|x| < 3.2$. This range in $x$ contains more than 99.8% of the area of the experimental spectra. The final data from each measured spectrum is the average of the left and right hand sides of that spectrum. From 4 to 10 measured spectra are averaged to obtain $S_e(x, y)$ for each value of $y$.

Experimental spectra $S_e(x, y)$ for xenon gas have been compared with the results of the kinetic model calculation (see sec. (IIC2c)) for both Maxwell and hard sphere molecules. The kinetic model calculation supplies spectra $S(x, y)$ normalized to unit area in $x$ (see fig. (5.2)). Using the methods described in sec (IV G2) the kinetic model spectra were numerically convolved with the instrumental profile $I(x)$, also normalized to unit area in $x$, to obtain $S_e(x, y) = S(x, y) \otimes I(x)$. Convolutions were performed with point spacings in $x$ of $\Delta x = 0.025$ for $y < 3$ and $\Delta x = 0.00625$ for $3 \leq y \leq 6$, and were accurate to better than 0.01%. The normalized instrumental profile of the FPS interferometer (free spectral range = 577MHz) used in the xenon experiment is given in Table (5.2). The profile $I(x)$ is symmetrical about $x = 0$. Since the measurements were made by changing pressure at constant scattering angle and therefore at constant $K$, the instrumental profile is the same for all values of $y$.

Figure (5.2) shows the normalized instrumental profile $I(x)$, Maxwell molecule spectra $S(x, y)$ calculated from the kinetic model, and the convolved spectra $S_e(x, y)$ for several values of $y$. The effect of the convolution becomes more serious as $y$ increases and the features of $S(x, y)$ become sharper.

The experimental data are shown plotted in fig. (5.3) along with $S_e(x, y)$ from the kinetic model for both Maxwell molecules and hard spheres. The results of the exact hydrodynamic calculation (see sec. (IIC3) have also been plotted for selected values of $x$. Each column of open circles in fig. (5.3) represents the experimentally determined spectrum $S_e(x, y)$ at the value of $y$ indicated. The curves presented here
Table 5.2: Instrumental Profile Used to Measure the Scattered Light Spectrum of Xenon Gas, Normalized to Unit Area in x. A Unit of x is 56.31 MHz.

<table>
<thead>
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<th>x</th>
<th>I(x)</th>
<th>x</th>
<th>I(x)</th>
<th>x</th>
<th>I(x)</th>
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Figure 5.2: Effect of the convolution of $S(x, y)$ with $I(x)$ for several values of $y$. Here $S(x, y)$ is from the exact solution of the Boltzmann equation for Maxwell molecules.
Figure 5.3: Comparison of measured and calculated spectra, $S_e(x,y)$ for xenon gas.
Data

- $S(x, y)$, Maxwell Molecules
- $S_e(x, y)$, Maxwell Molecules
- $S(x, y)$, Hard Spheres
- $S_e(x, y)$, Exact Navier-Stokes

$S_e(x, y)$ vs $y$ for various $x$ values:
- $x = 0.6$
- $x = 0.8$
- $x = 0.9$
- $x = 1.0$
- $x = 1.1$
- $x = 1.2$
- $x = 1.3$
- $x = 1.4$
- $x = 1.5$
- $x = 1.7$
- $x = 2.0$

The diagram shows the relationship between $S_e(x, y)$ and $y$ for different values of $x$, illustrating the data and various models for comparison.
show $S_e(x,y)$ as a function of $y$ at various values of frequency shift $x$. Considering fig. (5.2) to be a plot of $S_e(x,y)$ in the $x$ - $y$ plane, the curves of fig. (5.3) are obtained by cutting the function $S_e(x,y)$ in planes of constant $x$. Spectra increase with increasing $y$ in the vicinity of the central line ($x \sim 0$) and Brillouin line ($x \sim 0.9$), and decrease at the intermediate points ($x \sim 0.5$).

The asymptotic limits of the measured spectra for large $y$ ($y = \infty$) and small $y$ ($y = 0$) have been indicated. The $y=0$ points are determined from the convolution of $I(x)$ with the kinetic limit Gaussian distribution of eq. (2.166). In the large $y$ limit the widths of the central and Brillouin lines go to zero so the $y \to \infty$ limit $S_e(x,y)$ is $I(x)$ convolved with three properly weighted and spaced $\delta$ functions.

We have shown, in fig. (5.3a) the variation of $S(x,y)$ at $x = 0$ from the kinetic model calculation for Maxwell molecules. This is to indicate the comparative variations of $S(x,y)$ and $S_e(x,y)$ with $y$. Generally, the convolved spectra $S_e(x,y)$ change more slowly with $y$ than do $S(x,y)$, but in much the same way over the range of $y$ studied.

Figures (5.3a and b) show, in addition, for selected values of $x$, the variation with $y$ of the exact spectra calculated from the Navier-Stokes hydrodynamic equations (see eq (2.253)). As indicated in Table (2.5) these begin to deviate perceptibly from the kinetic model calculation for $y < 4$.

Errors in the measurement of $S_e(x,y)$ can be classified as random, arising from shot noise and in the determination of $x$ and $y$, or can be classified as systematic, arising in the determination of the instrumental profile and from the distribution of scattering angles in the spectral measurement. The significance of random error in the measurement of $S_e(x,y)$ is well indicated in fig. (5.3) by the fluctuation of the data about smooth functions of $y$. RMS fluctuation $\Delta S_e(x,y)$ in the measurement of a point of $S_e(x,y)$ was typically $\Delta S_e(x,y) < 0.006$, which is the diameter of the open circles in fig. (5.3). The RMS fluctuation was largest for values of $S_e(x,y)$ with the largest slope in $x$, e.g. $x=0.2, 0.3, 0.6, 0.7$ for $y > 1$. 
The effect of the error in the measurement of the instrumental profile $I(x)$ was determined by convolving the theoretical spectra with a number of profiles which deviated slightly from about the final $I(x)$. These profiles were selected from the measured transmission profiles which were averaged to give $I(x)$. The resulting variations in convolved spectra were negligible.

The distribution of scattering angles in the spectral measurement was discussed in sec. (IV C2) where it was pointed out that such a distribution leads to a spurious increase in the measured width of the Brillouin peak. For our experimental conditions the Brillouin width of the measured spectrum would be increased by $\sim 0.5\%$ at $y = 6$, $\sim 0.3\%$ at $y = 3$ and $\sim 0.2\%$ at $y = 2$. These errors are small compared to the random error in the measurements and do not substantially alter the data. Since they are difficult to accurately correct for, they were neglected.

4. Measured Spectra in Helium Gas

Measurements of $S_e (x, y)$ have also been made in pure helium gas at $\Theta = 10.6^\circ$, $T = 22^\circ$C for two pressures, 2.046 atm. ($y = 3.47$) and 3.055 atm. ($y = 5.18$). These spectra shown in fig. (5.4) along with spectra calculated from Mountain's exact solution of the Navier-Stokes hydrodynamic equations. (eq. 2.253). The difference between the hydrodynamic and kinetic model theories is too slight at $y = 3.47$ or 5.18 to be observed with the signal to noise available in helium, so comparison was made only with the hydrodynamic calculation.

These measurements in helium gas were made using the spherical Fabry-Perot interferometer of free spectral range 577 MHz which was employed in the xenon experiment. Because the Brillouin splitting, $Kc_o/2\pi$, in helium (from Table 5.1, $c_o = \sqrt{\frac{3}{6} v_o}$) is $\sim 295$ MHz, the Brillouin components from adjacent FPS transmission peaks overlap, as fig. (5.4) indicates. To compare these spectra with theory, then, it was necessary to convolve theoretical spectra with a periodic repetition of the instrumental profile, spaced by the free spectral range.

As may be seen, the Navier-Stokes hydrodynamic spectra agree to within the noise with the measured spectra for $y = 3.47$ and $y = 5.18$. 
Figure 5.4: The spectrum of light scattered by helium gas at $T = 22^\circ C$, $\Theta = 10.6^\circ$.

Spectrum of light scattered by helium gas

$T = 22^\circ C$ $\Theta = 10.6^\circ$

- Hydrodynamic spectra given by Mountain
- Stray light subtraction
- Dark current (11 counts/sec)

$y = 3.47$ 2.046 atm $577$ MHz

$y = 5.18$ 3.055 atm $577$ MHz

$y = 5.18$ 3.055 atm $577$ MHz
5. Discussion

We have compared in fig. (5.3) the spectra obtained from the exact solution of the Boltzmann equation for both the Maxwell molecule and hard sphere gas with the measured spectra in xenon gas for $0.1 < y < 5.4$, $T = 220^\circ C$ and $K = 2 \times 10^4$ cm$^{-1}$. This comparison shows very good agreement of the spectra for both the Maxwell molecule and hard sphere gases with the measured spectra in xenon gas.

The measurements do not allow a clear choice of Maxwell molecule or hard sphere intermolecular potential as being more appropriate to xenon under the conditions of the experiment. Over the range $1 < y < 4$, where the difference between the Maxwell molecule and hard sphere spectra is the greatest the Maxwell molecule spectrum is preferable. For $y \approx 0.7$, however, the hard sphere spectra show slightly better agreement with the measurements. The previous measurements of Greytak and Benedek in xenon at $y = 0.77$ were also fit better by the hard sphere spectra than by the Maxwell molecule spectra.$^2$

The overall agreement between theory and experiment indicates that the linearized Boltzmann equation, when solved using the kinetic model procedure, can provide accurately the density fluctuation spectrum of a dilute monatomic gas. The fact that such agreement is obtained between spectra calculated for crude molecular models like the Maxwell and hard sphere molecule and the spectra measured in xenon gas, which is known to have a Lennard-Jones type of intermolecular potential, is further evidence of the insensitivity of the density fluctuation spectrum to the form of the intermolecular potential. This insensitivity was first indicated by the similarity of the calculated spectra for Maxwell molecules and hard spheres,$^3$ and reflects the insensitivity of the relative magnitudes of the matrix elements $\lambda_{ij}$ of the Boltzmann collision operator $J$ to the form of the intermolecular potential.

The close relationship between the density fluctuation spectrum and the dispersion relation for forced sound propagation was pointed out in the introductory chapter* and discussed further in Chapter II.$^+$ It is

$^*$Sec. (I A 4)
$^+$Sec. (II C 2 c)
of interest, therefore, to compare the results obtained here in the measurement of the density fluctuation spectrum with the results of the forced sound propagation calculations and experiments. Using the kinetic model Sirovich and Thurber\(^4\) have calculated the dispersion relation for forced sound propagation for both Maxwell molecules and hard spheres and have compared their calculations with the measurements of Greenspan\(^5\) and Meyer and Sessler\(^6\). Over the range \(y\) of interest here, \(0.1 < y < 5.4\), the calculated Maxwell molecule and hard sphere dispersion relations are somewhat different with the Maxwell molecule calculation showing good agreement with the measurements. The difference between the hard sphere calculation of the dispersion relation and the measurements is too great to be consistent with the good agreement of our spectral measurements with the calculated hard sphere spectra. However, the calculated dispersion relations for Maxwell and hard sphere molecules also show considerably more difference than one would expect on the basis of a comparison of the calculated Maxwell and hard sphere spectra. This is probably because the kinetic model approximation was carried out only to order \(N = 11\) in the calculations of Sirovich and Thurber.

Sugawara, Yip, and Sirovich\(^3\) show that it is necessary to carry the kinetic model calculation to \(N = 21\) for the hard sphere gas to obtain sufficient convergence in the calculation of the spectra. One would expect the same kind of behavior for the dispersion relation. It may be, then, that some of the difference observed between the measured dispersion relation and the hard sphere calculation of the dispersion relation of Sirovich and Thurber is due to a lack of convergence.

We now briefly discuss the applicability of the various hydrodynamic calculations. The measurements presented here establish the exact solution of the Boltzmann equation as an accurate means of calculating the density fluctuation spectrum for a dilute monatomic gas. It would seem appropriate, therefore, to judge the hydrodynamic theories on the basis of the agreement of their spectra with the spectra calculated from the exact solution of the Boltzmann equation. This comparison was made and discussed in sec. (IIC3c) and Tables (2.5, 6). We repeat only the most important points here. First, none of the hydrodynamic theories was found to be useful for values of the uniformity parameter \(y\) further
into the kinetic regime than \( y = 3 \), i.e., for \( y < 3 \). The Burnett approximation, for \( y > 3 \), is found to be clearly better at describing the sound propagation mode than is the Navier-Stokes approximation. This is in accord with the sound propagation results of Greenspan. (5) The Burnett approximation, however, fails to adequately describe the thermal diffusion mode for \( y < 6 \) and in this regard represents no improvement over the Navier-Stokes approximation. The best hydrodynamic theory is found to be that of Selwyn which gives excellent agreement with the results of the exact solution of the Boltzmann equation for \( y > 3 \).

B. Helium-Xenon Mixture

1. Introduction

The data to be presented on the helium-xenon gas mixture consists of: i) the measurement of \( r_d \) and \( r_c \), the ratios of extinction for density and concentration fluctuations, respectively, as a function of xenon concentration and helium pressure; ii) the measurement of \( S_{xx}(K, \omega) \) as a function of helium pressure; iii) the measurement of the Brillouin splitting and line width at various values of xenon concentration and total pressure. We now discuss these in turn.

2. Measurement of the Extinction Ratios \( r_c \) and \( r_d \)

a) Introduction

The extinction ratio \( r_c \) was defined in sec. (IIIC1) as that fraction of the total optical power scattered from a dilute gas mixture in the hydrodynamic limit which is due to concentration fluctuations. Similarly \( r_d = 1 - r_c \) is that fraction arising from density fluctuations. So defined, then, \( r_c \) is the fraction of the area measured spectrum \( S(K, \omega) \) contained in the diffusion spectrum \( B(K, \omega) \) of eq. (3.71), and \( r_d \) is the fraction of the area contained in the density fluctuation spectrum \( A(K, \omega) \) of eq. (3.71). Expressions for \( r_c \) and \( r_d \), obtained from the hydrodynamic calculation of Mountain and Deutsch were given in eqs. (3.75) and fig. (3.1). The measurement of \( r_c \) and \( r_d \) in the hydrodynamic limit allows the testing of the values for these ratios predicted by the hydrodynamic theory. Furthermore, as was discussed in sec. (IIB5), measurement of the ratios \( r_c \) and \( r_d \) in the regime where the xenon motion is partially kinetic,
Figure 5.5: The spectrum of light scattered by a helium-xenon gas mixture in the hydrodynamic regime.

Theta = 10.6°
T = 22 °C
p_h = 4.53 atm
p_x = 0.029 atm

FWHH of instrument = 25.9 MHz
allows one to determine the area of the contribution of the spectral densities \( S_{\text{hx}}(K, \omega) \) and \( S_{\text{hx}}(K, \omega) \) to \( S(K, \omega) - r_d A(K, \omega) \). This information is required to estimate the possible effects of the presence of \( S_{\text{hx}} \) and \( S_{\text{hx}} \) in the determination of \( S_{\text{xx}} \) from \( S - r_d A \).

b) Determination of \( r_c \) and \( r_d \)

Measurements of \( r_c \) and \( r_d \) of the helium-xenon mixture were made at \( T = 22^\circ C \), \( \theta = 10.6^\circ \) both in the hydrodynamic regime and in the regime where the xenon motion is partially kinetic. The density fluctuation contribution was identified using the three Lorentzian approximation as was discussed in sec. (IIIID5), except at the lower helium pressures where it was sufficiently broad and small to be approximated by a constant. The area of the contributions on a trace was measured using a precision planimeter.

Figure (5.5) shows a portion of a typical spectrum in the hydrodynamic regime \( (p_h = 4.53 \text{ atm.}, x_x = 0.0064) \), taken using the FPS interferometer of free spectral range equal to 750 MHz. We have indicated on fig. (5.5) the total measured spectrum \( S(K, \omega) \) and the density fluctuation spectrum \( r_d A(K, \omega) \). The stray light contribution is also indicated and has been subtracted out to obtain \( S(K, \omega) \). The base line indicated in fig. (5.5) is the dark current. The Brillouin splitting \( f_B = \frac{Kc}{2\pi} \) is indicated. Since the Brillouin peaks of adjacent orders overlap to some extent they were fit simultaneously to a pair of Lorentzians to determine their height, width, and area. The procedure outlined in sec. (IIIID5) to determine \( r_d A(K, \omega) \) was then followed.

Figure (5.6) shows the evolution of the spectrum through the kinetic-hydrodynamic transition for \( p_x = 16.8 \text{ Hg (0.022 atm.)} \), \( p_h = 0, 0.41, 0.78, 1.69, \) and \( 3.10 \text{ atm.} \). These spectra were taken using the FPS of free spectral range equal to 577 MHz. The spectra shown in fig. (5.6) were obtained by tracing chart records for the various runs involved. They differ somewhat in frequency dispersion since the length along the chart corresponding to a frequency interval of a free spectra range varies somewhat from run to run.
Figure 5.6: The evolution of the spectrum of light scattered by a helium-xenon mixture through the kinetic-diffusion transition.
Each spectrum presented in fig. (5.6) covers a frequency interval equal to one free spectral range (577 MHz). Due to scale changes and variations in laser power from run to run the vertical scales of the various spectra are not related. Peak counting rates for the spectra of fig. (5.6) vary from 150 counts/sec for $p_h = 0$ to 300 counts/sec at $p_h = 3.10$ atm.

Since the Brillouin splitting is $\sim 290$ MHz, Stokes and anti-Stokes components from adjacent orders are in this case nearly superimposed. A pair of Lorentzians was again used to fit the Brillouin peaks. Estimates of the possible contribution of the tails of $S_{xx}(K, \omega)$ I (\omega), the central portion of the spectrum, in the vicinity of the Brillouin peaks was made using the Lorentzian $B(K, \omega)$ for $S_{xx}(K, \omega)$ in the hydrodynamic regime and spectra from the Fokker-Planck calculation for $S_{xx}(K, \omega)$ in the kinetic regime. On each of the traces in fig. (5.6) we have indicated the total spectrum $S(K, \omega)$, the base line (dark current), and the contribution of $r_d A(K, \omega)$ as determined by the methods described here and in sec. (IIID5). The stray light contribution, indicated for $p_h = 0$, is of the same relative magnitude for all the spectra in fig. (5.6) and has been subtracted from the spectrum on the chart record to obtain $S(K, \omega)$. These spectra may be compared with those from pure helium in fig. (5.4).

c) Results and Discussion

The measured values of $r_c$ and $r_d$ are shown in fig. (5.7), plotted for various helium pressures and xenon number fractions. Error bars indicate the r.m.s. fluctuations in the measurements. The solid line is $r_c$ and $r_d$ from the hydrodynamic calculation of Mountain and Deutsch (eqs. (3.75)). The hydrodynamic theory shows good agreement with measurements of $r_c$ and $r_d$ at helium pressures such that the system is into the hydrodynamic regime ($p_h \geq 2.4$ atm., $x_h \leq 0.4/K$). However, at low helium pressures, in the kinetic regime, this agreement deteriorates, with the area of the density fluctuation contribution falling below that predicted by hydrodynamics. As discussed in sec. (III D 5) this is the behavior to be expected if $S_{xx}(K, \omega)$, $S_{hx}(K, \omega)$, and the contribution of $S_{xx}(K, \omega)$ to $r_d A(K, \omega)$ go to zero in the kinetic limit. The dashed curve
in fig. (5.7) gives $r_c$ and $r_d$ if $S_{xh}$. $S_{hx}$ and the contribution of $S_{xx}$ to $A(K, \omega)$ is zero. As the kinetic regime is approached the contributions of $S_{xh}$ and of $S_{xx}$ to $A(K, \omega)$ can be expected to vanish more rapidly than that of $S_{hx}$ because the former contributions both involve the influence of the xenon distribution by the helium, which does not fully develop until $t = \tau_{xh}$, i.e., until a velocity correlation time of the xenon has elapsed. The distribution $p_{hx}(r^x_t)$, on the other hand, begins to develop after the first helium - xenon #1 collision, at $t \sim \tau_{xh}/12$, so that $S_{hx}(K, \omega)$ should persist further into the kinetic regime. In any case, the measurements of $r_c$ and $r_d$ indicate that the net area of the contribution of $S_{xh}$ and $S_{hx}$ to $S(K, \omega) - r_d A(K, \omega)$, for helium pressures less than $p_h = 2.4$ atm., falls below the hydrodynamic value of 10% to $\sim 5\%$ at $p_h = 0.78$ atm., and $\sim 0\%$ at $p_h = 0.41$ atm. These values tally well with the nearly Gaussian shape of $S_{xx}(K, \omega)$ for $p_h < 0.4$ atm ($\ell_{xh} > 2.5/\kappa$) and its nearly Lorentzian shape for $p_h > 2.4$ atm. ($\ell_{xh} < 0.4/\kappa$).

It may be noted that the measurements of $r_c$ in the hydrodynamic regime tend to fall slightly below the hydrodynamic calculation of $r_c$. This is suggestive of a systematic overestimation of the area of density fluctuation contribution of the spectrum. Such an error might be due to deviations of the density fluctuation spectrum from the simple hydrodynamic form which arise from the sound relaxation processes.*

3. Measurement of $S_{xx}^e(K, \omega)$

a) Introduction

We have measured the spectrum $S_{xx}^e(K, \omega)$ in a helium-xenon mixture at $T = 22^\circ C$, $\Theta = 10.6^\circ$, $p_x = 16.8$ mmHg and at 10 helium pressures, $p_h$, in the range $0 < p_h < 3.10$ atm. The FPS interferometer of free spectral range 577 MHz was employed for these measurements. Examples of the measured scattered light spectrum from the helium-xenon mixture under these conditions were given in fig. (5.6). According to the remarks of sec (IV G3) a measured total spectrum on a trace was corrected for the finite filter response time to determine the actual total spectrum from

*Sec. (III E)
Figure 5.7: Comparison of measured and calculated values of \( r_c \) and \( r_d \).
which $S_{xx}^e(K, \omega)$ was extracted using the methods described in secs. (III D5) and (V B2). Once $S_{xx}^e(K, \omega)$ was determined it was normalized to unit area in the reduced frequency parameter $x$ for xenon. To compare the various theoretical calculations of $S_{xx}(K, \omega)$ with the measurements, it is necessary to carry out numerically the convolution $S_{xx}^e(K, \omega) = S_{xx}(K, \omega) \otimes I(\omega)$ of $S_{xx}(K, \omega)$ with the instrumental profile, $I(\omega)$, of Table (5.2). The convolutions were carried out as described in secs. (IV G3) and (VA3) and the convolved spectra $S_{xx}^e(K, \omega)$ were then compared with the normalized data.

Under the above stated conditions, as discussed in sec. (III D3), the spectrum $S_{xx}(K, \omega)$ depends on both the collision lengths for xenon-xenon collisions and xenon-helium collisions. Two uniformity parameters, $y_c$ (conserving) for xenon-xenon collisions and $y_{nc}$ (nonconserving) for xenon-helium collisions are therefore required. $S_{xx}(K, \omega)$, normalized to unit area in the reduced frequency parameter $x = \omega / \sqrt{Kv_{ox}^v}$, will be written as $S_{xx}(x, y_c, y_{nc})$. The parameter $y_c$ is the kinetic model parameter for a pure gas and is determined by the xenon pressure and eq. (5.3). Table (5.1) shows that, at $p_x = 16.8$ mmHg, we have $y_c = 0.184$. The parameter $y_{nc}$ is given by eq. (3.105)

$$y_{nc} = \frac{2\nu x}{\sqrt{2}}$$

which, in practical units becomes

$$y_{nc} = 5.13 \times 10^{-6} \frac{\lambda(\lambda)}{D(cm^2/sec)\sin(\theta/2)(MW)} \left(\frac{T(\text{K})}{MW}\right)^{1/2} \left(\frac{I(\mu)}{\text{E}V}\right)$$

The mutual diffusion coefficient $D$ has been measured at $p = 1$ atm., $T = 22^\circ C$ in a helium-xenon mixture of equal number densities ($x_x = 0.5$) and is found to be $D = 0.530$ cm$^2$/sec $\pm 0.8\%$. The dependence of $D$ for a dilute binary gas mixture on the mixture composition has not been measured, but may be estimated using calculations of $D$ from the Chapman-Enskog procedure for a mixture of Lennard-Jones molecules. This
calculation shows that the dependence of $D$ on composition is weak. For the helium-xenon mixture we find

$$D_{x^2_0} = 0.974 \ D_{x^2_{0.5}} = 0.516 \text{ cm}^2/\text{sec},$$

and from eq. (5.5), $y_{nc} = 1.02 \ p_{tot} \ \text{atm}.$

b) The Measured Spectra $S_{xx}^e (x, y_{nc})$

The calculated and measured spectra $S_{xx}^e (x, y_c, y_{nc})$ are shown plotted in fig. (5.8) as a function of $y_{nc}$ for various values of $x.$

Since all measurements and calculations are for $y_c = 0.184$ the dependence of $S_{xx}$ on $y_c$ will not be noted further. The variation of these curves with $y_{nc}$ is similar to that obtained by cutting the unconvolved spectra of (fig. 5.2) in planes of constant $x.$ The results of four calculations of $S_{xx}^e (x, y_{nc})$ are presented: — — — hard collision model;

— modified Fokker-Planck model to include $x - x$ and $x - h$ collisions ($y_c = 0.184$);

— — — — pure Fokker-Planck model ($y_c = 0$);

— — — — extension of the Lorentzian of the diffusion limit into the kinetic regime. The $y_{nc} = \infty$ limit is the instrumental profile $I(x).$

At $y_{nc} = 0,$ the hard collision and Fokker-Planck spectra have the form of the Gaussian kinetic limit convolved with $I(x).$ The modified Fokker-Planck has the pure gas Maxwell molecule spectrum for $y_c = 0.184$ in the $y_{nc} = 0$ limit. Also indicated is the unconvolved spectrum $S_{xx} (x, y_{nc})$ for the Fokker-Planck model to indicate the effect of the convolution.

Root mean square fluctuation in the measurements of $S_{xx}^e (K, \omega)$ is less than the data point size unless otherwise indicated. Typically five spectra were averaged for each value of $y_{nc}.$

Measurements of $S_{xx}^e (K, \omega)$ were also made at $p_h = 4.53 \ \text{atm.}$

$p_x = 0.029, 0.066 \ \text{atm.}$ with the FPS of 750 MHz free spectral range.

The interferometer had an accurately Lorentzian instrumental profile with a FWHH of 25.89 ± 0.07 MHz. At $p_h = 4.53 \ \text{atm.}$ ($y_{nc} \approx 4.5$) $S_{xx} (K, \omega)$ is approximated by a Lorentzian of FWHH $DK^2/\pi \ \text{Hz},$ so that $S_{xx}^e (K, \omega)$ should also be Lorentzian. The measured spectra $S_{xx}^e (K, \omega)$ in this case could be least squares fit to a Lorentzian shape which they fit well. Fig.
Figure 5.8: Comparison of measured and calculated spectra $S_{xx}^e(x, y_{nc})$ for a helium-xenon mixture.
Figure 5.9: The spectrum $S_{xx}^e(K, \omega)$ from a helium-xenon mixture in the hydrodynamic regime.
(5.9) shows such a fit. The measured spectrum $S_{xx}^{e}(K, \omega)$ was found to be independent of xenon pressure and to have a FWHH of $39 \pm 1$ MHz. Subtracting the instrumental width gives $DK^2/\pi = 13.1 \pm 1$ MHz for the FWHH of $S_{xx}^{e}(K, \omega)$. This compares favorably with the value of $DK^2/\pi = 12.6$ MHz at $p_h = 4.53$ atm, calculated from the measured diffusion coefficient.

c) Discussion

The comparison in fig. (5.8) of the measurements and the four calculations of $S_{xx}^{e}(K, \omega)$ shows that the modified Fokker-Planck model provides the best description of the evolution of $S_{xx}^{e}(K, \omega)$ throughout the kinetic-hydrodynamic transition. The agreement is in fact remarkable in view of the approximations which have been made in obtaining $S_{xx}^{e}(K, \omega)$. These measurements demonstrate the appropriateness of the Fokker-Planck approximation for modeling the collisions of xenon with helium in a helium-xenon gas mixture, in so far as temporal evolution of $\rho_{xx}(\vec{r}, t)$ and the shape of the resulting spectrum $S_{xx}^{e}(K, \omega)$ are concerned. The hard collision model was included largely for comparison purposes since it represents the hard collision limit, whereas the Fokker-Planck model represents the soft collision limit. As can be seen the spectrum $S_{xx}^{e}(K, \omega)$ is not tremendously sensitive to the exact nature of the collision, but sensitive enough so that the soft collision limit is seen to be clearly preferred.

The Fokker-Planck model should become more appropriate to describe the motion of a particle of mass $M$ in a background of particles of mass $m$ as the ratio $M/m$ increases. Our measurements, therefore, indicate that the Fokker-Planck Model would be useful for any mass ratio $M/m$ such that $M/m > m_x/m_h \sim 30$. This may be put in another way by noting that for xenon moving in helium, thermalization occurs in about 12 x-h collisions. Therefore, the trajectories of particles undergoing thermalization in more than about 12 collisions may be replaced by the smooth trajectories of the Fokker-Planck Model.

As mentioned at the end of Chapter II*, the previous measurements

*Sec.II.C4
of collision narrowing of a Raman line in gaseous hydrogen by Murray and Javan indicate that the hard collision model is better suited to approximate collisions between particles of equal mass.

4. Sound Velocity and Attenuation Measurements

We have made some preliminary measurements of the Brillouin splitting \( f_B = K c_o'/2\pi \) and HWHH \( \delta f_H = \Gamma_B'/2\pi \) in a helium–xenon gas mixture. Figure (5.5) shows a typical scattered light spectrum. The Brillouin splitting \( f_B \) is indicated. Since Brillouin components from adjacent orders of the Fabry-Perot interferometer overlap to some extent, the splitting \( f_B \) and HWHH \( \delta f_H \) were determined by least squares fitting a pair of overlapping Lorentzians to the measured spectrum in the vicinity of the Brillouin components, as was described in sec. (III D5). The contribution of the diffusion and thermal diffusion components to the spectrum in the vicinity of the Brillouin components was subtracted before fitting the Brillouin components.

Measurements of \( f_B \) and \( \delta f_H \) were made initially in pure helium at pressures from 2 to 4.5 atm. At these pressures under our experimental conditions the uniformity parameter \( y \) ranges from 3.4 to 7.6 so that the helium is hydrodynamic and the Brillouin widths and splitting should take on their hydrodynamic values. The measurements in pure helium then serve to test for any instrumental effects which could lead to spurious splitting or broadening of the Brillouin components. No such effects were observed, the measured \( f_B \) and \( \delta f_H \) agreeing within experimental error with the values calculated from hydrodynamics.

Figure (5.10) shows measurements of \( f_B \) and \( \delta f_H \) taken in the helium–xenon mixture at total pressure \( p = 4.53 \) atm., \( \Theta = 10.6^\circ \), \( T = 22^\circ \)C, for various values of xenon concentration. The solid lines represent \( f_B \) and \( \delta f_H \) calculated from the low frequency forms for \( c_o' \) and \( \Gamma_B' \) in eqs. (3.36) and (3.41) respectively. The dashed lines are calculated from the Goldman-Sirovich theory for the binary gas mixture. The measurements of \( f_B \) and \( \delta f_H \) at \( p = 4.53 \) atm. show clearly the effects of a relaxation process on \( c_o' \) and \( \Gamma_B' \). Recalling our discussion of sec.
Figure 5.10: Comparison of the Brillouin splitting, $f_B$, and HWHH, $\delta f_H$, measured in a helium-xenon binary gas mixture, with $f_B$ and $\delta f_H$ of the low frequency limit and $f_B$ and $\delta f_H$ from the Goldman-Sirovich theory.
Figure 5.11: Comparison of the ratio of the measured HWHH with the prediction of the Goldman-Sirovich theory.

Goldman-Sirovich Theory

low frequency limit
(III E), this is to be expected since at \( p = 4.53 \text{ atm.} \) we have \( \omega/\omega_u = Kc_0/\omega_u \approx 0.7 \), i.e. we are well into the frequency regime where the relaxation in the velocity difference of the two mixture constituents sets in. The HWHH \( \delta f_H \) calculated from the Goldman-Sirovich theory shows reasonable agreement with the data at this range of \( \omega/\omega_u \). The Goldman-Sirovich theory, however, predicts considerably more dispersion in the sound speed than the measurements show. The measured sound speeds fall closely on the calculated low frequency values.

In fig. (5.11) we have plotted \( \delta f_H/\delta f_H^0 \), the ratio of the measured HWHH, \( \delta f_H \), to the low frequency HWHH \( \delta f_H^0 = \Gamma_B/2\pi \), calculated from eq. (3.41), as a function of \( \omega/\omega_u \). The solid line gives the ratio \( \delta f_H/\delta f_H^0 \) calculated from the Goldman-Sirovich theory. The agreement is good for frequencies \( \omega/\omega_u < 1 \). For \( \omega/\omega_u > 1 \), however, considerably more attenuation is observed than is predicted by the Goldman-Sirovich theory. This result is in agreement with the recent forced sound propagation measurements of Pragma, Jenkman, and Beenaker\(^{(9)}\) who have studied the sound attenuation coefficient, \( \alpha \), in the argon-helium gas mixture (we recall that the attenuation coefficient, \( \alpha \), is related to the Brillouin HWHH \( \delta f_H \) by \( \delta f_H = \alpha c_0/2\pi \)). Their results show that the measured attenuation coefficient, \( \alpha \), for low argon concentrations and \( \omega \geq \omega_u \) is larger than that predicted by the Goldman-Sirovich theory.

Our measurements show that the Goldman-Sirovich (G-S) theory represents a considerable improvement over the low frequency hydrodynamic theory in describing the sound attenuation in a binary gas mixture for frequencies \( \omega \) such that \( \omega \gtrsim \omega_u \). The breakdown of the G-S theory for \( \omega > \omega_u \), however, is not surprising in view of the nature of the approximations made in it. The essential generalization of the low frequency hydrodynamic theory introduced by the G-S theory, indicated in eq. (3.118), is to account for the finite time required for the equilibration of the velocity and temperature differences between the two components of the mixture. The form obtained for the relaxation of the
velocity and temperature differences from the G-S theory is a hydrodynamic one which cannot account for kinetic effects in the equilibration which are important over time intervals, $\tau$, short compared to $\tau_u = 1/\omega_u$, and thus for frequencies $\omega > \omega_u$. This is indicated clearly in the form of the concentration fluctuation spectrum which, for dilute xenon in helium, is $S_{xx}(K, \omega)$. Let us compare $S_{xx}(K, \omega)$ obtained from the G-S theory to that from the Fokker-Planck model, which our measurements show to accurately provide $S_{xx}(K, \omega)$.

To obtain the concentration fluctuation spectrum from the G-S theory we observe from fig. (5.11) that the relaxation of importance is the relaxation of the relative velocity, at frequency $\omega_u$. The concentration fluctuation spectrum including the effect of the velocity relaxation may be calculated using eq. (3.118). This equation along with the conservation equation (eq. (3.116)) yields the following equation for the concentration $c(\vec{r}, t)$

$$\frac{\partial c}{\partial t} = -\frac{1}{\omega_u} \frac{\partial^2 c}{\partial t^2} + D \nabla^2 c. \tag{5.5}$$

This equation may be solved for the G-S concentration fluctuation spectrum in the same way that the hydrodynamic equations were solved for the density fluctuation spectrum in a pure gas. We find for the G-S concentration fluctuation spectrum, $S_{GS}(K, \omega)$

$$S_{GS}(K, \omega) = \frac{2DK^2}{(DK^2 - \omega^2/\omega_u)^2 + \omega^2}. \tag{5.6}$$

The corresponding dimensionless spectrum, $S_{GS}(x, y_{nc})$ is

$$S_{GS}(x, y_{nc}) = \frac{(1/2y_{nc})}{(1/2y_{nc} - x^2/y_{nc})^2 + \chi^2}. \tag{5.7}$$

In the long wavelength low frequency limit ($y_{nc} \to \infty$), $S_{GS}(x, y_{nc})$

* sec. (II C 3 b)
reduces to the simple Lorentzian diffusion form of eq. (2.300). Numerical calculation of $S_{GS}(x, y_{nc})$ from eq. (5.7) shows that $S_{GS}(x, y_{nc})$ begins to deviate considerably from the measured spectra $S_{xx}(x, y_{nc})$ and the spectra of the Fokker-Planck model for $y_{nc} \lesssim 5$. This deviation shows that the G-S theory does not properly describe the evolution of the xenon distribution over short time intervals. The limit of applicability may be determined by recalling the definition of $y_{nc}$ in eq. (3.100)

$$y_{nc} = \frac{1}{\sqrt{2} K v_{ox} \tau_c}.$$  

(3.100)

At low xenon concentration the velocity correlation time, $\tau_c$, of a xenon atom is just $\tau_c = 1/\omega_u$ so that

$$\lim_{x_{\perp} \to 0} y_{nc} = \frac{\omega_u}{\sqrt{2} K v_{ox}}.$$  

Since $\omega = K c_o'$ and $c_o' \sim 6 v_{ox}$ we find $y_{nc} \sim 4 \omega_u/\omega$. The breakdown of the G-S spectra for $y_{nc} < 5$, then, indicates that we should not expect it to provide the sound propagation constants for frequencies $\omega$ such that $\omega \gtrsim 0.8 \omega_u$. 

*sec. (III C 3)
References: Chapter 5

1. The viscosity, $\eta$, of xenon at room temperature is nearly proportional to the temperature ($\eta \sim T$).


4. L. Sirovich and J. K. Thurber, J. Acoust. Soc. Am. 38, 478 (1965). The uniformity parameter, $r$, used in this paper and in reference #5 of this chapter is related to our parameter, $y$, by $r = 0.164y$.


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Biographical Note

Born December 17, 1940 in Cleveland, Ohio, Noel Anthony Clark attended primary school and St. Ignatius High School in Cleveland. He graduated from John Carroll University with a B.S. in 1963 and an M.S. in 1965. On June 18, 1966 he and Pauline Agnes Novak were married. A daughter, Caitlin, was born to them on July 18, 1967.