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SPECTRAL DISTRIBUTIONS OF LIGHT SCATTERED IN DILUTE GASES AND GAS MIXTURES

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Abstract. — The analysis of Rayleigh-Brillouin scattering in dilute gases requires a molecular treatment when the wavelengths of the fluctuations observed become comparable to the collision mean free path. An initial-value problem based on the linearized Boltzmann equation can be formulated to calculate density correlation functions at any ratio of the wavelength to mean free path. In the present paper this approach is applied to binary gas mixtures. The presence of different types of density fluctuations causes the spectral distribution of scattered light to have interesting variations with the density and polarizability of each species. As specific applications, results of the analysis of recent measurements on xenon-helium mixtures by Clark and Benedek are discussed and a similar experiment on xenon-argon mixtures is proposed.

1. Introduction. — Light scattering in a rarefied gas is among the simplest problems in the study of density fluctuations in fluids. Since in this case the dielectric constant is directly proportional to the density [1], the spectral distribution of the scattered light provides a direct measure of the time-dependent density correlation function [2]. From the standpoint of static correlations, the gas is structureless and is of no interest. However, collisions among the gas atoms give rise to dynamical correlations which are characteristic of a many-body system and which can be effectively investigated by Rayleigh-Brillouin scattering.

In discussing dynamical correlations in gases it is convenient to introduce a dimensionless collision parameter $y$, which is a measure of the ratio of wavelength to mean free path. The relevant wavelength here is $2\pi/k$, with $k$ being the wavenumber transfer in the scattering experiment. Each observed spectral distribution is characterized by a value of $y$ which varies with experimental conditions such as scattering angle and gas properties such as pressure and temperature. If $y \gg 1$, the spectrum has the well-known hydrodynamic form consisting of a central Rayleigh component and two displaced Brillouin-Mandel'stam components [3]. If $y \ll 1$, the line shape will be essentially Gaussian which is characteristic of Doppler broadening. This is the collisionless or Knudsen limit. In the intermediate (kinetic) region where $y \sim 1$, the spectrum cannot be discussed in such simple terms because both collision and streaming effects are important in the description of thermal fluctuations. A molecular theory is then needed to carry out the analysis. In practice all three regions of $y$ are accessible by light scattering in gases under normal conditions.

Previous experimental and theoretical investigations of light scattering spectra of gases are concerned mostly with single-component systems [4]. But recently measurements of binary mixtures have been made [5], [6]. The spectral distribution of a multi-component gas contains the effects of density fluctuations in each species weighted by the square of the polarizability, and cross correlation effects are also present. The additional variables of concentration, as determined by the partial pressure of each species, and polarizability, as determined by the choice of gases, give new dimensions to the experiment as well as the analysis.

The purpose of this paper is to describe a kinetic theory approach to the analysis of light scattering spectra of gases. In particular we are interested in analyzing the recent measurements of Clark and Benedek on dilute mixtures of xenon and helium [5]. The Xe-He system is an example of large mass and

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polarizability differences between the species, and has a number of interesting features. The experiments were carried out at very low concentration of Xe and various values of He density. Some of the conditions clearly do not satisfy the criteria for hydrodynamic behavior, therefore a complete kinetic theory treatment seems appropriate.

In Sec. 2 we introduce the density correlation functions in a binary mixture and the various collision parameters. By solving the system of linearized Boltzmann equations as a particular initial-value problem, one can obtain correlation functions which are valid for all values of the collision parameters. At the present time explicit calculations have been made only for a special repulsive interatomic potential and in the context of a kinetic model. The kinetic theory approach has been developed more extensively in the case of single-component gases, and we briefly discuss this problem in Sec. 3. In Sec. 4 we show that several decompositions of the spectral distribution of a binary mixture are possible. Specific results for Xe-He are presented and compared with the data of Clark and Benedek. We also propose an experiment on Xe-A as an example where the masses and polarizabilities of the two species are more similar.

2. Density Fluctuations in Gases.— In a simple gas of \( N \) particles the dynamical variable which describes the instantaneous change in the number density is

\[
\delta n(r, t) = \sum_{i=1}^{N} \delta (r - R_i(t)) - \left< \sum_{i=1}^{N} \delta (r - R_i(t)) \right> \tag{2.1}
\]

where \( R_i(t) \), \( i = 1, \ldots, N \), are the particle position coordinates, and \( < > \) denotes an average over a thermal equilibrium ensemble. Density fluctuations in the gas are then described by the time correlation function

\[
G(r, t) = \frac{1}{n} < \delta n(r, t) \delta n(0, 0) > \tag{2.2}
\]

which obeys the sum rule

\[
\int_{-\infty}^{\infty} \frac{d\omega}{2\pi} S(k, \omega) = 1 \tag{2.4}
\]

where \( n \) is the uniform gas density. For a dilute gas the initial value of \( G(r, t) \) is \( G(r, 0) = \delta (r) \). The Fourier-space-time transform of (2.2) is

\[
S(k, \omega) = \int d^3r \int_{-\infty}^{\infty} dt \, G(r, t) e^{-i(k \cdot r - \omega t)} \tag{2.3}
\]

with \( \beta = (k_B T)^{-1} \). By solving this set of coupled equations with initial conditions \( h_a(rv; t=0) = \delta (r) \), \( h_b(rv; t=0) = 0 \), one obtains \( G_{aa}(r, t) \) and \( G_{bb}(r, t) \) obtained by interchanging the indices \( a \) and \( b \). The Fourier transforms \( S_{aa}(k, \omega) \) and \( S_{bb}(k, \omega) \) are normalized as in (2.4), but the cross correlations give

\[
\int_{-\infty}^{\infty} \frac{d\omega}{2\pi} S_{ab}(k, \omega) = \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} S_{ba}(k, \omega) = 0 \tag{2.7}
\]

which is also correct to terms independent of the density. Using the correlation functions for each type of particles, we can construct other correlations in the mixture such as concentration, total number and mass densities. These will be discussed in Sec. 4.

A general method of calculating correlation functions in gases involves the solution of an initial-value problem based on a linearized kinetic equation [8]. The equations appropriate to a binary mixture are the system of Boltzmann equations [9],

where \( \sigma_a, \sigma_b, \sigma_{ab} \) are the differential scattering cross sections for \( a-a \), \( b-b \), and \( a-b \) (or \( b-a \) ) collisions respectively, and \( \Phi(v) \) is the absolute Maxwellian distribution

\[
\Phi(v) = \left( \frac{\beta m_v}{2\pi} \right)^{3/2} \exp \left( -\frac{\beta m_v v^2}{2} \right) \quad a = a, b \tag{2.10}
\]

with \( \beta = (k_B T)^{-1} \). By solving this set of coupled equations with initial conditions \( h_a(rv; t=0) = \delta (r) \), \( h_b(rv; t=0) = 0 \), one obtains

\[
G_{aa}(r, t) = \int d^3v \, \Phi_a(v) \, h_a(rv; t) \tag{2.11}
\]

\[
G_{bb}(r, t) = \int d^3v \, \Phi_b(v) \, h_b(rv; t). \tag{2.12}
\]
On the other hand, using the initial conditions, $h_a(r = 0) = 0$, $h_b(r = 0) = \delta(r)$, gives $G_{ab}(r, t)$ and $G_{bb}(r, t)$. Notice that (2.8) and (2.9) are valid only for $t > 0$; however, this presents no difficulty in carrying out the Fourier time transformation since all the correlation functions are even in $t$.

The various collision terms in (2.8) and (2.9) have simple interpretations. For example, in (2.8) the term proportional to $n_a$ describes the self collisions among the type $a$ particles, whereas the term containing $n_b$ describes the $a$-$b$ collisions. Of course, in a one-component gas only the self collisions are present. If we consider very low concentrations of the type $a$ particles ($n_a \to 0$) and ignore the density fluctuations among the $b$ particles ($h_b \to 0$), then (2.8) becomes the kinetic equation for the test particle problem and the solution gives the van Hove self correlation function [11], [12].

The initial-value problem based on the linearized Boltzmann equation has been solved only in the case of repulsive interatomic potentials. Of particular interest is the Maxwell molecule interaction [13]

$$\sigma(r) = \frac{\kappa}{4r^2}$$

(2.12)

where $\kappa$ is the force constant usually determined by fitting a certain transport coefficient. In this case, the cross section $\sigma(v_{\parallel}, \theta)$ becomes inversely proportional to the relative speed $v_{\parallel}$, and the eigenfunctions and eigenvalues of the collision operator are known explicitly. One can now take advantage of the known properties of the potential (2.12) and formulate the calculation in terms of kinetic models. This approach is quite successful in producing very accurate solutions in the numerical sense [14]. Similar calculations also have been carried out for a gas of hard spheres. Recently, the method of kinetic models has been applied to a binary mixture of Maxwell molecules [10], [15], [16]. Some of the results will be discussed in Sec. 4.

One of the basic properties of kinetic-model solutions is that the correlation functions are insured to have the proper behavior in the hydrodynamic and Knudsen regimes. In the kinetic regime, one obtains smooth interpolations which have been shown to converge with higher order models [14]. For a simple gas it is straightforward to define the collision parameter $\gamma$. In a binary mixture there are four mean free paths and therefore there will be four wavelength to mean free path ratios. For a mixture of Maxwell molecules we can define

$$y_a = \frac{n_a}{kT_a} \left( \frac{\kappa_a}{m_a} \right)^{\frac{1}{2}}$$

$$y_{ab} = \frac{n_a}{kT_a} \left( \frac{\kappa_{ab}}{2 \mu} \right)^{\frac{1}{2}}$$

$$y_{ba} = \frac{n_b}{kT_b} \left( \frac{\kappa_{ab}}{2 \mu} \right)^{\frac{1}{2}}$$

(2.13)

where $v_t$ is the thermal speed $(\beta m_o)^{-\frac{1}{2}}$, $\mu$ is the reduced mass, and $| \lambda_{11} | = 0.436 ...$ is an eigenvalue of the self collision operator. It is possible to discuss the criteria for hydrodynamic behavior in terms of these dimensionless ratios, and one can show that the conditions can be fulfilled by different sets of $\gamma$ values [10], [15].

3. Spectra of Simple Gases. — The kinetic theory formulation of density fluctuations has been used to analyze the spectral distribution of light scattered in monatomic gases [4]. Greytak and Benedek [17] and later Clark and Benedek [5] have carried out measurements on dilute xenon gas at room temperature and over a range of pressures up to an atmosphere. Expressed in terms of the collision parameter $\gamma$, the experimental data lie in the region $0.1 \leq \gamma \leq 6$. At the higher end of this region the spectra are essentially hydrodynamic while at the lower end they have a nearly Gaussian profile. The xenon data have been found to be in good agreement with theoretical results obtained from the linearized Boltzmann equation. Two potentials, the Maxwell molecule interaction (2.12) and the hard sphere interaction, have been considered. In these calculations the force constant $\kappa$ or the hard sphere diameter was chosen to give the observed shear viscosity of the gas; therefore the comparison of calculated and measured relative intensities of the scattered light involves no adjustable parameter.

Although the room temperature data are found to be rather insensitive to the details of the repulsive part of the interatomic potential, it remains to study more thoroughly the temperature dependence of the spectral distributions. By choosing the temperature and density range properly, one may be able to observe a more pronounced effect of the attractive interactions. It is to be expected that in using a kinetic theory description based on purely repulsive interatomic interactions the force constant becomes a temperature-dependent quantity. On the other hand, when calculations using potentials with an attractive tail become feasible, it should not be necessary to introduce a temperature-dependent interaction.

Another characteristic feature of the spectral distribution in dilute gases which has not yet been verified is the scaling property. Since the spectrum of density fluctuations is completely characterized by the parameter $\gamma$, measurements carried out at different temperatures and densities should give the same result provided the scattering angle is also varied to keep the value of $\gamma$ unchanged. This property is a direct consequence of the Boltzmann equation and is independent of kinetic models. It could be used, for example, to help determine whether density effects beyond those treated by the Boltzmann equation are important in a given experiment.

4. Spectra of Binary Mixtures. — When light is scattered from a multi-component system, the resulting...
Spectral distribution may be analyzed in terms of different dynamical variables [15], [18]. One can express the spectrum as a sum of density correlation functions of the type discussed in Sec. 2. Alternatively, the spectrum can be decomposed into contributions arising from the total number density and concentration fluctuations. Still other sets of variables may be used. Since the different variables are rather simply related, the choice of one set over another appears to depend on the type of information desired.

Consider first the density fluctuations defined in Sec. 2. The spectrum of scattered light, normalized on the basis of unit integrated intensity, can be written as

\[ I(k, \omega) = R_{nn}(k, \omega) \]  

where

\[ R_{nn} = \frac{n_a \alpha_a^2}{A} = 1 - R_{bb} \]  

\[ R_{bb} = \frac{2 \, n_b \alpha_a \alpha_b}{A} \]  

\[ A = n_a \alpha_a^2 + n_b \alpha_b^2 \]

where \( \alpha_a, \alpha_b \) are the atomic polarizabilities of the two species. In view of (2.7) we see that \( R_{aa} \) and \( R_{bb} \) give the fractions of integrated intensity arising from a-a and b-b density fluctuations respectively. As one would expect, the relative intensity of each contribution varies as the density and the square of the atomic polarizability.

We can construct another set of dynamical variables. Let

\[ n(r, t) = n_a(r, t) + n_b(r, t) \]  

\[ \rho(r, t) = m_a n_a(r, t) + m_b n_b(r, t) \]  

\[ c(r, t) = \frac{m_a n_a(r, t)}{\rho(r, t)} \]

be the total number density, mass density, and concentration variables. We define correlation functions \( S_{nn}, S_{pp}, S_{cc}, \) etc., in terms of the deviations of these variables from their equilibrium values. For example, if

\[ S_{nn}(k, \omega) = \int d^3r \int_{-\infty}^{\infty} dt \, <\delta n(r, t) \delta n(0, 0) > e^{-i(k \cdot r - \omega t)} . \]

Notice that unlike the correlation functions of Sec. 2 we do not include a multiplicative factor like \( 1/n_a \) (cf. (2.5)).

One can see that \( \delta n \) and \( \delta c \) are statistically independent in a dilute gas, since \( S_{nn}(k, \omega) \) has a vanishing frequency integral in the sense of (2.7). By choosing \( n(r, t) \) and \( c(r, t) \) as the dynamical variables, we find

\[ I(k, \omega) = R_{nn}(k, \omega) \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} S_{nn}(k, \omega) \]  

\[ + R_{cc}(k, \omega) \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} S_{cc}(k, \omega) \]

where

\[ R_{nn} = \frac{1}{nA} (n_a \alpha_a + n_b \alpha_b)^2 \]  

\[ R_{cc} = \frac{n_a n_b (\alpha_a - \alpha_b)^2}{nA} = 1 - R_{nn} \]  

\[ R_{cc} = \frac{2 n_a n_b}{c(1-c) n^2 A} (\alpha_a - \alpha_b) (n_a \alpha_a + n_b \alpha_b) . \]

The relative contributions to the integrated intensity from number density and correlation fluctuations are given by \( R_{nn} \) and \( R_{cc} \). If \( \alpha_a = \alpha_b, I(k, \omega) \) can depend only on \( S_{nn} \) for any ratio of \( n_a/n_b \). It is interesting to note that they can be rewritten as

\[ n^2 \bar{\alpha}^2 R_{nn} = \bar{\alpha}^2 \]  

\[ n^2 \bar{\alpha}^2 R_{cc} = \bar{\alpha}^2 - \bar{\alpha}^2 \]

where \( \bar{\alpha} \) is the average polarizability

\[ \bar{\alpha} = \frac{n_a \alpha_a + n_b \alpha_b}{n} . \]

According to (4.11') concentration fluctuations can be observed by light scattering whenever \( \bar{\alpha}^2 \neq \bar{\alpha}^2 \) that is, whenever there are fluctuations in the polarizability. One should in fact compare (4.10') and (4.11') with similar expressions for the coherent and incoherent neutron scattering lengths for a system of nuclei which have nonzero spin or a distribution of isotopes. This suggests that the concentration correlation function should have behavior similar to the van Hove self correlation function.

One can choose a third set of variables which include the mass density \( \delta \rho(r, t) \). The combination of density fluctuations which is statistically independent of \( \delta \rho(r, t) \) is

\[ \delta \sigma(r, t) = \rho_b \delta n_b(r, t) + \rho_a \delta n_a(r, t) \]  

The relative contribution to the integrated intensity from mass density fluctuations is

\[ R_{\delta \rho} = \frac{(\rho_a \alpha_a + \rho_b \alpha_b)^2}{A(m_a \rho_a + m_b \rho_b)} . \]
If \( \frac{\sigma_a}{\sigma_b} = \frac{m_a}{m_b} \), then \( R_{pp} = 1 \), \( R_{aa} = R_{pp} = 0 \), and

\[
I(k, \omega) = \frac{S_{pp}(k, \omega)}{\int_{-\infty}^{\infty} \frac{d\omega}{2\pi} S_{pp}(k, \omega)}. \tag{4.16}
\]

We now specialize our discussions to a dilute mixture of xenon and helium. Recently Clark and Benedek have carried out a series of spectral measurements on such a system using a 6 328 Å laser and a scattering angle of 10.6°. In these measurements the Xe density was fixed and the He density was varied. Table I shows the two cases which we will consider in some detail. We label the Xe and He atoms as a and b particles respectively. The low Xe concentration means that Xe-Xe collision effects will be small, but they are not entirely negligible because the deviation of the pure Xe spectrum from a strictly Gaussian distribution was quite observable in the data [5].

**Table I**

Partial pressures, collision parameters, and integrated intensity factors in the Clark-Benedek experiment. (xenon is the a-gas and helium is the b-gas.)

<table>
<thead>
<tr>
<th>Case A</th>
<th>Case B</th>
</tr>
</thead>
<tbody>
<tr>
<td>( P_a ) (atm)</td>
<td>0.022</td>
</tr>
<tr>
<td>( P_b ) (atm)</td>
<td>0.78</td>
</tr>
<tr>
<td>( \gamma_a )</td>
<td>0.184</td>
</tr>
<tr>
<td>( \gamma_{ab} )</td>
<td>31.34</td>
</tr>
<tr>
<td>( \gamma_b )</td>
<td>1.317</td>
</tr>
<tr>
<td>( \gamma_{ba} )</td>
<td>0.155</td>
</tr>
<tr>
<td>( R_{aa} )</td>
<td>0.915</td>
</tr>
<tr>
<td>( R_{bb} )</td>
<td>0.085</td>
</tr>
<tr>
<td>( R_{ab} )</td>
<td>0.200</td>
</tr>
<tr>
<td>( R_{ba} )</td>
<td>0.800</td>
</tr>
<tr>
<td>( R_{pp} )</td>
<td>0.986</td>
</tr>
<tr>
<td>( R_{uu} )</td>
<td>0.014</td>
</tr>
</tbody>
</table>

The various collision parameters given in Table 1 have been obtained by fitting the Maxwell molecule potential parameters \( \kappa_{aa} \), \( \kappa_{bb} \), and \( \kappa_{ab} \) to appropriate transport coefficients [10], [15]. For \( \gamma_a \) and \( \gamma_b \) we use the experimental values of shear viscosity of pure Xe and He respectively. For the cross collisions we find \( \kappa_{ab} \) by considering the shear viscosity and thermal conductivity of the mixture. The value of \( \kappa_{ab} \) deduced in this way gives a predicted diffusion coefficient that is within 2% of the measured value. In Case B the helium pressure has been increased by about a factor of 4. This increase in \( n_b \) leads to a corresponding increase in \( \gamma_b \) and \( \gamma_{ab} \). We can therefore expect the spectrum of Case B to show a more hydrodynamic behavior.

The different \( R \) factors in Table 1 give the relative contributions to the integrated intensity. In both cases \( R_{pp} \) is seen to be very nearly unity, which means that one is measuring mostly mass density fluctuations in this experiment. From the discussions above, this is not too surprising since \( \sigma \) is roughly proportional to the number of electrons and \( m \) is proportional to the number of nucleons. For the Xe-He system, \( (m_{He}/m_{Xe}) = 0.0305 \), and we have from dielectric data at 6 328 Å \( (\sigma_{He}/\sigma_{Xe}) = 0.0514 \). The variations in \( R_{aa} \) and \( R_{bb} \) from Case A to Case B are consistent with the increase in helium pressure. In Case B the helium pressure is about 100 times greater than the xenon pressure, but \( R_{aa} \) shows that about 65% of the total scattering is still due to xenon concentration fluctuations. The reason, of course, is that the scattering power of a xenon atom is almost 400 times that of a helium atom.

The comparison of calculated intensity spectra and experimental points is shown in figures 1 and 2. The theoretical results were obtained from a Maxwell molecule kinetic model [15] and each spectrum has been convolved with an instrumental resolution function. Since only relative intensities are measured, we have arbitrarily normalized the calculations to the data by requiring an overall fit. This procedure clearly has no effect on the relative intensities which are in excellent agreement between theory and experiment.
heat conduction and concentration diffusion effects are not separable, but in the absence of thermal diffusion the Rayleigh line, in the hydrodynamic regime, becomes a sum of two Lorentzians. This long wavelength limit behavior was first pointed out by Mountain and Deutch [19] and is also obtained in the present kinetic theory description.

When the collision parameters are of order unity, the fluctuations are no longer adequately described by hydrodynamic theory. In the Clark-Benedek experiment it appears that Case A is not likely to be hydrodynamic. The nonhydrodynamic behavior is illustrated in figure 3 which shows a comparison of the concentration fluctuations as obtained by kinetic theory and hydrodynamic calculations. The hydrodynamic result is a Lorentzian with half width \( Dk^2 \), where \( D \) is the diffusion coefficient. This is about 20% greater than the width of the kinetic theory spectrum, but when resolution effects are taken into account the difference is less pronounced.

The Xe-He mixture represents a system with large disparity in masses and polarizabilities. It is also interesting to examine a system where the two species are more similar. The mixture of Xe-Kr could be considered, but the transport properties of this system are not very well known. Therefore we choose to analyze the binary mixture of Xe-A. Figure 4a shows the theoretical spectra corresponding to \( y_a = 0.75 \), \( y_b = 0.233 \), \( y_{ab} = y_{ba} = 1.035 \). These values may be achieved with a scattering angle of 10.6° and partial pressures of 0.09 and 0.05 atmospheres for Xe (a-gas) and A (b-gas) respectively. Higher pressures can be used if the scattering angle is also increased. The various density fluctuation components are shown in figure 4a along with the hydrodynamic calculation. As in figures 1 and 2, we see a cancellation between \( R_{ba} S_{ab} \) and \( R_{ba} S_{ba} \) in the vicinity of the origin, and out in the wings their effects are additive. In this case the cross correlation effects are quite large and are

\[
I(k\omega) = R_{aa} S_{aa}(k\omega) + R_{bb} S_{bb}(k\omega) + R_{ba} S_{ba}(k\omega) + R_{ab} S_{ab}(k\omega)
\]

\[
I(k\omega) \quad \text{Hydrodynamic}
\]

(\( p_a = .09008 \ \text{atm}, \ p_b = .04968 \ \text{atm if scattering angle is 10.6°}).}
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primarily responsible for the pronounced shoulder in the spectral distribution. This behavior indicates that both species participate in the propagation of collective motions. In contrast, figure 2 shows that collective motions in the Xe-He mixture involve mostly only the helium atoms.

The results shown in figure 4a do not include instrumental resolution effects. When this broadening is taken into account, the kinetic and hydrodynamic spectra appear as shown in figure 4b. The structure in the kinetic theory prediction is lost, but there is still a difference of about 15% in the half width. Such deviations should be observable with present experimental precisions.

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