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BRILLOUIN AND RAYLEIGH SCATTERING
IN RELAXING LIQUIDS

by

EUGENE YUEN-CHING TONG

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The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies for acceptance, a thesis entitled BRILLOUIN AND RAYLEIGH SCATTERING IN RELAXING LIQUIDS, submitted by Eugene Yuen-Ching Tong in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

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ABSTRACT

Using Van Hove's density correlation-function technique we have calculated the intensity spectrum of light scattered by a relaxing liquid. Our treatment differs from the previous work on the subject, due to Mountain, in two respects: (a) the liquid is assumed to have a relaxing instead of a static shear viscosity, and (b) instead of using the time integral representation for the relaxing bulk viscosity, we consider it to arise from the relaxation of an ordering parameter, and apply the thermodynamic theory of relaxation processes to calculate the correlation function. The first modification is necessary if the theory is to explain the occurrence of Brillouin components in highly viscous liquids like glycerine. The second modification gives an insight into the nature of approximations involved in using the integral representation for the bulk viscosity.

We first solve the scattering problem for a model in which the shear and the bulk relaxation processes are each characterized by a single relaxation time. Our analysis shows that, provided the sound absorption per cycle is small compared with unity, the spectral intensity may be approximately written as a sum of five Lorentzians. Two of these represent the Brillouin components, and the other three form the central component. It is also shown that the time integral representation of the bulk viscosity cannot in general describe a temperature induced relaxation process, but is appropriate for a density induced relaxation process.

We next solve the scattering problem for the case when the relaxing viscosities are each described by a multiple or a distribution of relaxation times, instead of a single relaxation time. Both exact and approximate expressions for the intensity spectrum are obtained for this case.

Further it is pointed out that one should distinguish between the sound velocity v for a temporally absorbed hypersonic wave and the velocity v_B as determined from the Doppler-shifted Brillouin peaks. The dispersion relations for v and v_B for the case of a single relaxation time are discussed in detail, and the conditions for negative dispersion (decrease in v or v_B with increasing wave number) are obtained. The difference between v and v_B is significant whenever the sound absorption per cycle is not much smaller than unity.

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GENERAL INTRODUCTION

The subject of light scattering is nearly a hundred years old, dating back to the work of Rayleigh [1] and Einstein [2]. It has been a useful tool for the study of a variety of molecular phenomena. In the last decade, with the development of laser techniques and high-precision detection devices, light scattering has opened up new possibilities for the study of molecular kinetics and for the investigation of acoustic properties of fluids in the ultra high frequency (hypersonic) region (frequency $\gtrsim 10^{10}$ c/s), which is otherwise difficult to study by the usual ultrasonic methods.

It is well known that the scattering of light by a homogeneous medium mainly arises from the local fluctuations in the density ρ of the medium due to thermal agitations. These density fluctuations give rise to fluctuations in the dielectric constant ε of the medium and hence to scattering of light. A Fourier analysis of the density fluctuations over the volume of the scattering medium results in a very large number of hypersonic waves each specified by a wave vector $\vec{k}$. These sound waves act substantially as diffraction gratings for the scattering of light. The spectrum then consists of two Doppler shifted or Brillouin components corresponding to sound propagation in opposite directions (for a given $\vec{k}$). In addition there is a central or Rayleigh component which has a peak at the incident frequency. This component arises from a nonpropagating (diffusive) mode which decays as entropy fluctuations.

Both the Brillouin components and the Rayleigh component have certain line widths which depend on the rates at which the propagating (sound) and the diffusive modes decay. It is only in the last few years, with the advent of laser techniques and the availability of intense monochromatic light beams, that it is becoming increasingly possible to measure the widths and line shapes of the Rayleigh and Brillouin components. This in turn has revived interest in theoretical calculations of the spectral distribution of the scattered light.

In Chapter 1 of this thesis we briefly review some of the important early work on the subject. Some aspects of sound absorption in fluids and of the thermodynamic theory of relaxation processes are reviewed respectively in Chapters 2 and 3. Chapter 4 describes the Van Hove's density-correlation function technique, as adapted by Kamarov and Fisher [20] to calculate the spectral distribution of scattered light. These chapters form the prerequisite to our work which is described in subsequent pages.

In Chapter 5 we derive the spectral distribution for a fluid in which sound is absorbed owing to its thermal conductivity and to relaxing shear and bulk viscosities, each having a single relaxation time. The relationship of our work to those of previous authors is described in the Introduction to this Chapter. Chapter 6 points out the necessity of distinguishing between the sound velocity as measured by Brillouin scattering and that by other (ultrasonic) techniques. Chapter 7 is devoted to the extension of the theory of Chapter 5 to the case of a fluid in which the two viscosities are each characterized by a set (discrete and continuum) of relaxation times. A summary and discussion of the main results is given in Chapter 8. The calculation of the spectral intensities involves expressions for the mean square fluctuations in the various thermodynamic quantities. These are derived in the Appendix.

Chapter 1

EARLY WORK

§1.1 Rayleigh Scattering

In an experiment carried out by Tyndall in 1869 [3], in which he investigated the scattering of light by fine particles, he observed a bluish hue in the scattered spectrum and that the scattered light was polarized at an angle of 90° to the direction of the incident light. Theoretical investigation of the problem was later taken by Rayleigh in 1871 [1]. He applied the electromagnetic theory to a system of optically isotropic particles whose size is small compared with the optical wavelength. The incident field is then assumed to be practically uniform throughout each of the particles and induces oscillatory electric dipoles in them. These serve as secondary sources of light and radiate light in the form of scattering. For observation at a large distance from the scattering medium, it is enough to consider only dipole scattering. The total scattered intensity should depend on the superposition of the individual wavelets with the proper phases from each of the molecular dipoles. But Rayleigh assumed that these phases are at random so that the total intensity is the sum of the individual intensities. This is equivalent to assuming that there is no correlation between the molecules, which is justified for very dilute systems like an ideal gas. The expression for the scattered intensity per unit volume per unit incident intensity is

$$I = \frac{16\pi^4 n\alpha^2}{R^2\lambda^4} \sin^2 \phi, \tag{1}$$

where α is the average polarizability of the particles, λ the wavelength of incident light, n the number density of the particles, $\vec{R}$ is the point of observation assumed to be far away from the scattering medium, and ϕ the angle between $\vec{R}$ and the direction of the incident electric vector.

If the incident light is not polarized, Eq. (1) must be averaged over all directions of the electric vector in a plane perpendicular to the direction of propagation of the incident light. One then has

$$I = \frac{8\pi^4}{R^2} \frac{n\alpha^2}{\lambda^4} (1 + \cos^2\theta) , \tag{2}$$

where θ is the scattering angle.

§1.2 The work of Einstein and Smolukowski

As we stated before, the assumption which one makes in Rayleigh's theory of light scattering is that the particles are random scatterers. For dense fluid media, especially liquids, one should expect that the molecules will not move independently of each other, and therefore the above assumption will not be justified. Indeed, experiments show that the scattering formula given by Eq. (1) or (2) does not predict correct results for liquids.

Let us now consider a homogeneous liquid as the scattering medium. A simple application of Huygen's principle shows that such a medium can scatter no light because of the destructive interference from neighbouring small volumes, except, of course, in the forward direction. This is contrary to observations. One can therefore conclude from this that there must exist in the medium some inhomogeneities which are responsible for the observed scattering of light, although the liquid is on the average homogeneous. This problem was solved by Einstein and Smolukowski [2,4] who first used the concept of thermodynamic fluctuations to explain the large intensity of scattering observed for gases near their critical temperatures, a phenomenon known as critical opalescence. According to them, the molecules in a liquid are not distributed uniformly, but rather their number fluctuates from their mean value in any small volume element of the liquid. These fluctuations arise from thermal agitations of the molecules and they in turn produce fluctuations in the dielectric constant ε[†]. Thus the scattering system is really not homogeneous locally. So unlike the single particle scattering theory of Rayleigh, the theory of Smolukowski and Einstein considers scattering by small volumes in the fluid, so that though there may be molecular correlations, the small volumes are large enough to be statistically independent of each other, and scatter light incoherently.

Let us divide the scattering medium into small regions or cells whose linear dimensions are small compared with the optical wavelength λ but are large enough to contain sufficiently many molecules to allow one to use thermodynamic description. Consider a particular cell of volume δV_j. Let the dielectric constant at some instant of time be $\varepsilon_j = \varepsilon_o + \delta\varepsilon_j$, where ε_o is the mean dielectric constant of the medium and $\delta\varepsilon_j$ is the fluctuation.

The relevant electromagnetic equations (in Gaussian units) for our system are

---

[†] The fluctuations in the dielectric constant can also arise from the fluctuations in the orientation of the molecules, if they are anisotropic. This effect will not be considered here.

$$\text{curl } \vec{H} = \frac{1}{c}\dot{\vec{D}} \ , \quad \text{div } \vec{D} = 0$$

$$\text{curl } \vec{E} = -\frac{1}{c}\dot{\vec{H}} \ , \quad \text{div } \vec{H} = 0$$

$$\vec{D} = \ \varepsilon\ \vec{E} = \vec{E} + 4\pi\ \vec{P} \ , \quad \vec{P} = \frac{\varepsilon-1}{4\pi}\vec{E} \tag{3}$$

Hence a fluctuation $\delta\varepsilon_j$ will result in an additional polarization $\Delta\vec{P}$, giving rise to the scattered fields $\vec{E}'$, $\vec{D}'$ and $\vec{H}'$. We are only interested in linear effects. Assuming that $|\delta\varepsilon_j| \ll \varepsilon_o$, $|\vec{E}'| \ll |\vec{E}|$ etc., we have

$$\text{curl } \vec{H}' = \frac{1}{c}\dot{\vec{D}}' \ , \quad \text{div } \vec{D}' = 0$$

$$\text{curl } \vec{E}' = -\frac{1}{c}\dot{\vec{H}} \ , \quad \text{div } \vec{H}' = 0$$

$$\vec{D}' = \varepsilon_o\vec{E}' + \delta\varepsilon\vec{E}_o = \varepsilon_o\vec{E}' + 4\pi\Delta\vec{P}$$

$$\Delta\vec{P} = \frac{\Delta\varepsilon}{4\pi}\vec{E}_o \ , \tag{4}$$

where $\vec{E}_o$ is the incident electric vector. Eliminating $\vec{H}'$ and $\vec{E}'$ from (4), one gets

$$\nabla^2\vec{D}' - \frac{\varepsilon_o}{c^2}\ddot{\vec{D}}' = -\text{ curl curl } (\delta\varepsilon_j\vec{E}_o) \quad . \tag{5}$$

We now define $\sqrt{\varepsilon_o}\ \tau = t$, so that (5) is transformed into

$$\nabla^2\vec{D}' - \frac{1}{c^2}\frac{\partial^2}{\partial\tau^2}\vec{D}' = -\text{ curl curl } (\delta\varepsilon_j\vec{E}_o) \ . \tag{6}$$

The solution of this equation is readily obtained in terms of retarded potential

$$\vec{D}' = \text{curl curl } \vec{\Pi}$$

$$\vec{\Pi} = \int_{\delta V_j} \frac{\Delta\vec{P}(\vec{r},\tau)}{|\vec{R} - \vec{r}|} \bigg|_{\tau - \frac{|\vec{R}-\vec{r}|}{c}} d^3\vec{r}$$

$$= \frac{1}{4\pi} \int_{\delta V_j} \frac{(\delta\varepsilon_j \vec{E}_o)}{|\vec{R}-\vec{r}|} \bigg|_{\tau - \frac{|\vec{R}-\vec{r}|}{c}} d^3\vec{r} \qquad (7)$$

As the volume δV_j has dimensions much smaller than λ, (7) can be written as

$$\vec{\Pi} \simeq \frac{1}{4\pi} \frac{(\delta\varepsilon_j \vec{E}_o)\delta V_j}{|\vec{R}-\vec{r}_j|} \bigg|_{\tau - \frac{|\vec{R}-\vec{r}_j|}{c}} \quad , \qquad (8)$$

Here R is the point of observation and $\vec{r}_j$ is the position of the volume δV_j.

We shall be interested only in observations at large distances from the scattering medium, so that $|\vec{R}-\vec{r}_j| \simeq R$.

The incident electric vector E_o can be written as

$$\vec{E}_o = \vec{E}_1 \, e^{-i(\vec{\kappa}_o \cdot \vec{r}_j - \Omega_o t)} \quad , \qquad (9)$$

where Ω_o is the angular frequency of the incident light and $\vec{\kappa}_o$ is its wave vector. Since the wave number of the scattered wave κ' is equal to $\frac{\Omega_o\sqrt{\varepsilon_o}}{c}$, (8) can be written as

$$\vec{\Pi} = \frac{\vec{E}_1 e^{i\Omega_o t}}{4\pi R} \, e^{-i\vec{\kappa}' \cdot \vec{R}} (\delta\varepsilon_j \delta V_j) \, e^{i(\vec{\kappa}' - \vec{\kappa}_o) \cdot \vec{r}_j} \quad . \qquad (10)$$

Now regarding ε as a function of ρ and T, one has

$$\delta\varepsilon_j = \left(\frac{\partial\,\varepsilon_j}{\partial\,\rho}\right)_T \delta\rho + \left(\frac{\partial\,\varepsilon_j}{\partial\,T}\right)_\rho \delta T\ . \qquad (11)$$

We assume, as customary, that the second term can be neglected compared with the first†. Hence,

$$\delta\varepsilon_j \simeq \left(\frac{\partial\,\varepsilon}{\partial\,\rho}\right)_T \delta\rho_j = \left(\frac{\partial\,\varepsilon}{\partial\,n}\right)_T \delta n_j \qquad (11')$$

and (10) becomes

$$\vec{\Pi} = \vec{E}_1 e^{i\Omega_o t}\, e^{-i\vec{\kappa}'.\vec{R}}\, \frac{1}{4\pi R} \left(\frac{\partial\,\varepsilon}{\partial\,n}\right)_T \delta N_j\, e^{i(\vec{\kappa}'-\vec{\kappa}_o).\vec{r}_j} \qquad (12)$$

where $\delta N_j (\equiv \delta n_j \delta V_j)$ is the number fluctuation in the volume δV_j. To get $\vec{E}'$, one must evaluate curl curl $\vec{\Pi}$. For large R,

$$\text{curl curl}\ \frac{\vec{E}_1 e^{i\vec{\kappa}'.\vec{R}}}{R} \simeq \frac{1}{R}\ \text{curl curl}\ \vec{E}_1 e^{i\vec{\kappa}'.\vec{R}}$$

$$= \frac{1}{R} \{\text{grad}(\text{div}\ \vec{E}_1 e^{i\vec{\kappa}'.\vec{R}}) - \nabla^2(\vec{E}_1 e^{i\vec{\kappa}'.\vec{R}})\}$$

$$\simeq \frac{1}{R} \{-|\vec{E}_1|\kappa'\vec{\kappa}'\cos\phi\ e^{i\vec{\kappa}'.\vec{R}} + \kappa'^2 \vec{E}_1 e^{i\vec{\kappa}'.\vec{R}}\} \equiv \vec{G} \propto \vec{E}' \qquad (13)$$

---

† This neglect implies that $\left(\frac{\partial\,\varepsilon}{\partial\,T}\right)^2_\rho \langle\delta T^2\rangle \ll \left(\frac{\partial\,\varepsilon}{\partial\,\rho}\right)^2_T \langle\delta\rho^2\rangle$, where $\langle\delta T^2\rangle$ and $\langle\delta\rho^2\rangle$ are the mean square fluctuations of temperature and density respectively. There is some evidence, though not conclusive, that for water this assumption may not be a very good approximation. See [5].

where ϕ is the angle between $\vec{\kappa}'$ and $\vec{E}_1$. From (13), it can be verified easily that $\vec{E}'.\vec{\kappa}' = 0$, and that

$$|\vec{G}| = \frac{|E_1|}{R} \kappa'^2 \sin\phi \quad . \tag{14}$$

Now far away from the scattering medium, we have $\Delta\vec{P} = 0$, so that (4) and (14) give

$$\vec{E}' = \frac{1}{\varepsilon_o} \vec{D}' = \frac{1}{4\pi\varepsilon_o} \vec{G} \left(\frac{\partial \varepsilon}{\partial n}\right)_T \delta N_j \, e^{i(\vec{\kappa}'-\vec{\kappa}_o).\vec{r}_j} \quad . \tag{15}$$

Hence

$$|\vec{E}'|^2 = \frac{|\vec{E}_1|^2}{16\pi^2 R^2 \varepsilon_o^2} \kappa'^4 \sin^2\phi \left(\frac{\partial \varepsilon}{\partial n}\right)_T^2 \delta N_j^2 \quad . \tag{16}$$

The intensity per unit incident intensity is then given by

$$I_j = \frac{\Omega_o^4}{16\pi^2 R^2 c^4} \sin^2\phi \left(\frac{\partial \varepsilon}{\partial n}\right)_T^2 < \delta N_j^2 > \quad . \tag{17}$$

We can now make the assumption that for a liquid not close to its critical point, fluctuations in different cells are statistically independent, since then molecular correlation extends only to molecular distances. Therefore, the total intensity will be the sum of the contributions from all the cells, i.e. $I=\sum_j I_j$. From the thermodynamic theory of fluctuations [see Appendix],

$$<\delta N_j^2> = \frac{k_B T_o n_o^2 \delta V_j}{B_T} \quad , \tag{18}$$

where n_o and T_o are the equilibrium number density and temperature respectively. Therefore the total intensity is

$$I = \frac{V\ k_B T_o}{16\pi^2 B_T R^2} \left(\frac{\Omega_o}{c}\right)^4 \left[\rho\left(\frac{\partial \varepsilon}{\partial \rho}\right)_T\right]^2_{\rho=\rho_o} \sin^2\phi \tag{19}$$

where V is the total scattering volume. The expression (19) is the well-known result of Einstein.

For an ideal gas, $PV=N\,k_B\,T_o$, so that $B_T=n_o k_B T$. Further the polarizability $\alpha=(\varepsilon-1)/4\pi n_o$, so that one may write

$$\alpha = \frac{1}{4\pi n_o}\ \rho_o \left(\frac{\partial \varepsilon}{\partial \rho}\right)_T \quad . \tag{20}$$

If one substitutes (20) into (19), one sees that (19) becomes identical with the Rayleigh formula, eq. (1) above.

Now in order to make (19) useful for practical purposes, one needs to know how ε and ρ depend on each other. Einstein used the Clausius-Mossotti or Lorentz-Lorenz relation

$$\frac{\varepsilon-1}{\varepsilon+2}\,\frac{1}{\rho} = \text{constant} \tag{21}$$

Therefore

$$\rho_o\left(\frac{\partial \varepsilon}{\partial \rho}\right)_T = \frac{(\varepsilon_o - 1)(\varepsilon_o + 2)}{3} \quad . \tag{22}$$

If (22) is substituted into (19), the resulting formula is known to hold well for dilute gases ($\varepsilon_o \simeq 1$) but not as well in dense fluids and rather poorly for polar molecules. Ramanathan and others [6,7] have ascribed this to the inadequacy of using the Lorentz local field approximation. According to these authors, a more satisfactory relation to use, for light scattering problems, is[†]

$$\frac{\varepsilon - 1}{\rho} = \text{constant} \tag{23}$$

If we substitute (23) into (19), we have

$$I = \frac{V\, k_B T_o}{16\pi^2 B_T R^2} \left(\frac{\Omega_o}{c}\right)^4 (\varepsilon_o - 1)^2 \sin^2\phi\ . \tag{24}$$

Expression (24) is known to give better agreement with experiments for most liquids than the use of (21) in (19) [6,7].

§1.3 Fine Structure of the Rayleigh Line

A. Brillouin Mandelstam Doublets

The fine structure of the Rayleigh line was first predicted by Brillouin in 1922 [8], and later also by Mandelstam [9]. In analogy to the Debye waves in solids,

---

[†] Mathematical justification for this step is lacking at the present time.

Brillouin considered that the description of the thermal motions of the molecules in a liquid is equivalent to a superposition of a large number of elastic sound waves of different wave vectors $\vec{k}$. Provided such a Fourier analysis is carried out over a volume of the scattering medium whose linear dimensions are all large compared with the wavelength of light, each Fourier component substantially acts as a diffraction grating. In other words the wave-vectors $\vec{\kappa}_0$ and $\vec{\kappa}'$ of the incident and scattered light beams respectively are related to the wave-vector $\vec{k}$ of the sound wave by the well known Bragg condition $\vec{\kappa}'-\vec{\kappa}_0 = \vec{k}$. One can arrive at this formula most easily if in (7), one considers the contribution to $\vec{\Pi}$ from the whole scattering volume, so that

$$\vec{\Pi} = \frac{1}{4\pi}\int_V \frac{(\delta\varepsilon\vec{E})}{|\vec{R}-\vec{r}|}\Bigg|_{\tau - \frac{|\vec{R}-\vec{r}|}{c}} dV \quad . \tag{25}$$

Then (15) becomes

$$\vec{E}' = \frac{1}{4\pi\varepsilon_0}\vec{G}\left(\frac{\partial\varepsilon}{\partial\rho}\right)_T \int_V \delta\rho e^{i(\vec{\kappa}'-\vec{\kappa}_0).\vec{r}}\, d^3\vec{r} \ . \tag{26}$$

Fourier analysing $\delta\rho$, noting that the elastic sound waves are standing waves, we write

$$\begin{aligned}\delta\rho &= \sum_{\vec{k}} \rho(\vec{k}) \cos \vec{k}.\vec{r} \\ &= \tfrac{1}{2}\sum_{\vec{k}} \rho(k)\left[e^{i\vec{k}.\vec{r}} + e^{-i\vec{k}.\vec{r}}\right] \quad .\end{aligned} \tag{27}$$

Substituting this into (26), and making use of the fact that the integral $\int_V e^{i\vec{q}\cdot\vec{r}}\, d^3\vec{r}$ differs from zero for large volumes of V and is equal to V only under the condition q=0, we obtain

$$\vec{E}' = \frac{1}{4\pi\varepsilon_0} \vec{G} \left(\frac{\partial\varepsilon}{\partial\rho}\right)_T \tfrac{1}{2} V[\rho(k) + \rho(-k)] \ , \tag{28}$$

with the condition

$$\pm\vec{k} = \vec{\kappa}' - \vec{\kappa}_0 \ . \tag{29}$$

Expression (28) will lead to Einstein's formula (19) if one makes use of the following results from the theory of fluctuations [see Appendix]

$$< \rho(k)\rho(-k)> = \frac{\rho_0^2 k_B T_0}{V\ B_T} \tag{30}$$

$$< \rho(k)\rho(k) > = 0 \ . \tag{31}$$

If θ denotes the angle of scattering, then the Bragg condition (29) may be written in the more familiar form as

$$k = \frac{2\Omega_0\mu}{c} \sin \tfrac{1}{2}\theta \tag{32}$$

or

$$2\Lambda \sin\tfrac{1}{2}\theta = \lambda \ , \tag{33}$$

where μ is the refractive index of the medium, Λ is the wavelength of the sound wave and λ is the optical wavelength in the medium.

Now if the homogeneities were static, the scattered light would have the same frequency as the incident beam. Since the sound waves are moving, the time varying inhomogeneities will modulate the scattered light. Let the latter be denoted by

$$\vec{E}'_p \ \alpha \ e^{i\Omega_o t} \ \phi(t) \ , \qquad (34) \qquad \propto$$

where $\phi(t)$ is the modulation function. We shall see later that $\phi(t)$ arises from fluctuations in pressure or density at constant entropy, which propagate through the medium with the sound velocity v. Hence to a first approximation $\phi(t)$ may be expected to obey the wave equation

$$\ddot{\phi}(t) - v^2\nabla^2\phi = 0 \ . \qquad (35)$$

Since the standing wave solution of (35) is relevant, we have

$$\phi(t) \ \alpha \ \cos \omega t \ \cos \vec{k}.\vec{r} \ , \qquad (36) \qquad \propto$$

where $\omega = vk$. Therefore, we have

$$\begin{aligned} \vec{E}'_p \ \alpha \ & e^{i\Omega_o t} \ [e^{i\omega t} + e^{-i\omega t}] \qquad \propto \\ & = e^{i[(\Omega_o+\omega)t]} + e^{i[(\Omega_o-\omega)t]} \ . \qquad (37) \end{aligned}$$

Thus in the scattered light there are two components. One has angular frequency $\Omega_o - \omega$, and is called the Stokes line. The other has angular frequency $\Omega_o + \omega$, and is called the anti-Stokes line. From (32), the shift in frequency is given by

$$\Delta\Omega = \omega(\vec{k}) = 2 \frac{v}{c}\mu \, \Omega_o \sin \tfrac{1}{2} \theta \ . \tag{38}$$

This result is consistent with the fact that two opposite going sound waves give rise to a Doppler shift effect of precisely the same quantity as (38).

The Brillouin components obtained from (37) are infinitely sharp. In practice they have finite line widths. We shall see later that this is because sound waves are absorbed in the medium.

From (33) it can be seen that for incident light in the visible spectrum, λ is of the order of 5×10^{-5} cm. Since the velocity of sound is of the order 10^4 cm/sec, the frequency of sound wave involved is of the order of 10^9 or 10^{10} cycles per second. Sound waves of such high frequencies are called hypersonic or ultra high frequency waves.

In liquids since shear waves are highly damped, only longitudinal hypersonic waves are propagated. Therefore only a single pair of Brillouin lines are observed.

B. The Central or Rayleigh Component

In the first experimental determination of the frequency distribution of the light scattered by a liquid, Gross [10] observed that in addition to the doublet predicted by Brillouin's theory, a central line was also present. The explanation of this was given by Landau and Placzek [11] who considered that the spontaneous density fluctuations in a liquid, besides having an adiabatic pressure fluctuation part to give rise to Brillouin's doublets, also has a part due to isobaric entropy fluctuation. The latter will also scatter light. Let this be described by another modulation function $\psi(t)$. The contribution to the scattered light will be

$$\vec{E}_s' \;\; \alpha \;\; e^{i\Omega_o t} \; \psi(t) \; . \qquad (39)$$

$\propto$

The heat transport equation is normally given by [see Sec 2.3]

$$\rho_o T_o \frac{\partial s}{\partial t} = \chi \, \nabla^2 \, T \; , \qquad (40)$$

where χ is the thermal conductivity, and all quantities are referred to unit mass. For isobaric fluctuation, (40) can be written as

$$\frac{\partial T}{\partial t} = \frac{\chi}{\rho_o c_p} \nabla^2 \, T \; . \qquad (41)$$

If we assume that $\psi(t)$ satisfies a similar equation, then

$$\dot{\psi}(t) = \frac{\chi}{\rho_o c_p} \; \nabla^2 \, \psi \; . \qquad (42)$$

Eq. (42) can be solved easily and (39)becomes

$$\vec{E}_s' \; \alpha \; e^{i\Omega_o t} \; e^{-\frac{\chi k^2}{\rho_o c_p} t} \tag{43}$$

This means that the entropy wave is nonpropagative and damped out temporally. This mode therefore represents an unshifted line, and is conventionally called the Rayleigh component.

C. Temporal Absorption and Linewidths

A damping factor such as $e^{-\chi k^2 t/\rho_o c_p}$ in (43) is equivalent to temporal absorption. The spectral distribution of the intensity can be obtained by a Fourier transform of (43). Writing

$$\vec{E}_s' \; (t) = \int_{-\infty}^{\infty} \vec{E}_s'(\omega') \; e^{i\omega' t} \; d\omega' \tag{44}$$

we have†

$$\vec{E}_s' \; (\omega'') = \frac{1}{\pi} \int_0^{\infty} \vec{E}_s'(t') \; e^{-i\omega'' t'} \; dt' \; . \tag{45}$$

Putting (43) into (45), and defining the frequency of the scattered light in terms of the frequency shift,

$$\omega' = \omega'' - \Omega_o \tag{46}$$

---

† We have restricted to positive t. This is equivalent to assuming $\vec{E}_s'(t) = \vec{E}_s'(|t|)$. See for example Ref. 29 or (5 - 14).

we get

$$I_s'(\omega') \; \alpha \; \frac{1}{\omega'^2 + \left(\frac{\chi k^2}{\rho_o c_p}\right)^2} \; . \tag{47}$$

This is a Lorentzian distribution with maximum at the unshifted frequency i.e. $\omega'=0$ and with half width equal to $\frac{\chi k^2}{\rho_o c_p}$.

Now consider the Brillouin components. Temporal absorption can be formally described by letting the angular frequency ω in (37) be complex. Denoting the real part of the angular frequency to be ω again, we can write (37) as

$$\vec{E}_p'(t) \; \alpha \; e^{-\Gamma t} \left[e^{i(\Omega_o+\omega)t} + e^{i(\Omega_o-\omega)t}\right] , \tag{48}$$

where $\omega=vk$, v being the sound velocity, and Γ is the temporal absorption and arises from the imaginary part of the complex frequency. The result of (48) can also be obtained if one adds to (35) a loss term $-\Gamma\nabla^2\phi$.

If we now do similar thing as before and evaluate $\vec{E}_p'(\omega')$ from (48), using (46), one obtains, for small sound absorption (i.e. $\Gamma/vk << 1$),

$$\vec{I}_p' \simeq \text{const.} \left\{\frac{1}{\Gamma^2+(\omega'-vk)^2} + \frac{1}{\Gamma^2+(\omega'+vk)^2}\right\} \; . \tag{49}$$

Thus we obtain a doublets which are symmetrically centred at $\omega' = \pm vk$ with half width Γ for each of the two components.

D. Ratio of the Intensities of the Fine Structure

The ratio of the integrated intensity of the central Rayleigh component, denoted by I_c, to the intensities of the displaced Brillouin doublets, denoted by $2\ I_B$, was first given by Landau and Placzek [11]. Their result is

$$\frac{I_c}{2I_B} = \frac{c_p - c_V}{c_V} = \gamma - 1 \ , \tag{50}$$

where c_p and c_V are the specific heats at constant pressure and volume respectively; and γ is the specific heats ratio. (50) is then known as the Landau-Placzek ratio. This can be derived as follows:

The total intensity of the scattered light is proportional to $< \delta\varepsilon^2 >$, where $\delta\varepsilon$ is the dielectric fluctuation. If one neglects $(\frac{\partial \varepsilon}{\partial T})_\rho$, then one can write $< \delta\varepsilon^2 > \simeq (\frac{\partial \varepsilon}{\partial \rho})_T^2 < \delta\rho^2 >$.

Now $\delta\rho = (\frac{\partial \rho}{\partial s})_p \ \delta S + (\frac{\partial \rho}{\partial p})_s \ \delta p$.

From thermodynamic calculations [see Chapter 3],

$$(\frac{\partial \rho}{\partial p})_s = \frac{\rho_o}{B_s} \ ; \ (\frac{\partial \rho}{\partial s})_p = - \frac{\rho_o \beta T_o}{c_p}; \quad \beta^2 = \rho_o \frac{c_p - c_V}{TB_T} \ . \tag{51}$$

From fluctuation theory [see Appendix],

$$< \delta s^2 > = k_B c_p \quad , \quad < \delta p^2 > = \rho_o k_B T_o B_s$$

$$< \delta s \ \delta p > = 0 \tag{52}$$

Making use of (51) and (52), one obtains

$$< \delta\rho^2 > = \frac{\rho_o^3 k_B T_o}{B_T} \{(1 - \frac{1}{\gamma}) + \frac{1}{\gamma}\} \quad . \tag{53}$$

Hence

$$\frac{I_c}{2I_B} = (1 - \frac{1}{\gamma})/\frac{1}{\gamma} = \gamma - 1 \ . \tag{50}$$

A good account of what we have just described in this chapter can be found in "Molecular Scattering of Light" by Fabelinskii [37].

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Chapter 2

SOUND ABSORPTIONS IN VISCOUS LIQUIDS

§2.1 Preliminary Remarks

We have seen in the last section that the absorptions of sound waves in a liquid modulate the scattered light. Landau and Placzek [11] first related the width of the central line of the Rayleigh fire structure to the heat conductivity and the width of the doublets to the absorption of sound in the liquid. Later works [12] have confirmed this theory. In this section we shall discuss some of the major causes of sound absorption, namely the shear and bulk viscosities and the thermal conductivity [13]. We have said that a calculation of density fluctuations by thermodynamic theory alone cannot give the line widths. In the most general case, the kinetic motions of the molecules in the liquid should be understood from a formalism based on a microscopic theory. But this is extremely difficult to do. However, for the problem of light scattering or ultrasonic absorptions in liquids, since the wavelengths of disturbances are much larger than the intermolecular distances, one can use macroscopic treatment of the problem, and the dissipative mechanisms can be conveniently discribed by macroscopic equations of hydrodynamics and thermodynamics of irreversible processes.

§2.2 Hydrodynamical Equations

In a fluid, conservation of matter implies that if ρ is the density of the fluid and $\vec{u}$, the velocity at a given point in the fluid, we have

$$\int (\rho\vec{u}).d\vec{S} = -\frac{\partial}{\partial t} \int \rho dV \; . \qquad (1)$$

This holds for any arbitrary volume. Hence we have

$$\frac{\partial \rho}{\partial t} + \text{div}\;(\rho\vec{u}) = 0 \; , \qquad (2)$$

which is the continuity equation. For small disturbances, (2) can be linearized, which then becomes

$$\frac{\partial \rho}{\partial t} + \rho_o \;\text{div}\; \vec{u} = 0 \; . \qquad (3)$$

For a force-free fluid, the force required to move an element of fluid is only to overcome the hydrostatic pressure, which acts normal to the surface of the element. Thus

$$\int \rho\frac{d\vec{u}}{dt}\, dV = -\int p d\vec{S} = -\int \nabla p dV \; . \qquad (4)$$

Hence

$$\rho_o \frac{\partial \vec{u}}{\partial t} = -\nabla p \; , \qquad (5)$$

which is the linearized Euler's equation.

In a real fluid, however, the stress on a surface element contains both the normal and the tangential components, so that one has to describe it by a symmetric tensor σ_{ij} of rank 2. Hence the force density equation of Euler becomes

$$\rho_o \frac{\partial u_i}{\partial t} = \frac{\partial \sigma_{ji}}{\partial x_j} = - \sum_j \frac{\partial p}{\partial x_j} \delta_{ij} + \sum_j \frac{\partial \pi_{ji}}{\partial x_j} \quad , \tag{6}$$

where

$$\sigma_{ij} = - p\delta_{ij} + \pi_{ij} \quad , \tag{7}$$

and π_{ij} $(=\pi_{ji})$ is called the viscosity stress tensor. We assume that the rates of strain $\partial u_i/\partial x_j$ are small so that the stress can be taken to depend linearly on them, and that the fluid is isotropic, so that the properties along any axis are the same. Therefore,

$$\begin{aligned} \pi_{ii} &= \eta' \text{ div } \vec{u} + 2\eta \frac{\partial u_i}{\partial x_i} \\ \pi_{ij} &= \eta\left\{\frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i}\right\} \quad , \quad i \neq j \end{aligned} \tag{8}$$

where η and η' are constants.

Putting (8) into (6), we obtain

$$\begin{aligned} \rho_o \frac{\partial u}{\partial t} &= - \nabla p + b \text{ grad } (\text{div } \vec{u}) \\ &\quad + \frac{1}{3} \eta \text{ grad } (\text{div } \vec{u}) + \eta\nabla^2\vec{u} \quad , \end{aligned} \tag{9}$$

where

$$b = \eta' + \frac{2}{3} \eta \ . \tag{10}$$

Stokes assumed the special case b=0, so that (9) is reduced to the Navier-Stokes Equation.

η is called the shear viscosity and b the bulk viscosity.

§2.3 Bulk Viscosity and Sound Absorption

It can be shown that for ideal monatomic gas b=0 [14]. In general b≠0 [13,15].

For a nonzero b, the sound absorption α (per wavelength) due to viscosities alone can be calculated as follows:

We assume that sound waves are of weak intensity so that linearized hydrodynamical equations may be used. This is often referred to as the acoustic approximation. Combining (9) with (3), we obtain for one dimensional flow,

$$\rho_o \frac{\partial^2 u}{\partial t^2} = \rho_o \frac{\delta p}{\delta \rho} \frac{\partial^2 u}{\partial x^2} + (b + \tfrac{4}{3}\eta) \frac{\partial}{\partial t} \frac{\partial^2 u}{\partial x^2} \quad . \tag{11}$$

Eq. (11) can be solved for a solution of $u \; \alpha \; e^{i(\omega t - kx)}$, giving ∝

$$k^2 = \omega^2 \left(\frac{\delta p}{\delta \rho}\right)^{-1} \{1 + i\omega(b + \tfrac{4}{3}\eta)\frac{1}{\rho_o}\left(\frac{\partial p}{\partial \rho}\right)^{-1}\}^{-1} \tag{12}$$

$$= \omega^2 \frac{\rho_o}{B_s} \frac{1}{1 + i\omega/\omega_v} \quad , \tag{13}$$

where

$$\omega_v = \frac{B_s}{b + \frac{4}{3}\eta} \quad . \tag{14}$$

For $k=k_1-ik_2$, $u \;\alpha\; e^{-k_2x}\, e^{i(\omega t-k_1x)}$ the sound attenuation per wavelength is defined as

$$\alpha = \frac{2\pi k_2}{k_1} \quad . \tag{15}$$

Substituting (15) into (13), we have

$$\alpha = \frac{\pi v^2 \rho_o}{B_s} \; \frac{\omega/\omega_v}{1+(\omega/\omega_v)^2} \tag{16}$$

$$v^2 = \frac{2B_s}{\rho_o} \; \frac{1+ (\omega/\omega_v)^2}{1+\{1+(\omega/\omega_v)^2\}^{\frac{1}{2}}} \quad . \tag{17}$$

For the low frequency case,

$$\omega << \omega_v \tag{18}$$

Then

$$\alpha = \frac{\pi k}{\rho_o v_o} (b + \frac{4}{3} \eta) \tag{19}$$

$$v = v_o = (B_s/\rho_o)^{\frac{1}{2}} \quad . \tag{20}$$

For b=0, Eq. (19) together with the contribution to sound absorption from thermal conductivity is frequently called the classical absorption. It has been established [13, 16] that the classical absorption is too small to account for the observed absorption in many liquids and that a nonzero b is necessary to explain the additional absorption. Eq. (19) is about the only means of determining b experimentally.

To understand the meaning of b, let us calculate the mean pressure from (7), (8) and (3).

$$-\frac{1}{3}\sum_i \sigma_{ii} = p + \frac{b}{\rho_0}\frac{\partial \rho}{\partial t} \quad . \qquad (21)$$

We see that b is a measure of the resistance to the rate of change of density of the fluid, which may be caused by different mechanisms. In a monatomic fluid a nonzero b can arise only from the local spatial rearrangement of the atoms i.e. structural relaxation [see Chapter 3], and b=0 for a very dilute system of such constituents. For more complicated molecules, b can arise also from other types of relaxation processes.

In some liquids [13, 16], the observed sound attenuation α shows a maximum, when plotted against ω/ω_v, at some finite value of ω/ω_v. Moreover the calculated values of both v and α for $\omega \gtrsim \omega_v$ are much larger than the observed values. All these results contradict the predictions of Eqs. (16) and (17) in which b and η are constants independent of frequency. One is led to conclude that for these liquids some relaxation processes must be taking place and that b and η only describe the low frequency limits of these processes. We recall that b and η were introduced in (8) under the assumption that only the first space derivatives of the particle velocity $\vec{u}$ are kept. For higher frequencies, this will be a poor approximation and the hydrodynamical equation (9) will break down. Hence a proper way of modifying the stress tensor seems to be needed. Since this is not easy as molecular motions in liquids are in general very complicated, one finds it more convenient to assume some relaxing forms of the viscosities in a modified hydrodynamical equation, or in the case of bulk viscosity, one can introduce thermodynamic relaxation theory, as will be discussed in Chapter 3. In some liquids like CS_2 [17], it is sufficient to consider b to arise from a single relaxation time; in others [13, 16], more than one relaxation time, or even a distribution of relaxation times, is needed.

In viscous liquids, both shear and bulk viscosities are relaxing as the condition $\omega \overset{\sim}{>} \omega_v$ is easily satisfied.

§2.4 Sound Absorption due to Thermal Conductivity

We assume, for simplicity, that the only loss mechanism in a fluid is due to thermal conductivity; that is, there are no viscosities. The heat transfer equation is

$$\frac{dQ}{dt} = T\,\frac{ds}{dt} = \frac{\chi}{\rho_o}\,\nabla^2 T \,, \tag{22}$$

where x is the thermal conductivity and s is the entropy per unit mass.

Using thermodynamic relations (see Chapter 3) one can write

$$T_o \frac{\partial s}{\partial t} = T_o\left(\frac{\partial s}{\partial p}\right)_\rho \frac{\partial p}{\partial t} + T_o\left(\frac{\partial s}{\partial \rho}\right)_p \frac{\partial \rho}{\partial t}$$

$$= \frac{c_V}{\beta B_T}\frac{\partial p}{\partial t} - \frac{c_p}{\rho_o \beta}\frac{\partial \rho}{\partial t} \qquad (23)$$

$$\nabla^2 T = \left(\frac{\partial T}{\partial p}\right)_\rho \nabla^2 p + \left(\frac{\partial T}{\partial \rho}\right)_p \nabla^2 \rho$$

$$= \frac{1}{\beta B_T}\nabla^2 p - \frac{1}{\rho_o \beta}\nabla^2 \rho \ . \qquad (24)$$

For δp, $\delta \rho$ etc. α $e^{i(\omega t - \vec{k}.\vec{r})}$, (24) gives $\propto$

$$\frac{\delta p}{\delta \rho} = \frac{B_T}{\rho_o} \frac{\left(\frac{\chi k^2}{\rho_o} + i\omega c_p\right)}{\left(\frac{\chi k^2}{\rho_o} + i\omega c_V\right)} \ . \qquad (25)$$

Putting this into (11), and neglecting viscosity, we proceed as we did to obtain

$$k^2 = \frac{\rho_o \omega 2}{B_T} \frac{\chi k^2 + i\omega\rho_o c_V}{\chi k^2 + i\omega\rho_o c_p} \ . \qquad (26)$$

Again writing $k = k_1 - ik_2$, the low frequency limit

$$\omega << \frac{c_p \rho_o v^2}{\chi} \qquad (27)$$

yields for α and v the expressions

$$\alpha = \frac{\pi(\gamma - 1)\chi k}{\rho_o v_o c_p} \qquad (28)$$

$$v^2 = v_o^2 = B_s/\rho_o \ . \qquad (29)$$

If viscosities are not neglected, it can be shown easily that provided (27) and (18) hold, the sound absorptions due to heat conductivity and viscosities are additive. That is

$$\alpha = \frac{\pi k}{\rho_o v_o} \left[b + \frac{4}{3}\eta + \frac{\gamma - 1}{c_p}\right] . \qquad (30)$$

Chapter 3

THERMODYNAMIC THEORY OF RELAXATION

We have mentioned in Chapter 2 that in certain liquids, sound absorptions can be considered to arise from relaxation processes with either a single relaxation time or more. It was also pointed out that the usual hydrodynamic equation with nonrelaxing viscosities is then not applicable. Since a derivation of relaxing viscosities from the detailed molecular motions does not seem possible, attempts have been made to describe instead the general relaxation features of such processes. We shall describe in this chapter a very general formalism called the thermodynamic theory of relaxation, which was first introduced by Mandelstam and Leontovich [18], and then developed by others; in particular, very extensively done by Meixner [19]. In the following, we shall follow the description in Ref. 13.

§3.1 Formulation of the Theory

Consider a liquid which contains a single ordering mechanism. Such a system needs for its specification three independent thermodynamic variables. Two of these may be chosen from S, T, ρ and P, and the third is the "order" parameter (which we denote here by ξ) or the variable Z conjugate to ξ[†]. For thermodynamic reasoning it is not necessary to specify ξ. For example, it may refer to the temperature of the internal degrees of freedom of the molecules - the relaxation of ξ then gives rise to the so called thermal relaxation process; for a chemical reaction, ξ would represent the degree of reaction.

In all the thermodynamic descriptions throughout this chapter we shall refer extensive quantities to unit mass. The first law of thermodynamics may be written as

$$\delta u = T\delta S + \frac{P}{\rho_o^2}\,\delta\rho + z\delta\xi \qquad (1)$$

The Gibb's free energy is

$$\delta G = - S\delta T + \frac{1}{\rho_o}\,\delta P + Z\delta\xi \qquad (2)$$

When the system is at equilibrium at constant T and P, G is a minimum so that we have

$$Z(T,\ P,\ \xi) = 0\ , \qquad (3)$$

which determines the equilibrium value of ξ as a function of T and P. For equilibrium at constant T and ρ, the Helmholtz free energy is a minimum:

$$\delta A = -S\delta T + \frac{P}{\rho_o^2}\,\delta\rho + Z\delta\xi = 0\ , \qquad (4)$$

[†] The theory can be easily extended to the case of several order parameters.

so that

$$Z(T,\rho,\xi) = 0 \, . \tag{5}$$

A thermodynamic quantity measured at constant $Z(=0)$ corresponds to the value measured in the equilibrium state, i.e. at zero frequency. On the other hand, a measurement of quantities at constant value of the relaxation parameter ξ corresponds to the infinite frequency case, when things happen at too fast a rate for ξ to attain its equilibrium value $\bar{\xi}$, which is determined by (3) or (5). Such quantities are sometimes called 'frozen' quantities and are denoted usually with a superscript ∞. A quantity without a superscript will, for simplicity, correspond to one measured at zero frequency.

Since when ξ has its equilibrium value $\bar{\xi}$, one may to a first approximation assume that for small deviation $\delta\xi=\xi-\bar{\xi}$, the system returns to equilibrium according to the equation

$$\frac{d\delta\xi}{dt} = - L\delta Z \; , \tag{6}$$

where δZ may be regarded as the ordering force, and L is a constant or a slowly varying function of the thermodynamic variables ρ, T, etc.

If we write

$$\delta Z = \left(\frac{\partial Z}{\partial T}\right)_{\rho,\xi} \delta T + \left(\frac{\partial Z}{\partial \rho}\right)_{T,\xi} \delta\rho + \left(\frac{\partial Z}{\partial \xi}\right)_{T,\rho} \delta\xi, \tag{7}$$

and make use of (5), Eq. (6) becomes

$$\frac{d\delta\xi}{dt} = -\frac{\delta\xi - \delta\bar{\xi}}{\tau_{TV}} , \qquad (8)$$

where

$$\tau_{TV}^{-1} \equiv L \left(\frac{\partial Z}{\partial \xi}\right)_{T,\rho} . \qquad (9)$$

For $\delta\xi$ to relax at constant T and P, we have

$$\frac{d\delta\xi}{dt} = -\frac{\delta\xi - \delta\bar{\xi}}{\tau_{TP}} , \qquad (10)$$

where $\delta\bar{\xi}$ is now to be determined by (3), and

$$\tau_{T}^{-1} \equiv L \left(\frac{\partial Z}{\partial \xi}\right)_{T,P} \qquad (11)$$

Similarly one can define τ_{SV} and τ_{SP} .

§3.2 Some Useful Formulae

We shall in this section give some thermodynamic relations which will be useful to us later. First we recall some of the general thermodynamic quantities and relations for the zero frequency limit.

$$B_S = \rho_o \left(\frac{\partial P}{\partial \rho}\right)_{S,Z} \quad ; \quad B_T = \rho_o \left(\frac{\partial P}{\partial \rho}\right)_{T,Z} \quad ;$$

$$c_V = T_o \left(\frac{\partial S}{\partial T}\right)_{\rho,Z} \quad ; \quad c_P = T_o \left(\frac{\partial S}{\partial T}\right)_{P,Z} \quad ;$$

$$\beta = -\frac{1}{\rho_o}\left(\frac{\partial \rho}{\partial T}\right)_{P,Z} = -\rho_o \left(\frac{\partial S}{\partial P}\right)_{T,Z} \; ; \; \beta B_T = \left(\frac{\partial P}{\partial T}\right)_{\rho,Z} = -\rho_o^2 \left(\frac{\partial S}{\partial \rho}\right)_{T,Z} \; ;$$

$$\gamma = \frac{B_S}{B_T} = \frac{c_P}{c_V} \quad ; \quad B_S - B_T = \frac{T_o}{\rho_o c_V} \beta^2 B_T^2 \quad ;$$

$$\beta = \frac{\rho_o}{T_o} (c_P - c_V) \frac{1}{B_T} \quad , \tag{12}$$

where B_S and B_T are the adiabatic and isothermal bulk modulus respectively; c_P and c_V are the isobaric and isochoric specific heats respectively; γ is the specific heats ratio and β is the coefficient of volume expansion. For infinite frequency case, we immediately have

$$B_S^\infty = \rho_o(\frac{\partial P}{\partial \rho})_{S,\xi} \quad ; \quad B_T^\infty = \rho_o(\frac{\partial P}{\partial \rho})_{T,\xi} \quad ;$$

$$c_V^\infty = T_o(\frac{\partial S}{\partial T})_{\rho,\xi} \quad ; \quad c_P^\infty = T_o(\frac{\partial S}{\partial T})_{P,\xi} \quad ;$$

$$\beta^\infty = -\frac{1}{\rho_o}(\frac{\partial \rho}{\partial T})_{P,\xi} = -\rho(\frac{\partial S}{\partial P})_{T,\xi} \ : \ \beta^\infty B_T^\infty = (\frac{\partial P}{\partial T})_{\rho,\xi} = -\rho^2(\frac{\partial S}{\partial \rho})_{T,\xi} ;$$

$$\gamma^\infty = \frac{B_S^\infty}{B_T^\infty} = \frac{c_P^\infty}{c_V^\infty} \quad ; \quad B_S^\infty - B_T^\infty = \frac{T_o}{\rho_o c_V^\infty} \beta^{\infty^2} B_T^{\infty^2} \quad ;$$

$$\beta^{\infty^2} = \frac{\rho_o}{T_o} (c_P^\infty - c_V^\infty) \frac{1}{B_T^\infty} \tag{13}$$

From (4), one gets

$$(\frac{\partial S}{\partial \rho})_{T,Z} = - \frac{1}{\rho_o^2} (\frac{\partial P}{\partial T})_{\rho,Z} = - \frac{\beta B_T}{\rho_o^2}$$

$$(\frac{\partial S}{\partial Z})_{\rho,T} = (\frac{\partial \xi}{\partial T})_{\rho,Z}$$

$$\frac{1}{\rho_o^2} (\frac{\partial P}{\partial Z})_{T,\rho} = -(\frac{\partial \xi}{\partial \rho})_{T,Z} \quad . \tag{14}$$

Similar relations can be obtained from the other Legendre transforms of (1). Consider now

$$\delta P = \left(\frac{\partial P}{\partial T}\right)_{\rho,\xi}\delta T + \left(\frac{\partial P}{\partial \rho}\right)_{T,\xi}\delta\rho + \left(\frac{\partial P}{\partial \xi}\right)_{T,\rho}\delta\xi$$

$$= \beta^{\infty}B_T^{\infty}\delta T + \frac{B_T^{\infty}}{\rho_o}\delta\rho + \left(\frac{\partial P}{\partial \xi}\right)_{T,\rho}\delta\xi \qquad (15)$$

Therefore,

$$\frac{B_T}{\rho_o} = \left(\frac{\partial P}{\partial \rho}\right)_{T,Z} = \frac{B_T^{\infty}}{\rho_o} + \left(\frac{\partial P}{\partial \xi}\right)_{T,\rho}\left(\frac{\partial \xi}{\partial \rho}\right)_{T,Z}$$

or

$$B_T^{\infty} - B_T = \rho_o^{-1}\left(\frac{\partial P}{\partial \xi}\right)_{T,\rho}\left(\frac{\partial P}{\partial Z}\right)_{T,\rho} \qquad (16)$$

Similarly

$$B_S^{\infty} - B_S = \rho_o^{-1}\left(\frac{\partial P}{\partial \xi}\right)_{S,\rho}\left(\frac{\partial P}{\partial Z}\right)_{S,\rho} \qquad (17)$$

(15) also gives

$$\beta B_T - \beta^{\infty}B_T^{\infty} = \left(\frac{\partial P}{\partial \xi}\right)_{T,\rho}\left(\frac{\partial \xi}{\partial T}\right)_{\rho,Z} = \left(\frac{\partial P}{\partial \xi}\right)_{T,\rho}\left(\frac{\partial S}{\partial Z}\right)_{T,\rho} . \qquad (18)$$

Consider now

$$\delta S = \left(\frac{\partial S}{\partial T}\right)_{P,\xi}\delta T + \left(\frac{\partial S}{\partial P}\right)_{T,\xi}\delta P + \left(\frac{\partial S}{\partial \xi}\right)_{T,P}\delta\xi$$

$$= \frac{c_P^{\infty}}{T_o}\delta T - \frac{\beta^{\infty}}{\rho_o}\delta P + \left(\frac{\partial S}{\partial \xi}\right)_{T,P}\delta\xi \qquad (19)$$

Therefore,

$$\beta - \beta^{\infty} = -\rho_o\left(\frac{\partial S}{\partial \xi}\right)_{T,P}\left(\frac{\partial \xi}{\partial P}\right)_{T,Z}$$

$$= -\rho_o^{-1}\left(\frac{\partial S}{\partial \xi}\right)_{T,P}\left(\frac{\partial \rho}{\partial Z}\right)_{T,P} \qquad (20)$$

$$c_P - c_P^{\infty} = T_o\left(\frac{\partial S}{\partial \xi}\right)_{T,P}\left(\frac{\partial \xi}{\partial T}\right)_{P,Z}$$

$$= T_o\left(\frac{\partial S}{\partial \xi}\right)_{T,P}\left(\frac{\partial S}{\partial Z}\right)_{T,P} \tag{21}$$

Similarly,

$$c_V - c_V^{\infty} = T_o\left(\frac{\partial S}{\partial \xi}\right)_{T,\rho}\left(\frac{\partial S}{\partial Z}\right)_{T,\rho} \quad . \tag{22}$$

Also, from (19), we have

$$\left(\frac{\partial T}{\partial S}\right)_{P,Z} = \frac{T_o}{c_P} = \frac{T_o}{c_P^{\infty}} - \left(\frac{\partial S}{\partial \xi}\right)_{T,P}\left(\frac{\partial \xi}{\partial S}\right)_{P,Z}\frac{T}{c_P^{\infty}}$$

or

$$\frac{1}{c_P} - \frac{1}{c_P^{\infty}} = -\,T_o^{-1}\left(\frac{\partial S}{\partial \xi}\right)_{T,P}\left(\frac{\partial \xi}{\partial S}\right)_{P,Z}\left(\frac{\partial T}{\partial S}\right)_{P\xi}$$

Using

$$\left(\frac{\partial \xi}{\partial S}\right)_{P,Z} = -\left(\frac{\partial T}{\partial Z}\right)_{S,P}$$

$$\left(\frac{\partial S}{\partial \xi}\right)_{T,P}\left(\frac{\partial T}{\partial S}\right)_{P,\xi} = -\left(\frac{\partial T}{\partial \xi}\right)_{S,P} \quad ,$$

we have

$$\frac{1}{c_P} - \frac{1}{c_P^{\infty}} = -T_o^{-1}\left(\frac{\partial T}{\partial Z}\right)_{S,P}\left(\frac{\partial T}{\partial \xi}\right)_{S,P} \tag{23}$$

Similarly

$$\frac{1}{c_V} - \frac{1}{c_V^{\infty}} = -T_o^{-1}\left(\frac{\partial T}{\partial Z}\right)_{S,\rho}\left(\frac{\partial T}{\partial \xi}\right)_{S,\rho} \quad . \tag{24}$$

It can be easily verified that we also have

$$\frac{1}{B_T} - \frac{1}{B_T^{\infty}} = \rho_o^{-3}\left(\frac{\partial \rho}{\partial \xi}\right)_{T,P}\left(\frac{\partial \rho}{\partial Z}\right)_{T,P} \tag{25}$$

$$\frac{1}{B_S} - \frac{1}{B_S^\infty} = \rho_o^{-3}\left(\frac{\partial \rho}{\partial \xi}\right)_{S,P} \left(\frac{\partial \rho}{\partial Z}\right)_{S,P} \tag{26}$$

$$\frac{\beta B_T}{c_V} - \frac{\beta^\infty B_T^\infty}{c_V^\infty} = -T_o^{-1}\left(\frac{\partial P}{\partial Z}\right)_{S,\rho}\left(\frac{\partial T}{\partial Z}\right)_{S,\rho}\left(\frac{\partial Z}{\partial \xi}\right)_{S,\rho} . \tag{27}$$

Combining (20),(21) and (25), we have

$$\frac{\rho_o}{T_o}\,(c_P - c_P^\infty)\left(\frac{1}{B_T} - \frac{1}{B_T^\infty}\right) = (\beta - \beta^\infty)^2 . \tag{28}$$

Combining (16), (22) and (18), we have

$$\frac{\rho_o}{T_o}\,(c_V - c_V^\infty)(B_T^\infty - B_T) = (\beta B_T - \beta^\infty B_T^\infty)^2 . \tag{29}$$

Also, from (12), (13) and (28), we have

$$2\beta\beta^\infty = \frac{\rho_o}{T_o}\left\{\frac{c_P}{B_T^\infty} - \frac{c_V^\infty}{B_T^\infty} + \frac{c_P^\infty}{B_T} - \frac{c_V}{B_T}\right\} . \tag{30}$$

We shall now obtain relations between the various relaxation times.

From (9) and (11), we have

$$\frac{\tau_{TV}}{\tau_{TP}} = \left(\frac{\partial Z}{\partial \xi}\right)_{T,P} \Big/ \left(\frac{\partial Z}{\partial \xi}\right)_{T,\rho}$$

Now

$$\left(\frac{\partial Z}{\partial \xi}\right)_{T,P}\left(\frac{\partial \xi}{\partial P}\right)_{T,Z}\left(\frac{\partial P}{\partial Z}\right)_{T,\xi} = -1$$

$$\left(\frac{\partial Z}{\partial \xi}\right)_{T,\rho}\left(\frac{\partial \xi}{\partial \rho}\right)_{T,Z}\left(\frac{\partial \rho}{\partial Z}\right)_{T,\xi} = -1$$

Therefore

$$\frac{\tau_{TV}}{\tau_{TP}} = \frac{(\frac{\partial P}{\partial \xi})_{T,Z}(\frac{\partial Z}{\partial P})_{T,\xi}}{(\frac{\partial \rho}{\partial \xi})_{T,Z}(\frac{\partial Z}{\partial \rho})_{T,\xi}} = \frac{(\frac{\partial P}{\partial \rho})_{T,Z}(\frac{\partial Z}{\partial P})_{T,\xi}}{(\frac{\partial Z}{\partial \rho})_{T,\xi}}$$

$$= (\frac{\partial P}{\partial \rho})_{T,Z}(\frac{\partial \rho}{\partial P})_{T,\xi} = B_T/B_T^{\infty}$$

or

$$\tau_{TV} = \frac{B_T}{B_T^{\infty}}\,\tau_{TP} \quad . \tag{31}$$

Similarly

$$\tau_{SV} = \frac{B_S}{B_S^{\infty}}\,\tau_{SP} \quad . \tag{32}$$

Also

$$\frac{\tau_{SP}}{\tau_{TP}} = (\frac{\partial Z}{\partial \xi})_{T,P}/(\frac{\partial Z}{\partial \xi})_{S,P} = \frac{(\frac{\partial T}{\partial \xi})_{P,Z}(\frac{\partial Z}{\partial T})_{P,\xi}}{(\frac{\partial S}{\partial \xi})_{P,Z}(\frac{\partial Z}{\partial S})_{P,\xi}}$$

$$= (\frac{\partial S}{\partial T})_{P,\xi}/(\frac{\partial S}{\partial T})_{P,Z} = c_P^{\infty}/c_P$$

or

$$\tau_{SP} = \frac{c_P^{\infty}}{c_P}\,\tau_{TP} \quad . \tag{33}$$

Combining (31), (32) and (33), we have

$$\tau_{SV} = \frac{c_V^{\infty}}{c_V}\,\tau_{TV} \quad . \tag{34}$$

§3.3 Relaxation Processes

A. Adiabatic Processes

This is the case relevant to sound propagation. Expanding δP in S, ρ and ξ, and putting $\delta S=0$, we have

$$\delta P = \frac{B_S^\infty}{\rho}\,\delta\rho + \left(\frac{\partial P}{\partial \xi}\right)_{S,\rho}\delta\xi \tag{35}$$

Now

$$\left(\frac{\partial P}{\partial \xi}\right)_{S,\rho} = -\left(\frac{\partial \rho}{\partial \xi}\right)_{S,P}\left(\frac{\partial P}{\partial \rho}\right)_{S,\xi} = -\frac{B_S^\infty}{\rho}\left(\frac{\partial \rho}{\partial \xi}\right)_{S,P} .$$

Therefore,

$$\delta P = \frac{B_S^\infty}{\rho_o}\left\{\delta\rho - \left(\frac{\partial \rho}{\partial \xi}\right)_{S,P}\delta\xi\right\} . \tag{36}$$

We can eliminate $\delta\xi$ as follows: From (6), we have

$$\frac{d}{dt}\,\delta\xi = -\frac{\delta\xi-\delta\bar{\xi}}{\tau_{SP}} , \tag{37}$$

where $\delta\bar{\xi}$ is to be determined by

$$0 = \left(\frac{\partial Z}{\partial P}\right)_{S,\xi}\delta P + \left(\frac{\partial Z}{\partial \xi}\right)_{S,P}\delta\bar{\xi} ,$$

or

$$\delta\bar{\xi} = -\left(\frac{\partial Z}{\partial P}\right)_{S,\xi}\left(\frac{\partial \xi}{\partial Z}\right)_{S,P}\delta P = \frac{1}{\rho_o^2}\left(\frac{\partial \rho}{\partial Z}\right)_{S,P}\delta P . \tag{38}$$

Therefore, from (36), we have

$$\tau_{SP}\frac{d}{dt}\,\delta P = \frac{\tau_{SP}B_S^\infty}{\rho_o}\left\{\frac{d}{dt}\,\delta\rho + \frac{1}{\tau_{SP}}\left(\frac{\partial \rho}{\partial \xi}\right)_{S,P}\delta\xi - \frac{1}{\tau_{SP}\rho_o^2}\left(\frac{\partial \rho}{\partial \xi}\right)_{S,P}\left(\frac{\partial \rho}{\partial Z}\right)_{S,P}\delta P\right\} . \tag{39}$$

Adding (39) to (36) and using (26) and (32), we have

$$(1 + \tau_{SP} \frac{d}{dt})\delta\rho = \frac{\rho_o}{B_S} (1 + \tau_{SV} \frac{d}{dt})\delta P \ . \tag{40}$$

For $\delta\rho$, $\delta P \propto e^{i\omega t}$, we have from (40),

$$B_S(i\omega) = \frac{\delta P}{\delta\rho} = B_S + \frac{(B_S^{\infty}-B_S)i\omega\tau_{SV}}{1+i\omega\tau_{SV}} \ . \tag{41}$$

Thus we have arrived at a complex frequency-dependent bulk modulus.

B. Isothermal Processes

If we consider $\delta T=0$ and do similar things as in A, we would obtain, similar to (40) and (41), the following results

$$(1+\tau_{TP} \frac{d}{dt})\delta\rho = \frac{\rho_o}{B_T}(1 + \tau_{TV} \frac{d}{dt})\delta P \tag{42}$$

$$B_T(i\omega) = B_T + \frac{(B_T^{\infty}-B_T)i\omega\tau_{TV}}{1+i\omega\tau_{TV}} \ . \tag{43}$$

C. Temperature Induced or Thermal Relaxation Processes

This is a very important kind of relaxation process, and is one induced by a change of temperature only. Thus for such a process, isothermal changes of pressure and volume occur without relaxation effects. The condition then is given by

$$(\frac{\partial \rho}{\partial \xi})_{T,P} = (\frac{\partial P}{\partial \xi})_{T,\rho} = 0 \ . \tag{44}$$

In (44), since $(\frac{\partial \rho}{\partial \xi})_{T,P} = - \frac{\rho_o}{B_T^\infty} (\frac{\partial P}{\partial \xi})_{T,\rho}$, one of the two conditions in (44) will suffice. From (25), this condition is also equivalent to

$$B_T = B_T^\infty \quad , \tag{45}$$

or from (43), $B_T(i\omega) = B_T$ is real and independent of ω. Therefore there is no relaxation of the isothermal bulk modulus.

If a process is thermally induced, then from (28), we have $\beta = \beta^\infty$, which together with (45), (12) and (13) imply that $c_P - c_V = c_P^\infty - c_V^\infty$. These are the consequences, not the condition for thermal relaxation.

D. Pressure Induced Relaxation Processes

These are processes which are induced by a change of pressure only, irrespective of whether the relaxation takes place adiabatically or isothermally. Such processes are designated by

$$(\frac{\partial S}{\partial \xi})_{T,P} = (\frac{\partial T}{\partial \xi})_{S,P} = 0 \ . \tag{46}$$

From (21), this condition is also equivalent to

$$c_P^\infty = c_P \quad . \tag{47}$$

If we write

$$\delta\rho = (\frac{\partial \rho}{\partial S})_{P,\xi}\delta S + (\frac{\partial \rho}{\partial P})_{S,\xi}\delta P + (\frac{\partial \rho}{\partial \xi})_{S,P}\,\delta\xi$$

Then

$$\left(\frac{\partial \rho}{\partial \xi}\right)_{T,P} = \left(\frac{\partial \rho}{\partial S}\right)_{P,\xi}\left(\frac{\partial S}{\partial \xi}\right)_{T,P} + \left(\frac{\partial \rho}{\partial \xi}\right)_{S,P}$$

or

$$\left(\frac{\partial \rho}{\partial \xi}\right)_{T,P} = \left(\frac{\partial \rho}{\partial \xi}\right)_{S,P} \quad . \tag{48}$$

From (25), (26) and (33), we can write

$$\frac{\kappa_T-\kappa_T^{\infty}}{\kappa_S-\kappa_S^{\infty}} = \frac{\left(\frac{\partial \rho}{\partial \xi}\right)^2_{T,P} c_P}{\left(\frac{\partial \rho}{\partial \xi}\right)^2_{S,P} c_P^{\infty}} \tag{49}$$

Now

$$\left(\frac{\partial \rho}{\partial \xi}\right)_{S,P} = \left(\frac{\partial \rho}{\partial \xi}\right)_{T,P} + \left(\frac{\partial \rho}{\partial T}\right)_{P,\xi}\left(\frac{\partial T}{\partial \xi}\right)_{S,P}$$

$$= \left(\frac{\partial \rho}{\partial \xi}\right)_{T,P} + \frac{\rho T \beta^{\infty}}{c_P^{\infty}} \left(\frac{\partial S}{\partial \xi}\right)_{T,P} \quad . \tag{50}$$

Using (20) and (21), we have

$$\frac{c_P^{\infty}}{c_P} \left(\frac{\partial \rho}{\partial \xi}\right)_{S,P} = \left(\frac{\partial \rho}{\partial \xi}\right)_{T,P} + \frac{\rho_o \beta T_o}{c_P} \left(\frac{\partial S}{\partial \xi}\right)_{T,P} \quad . \tag{51}$$

Hence (49) becomes

$$\frac{\kappa_T-\kappa_T^{\infty}}{\kappa_S-\kappa_S^{\infty}} = \frac{\left(\frac{\partial \rho}{\partial \xi}\right)^2_{T,P} c_P^{\infty}}{c_P\left[\left(\frac{\partial \rho}{\partial \xi}\right)_{T,P} + \frac{\rho \beta T}{c_P}\left(\frac{\partial S}{\partial \xi}\right)_{T,P}\right]^2} \tag{52}$$

Eq. (52) provides us with a criteria for temperature or pressure induced relaxation process. Thus if

$$\left|\left(\frac{\partial \rho}{\partial \xi}\right)_{T,P}\right| \ll \left|\frac{\rho_o \beta T_o}{c_P}\left(\frac{\partial S}{\partial \xi}\right)_{T,P}\right| \quad , \tag{53}$$

or

$$\kappa_T - \kappa_T^{\infty} \ll \kappa_S - \kappa_S^{\infty} \quad , \tag{54}$$

we have thermal relaxation, and

$$\kappa_T \approx \kappa_T^{\infty} \qquad \text{or} \qquad B_T \approx B_T^{\infty} \quad . \tag{55}$$

On the other hand, if

$$\left|\left(\frac{\partial \rho}{\partial \xi}\right)_{T,P}\right| \gg \left|\frac{\rho_o \beta T_o}{c_P}\left(\frac{\partial S}{\partial \xi}\right)_{T,P}\right| \quad , \tag{56}$$

we have

$$\kappa_T - \kappa_T^{\infty} \approx \kappa_S - \kappa_S^{\infty} \quad . \tag{57}$$

This corresponds to pressure induced relaxation.

In analogy with the above discussion, we may define also a density or volume induced relaxation process by requiring that

$$\left(\frac{\partial S}{\partial \xi}\right)_{T,\rho} = \left(\frac{\partial T}{\partial \xi}\right)_{S,\rho} = 0 \quad , \tag{58}$$

which differs from (46) in that the role ρ and P have been exchanged. For this case, we have

$$c_V = c_V^{\infty} \quad , \tag{59}$$

and

$$\left(\frac{\partial P}{\partial \xi}\right)_{T,\rho} = \left(\frac{\partial P}{\partial \xi}\right)_{S,\rho} \quad . \tag{60}$$

Similar to (53) and (56), we have now the condition

$$\left|\left(\frac{\partial P}{\partial \xi}\right)_{T,\rho}\right| << \left|\frac{\beta B_T T_o}{c_V} \left(\frac{\partial S}{\partial \xi}\right)_{T,\rho}\right| \quad , \tag{61}$$

or

$$B_T^\infty - B_T << B_S^\infty - B_S \tag{62}$$

for temperature induced processes, and

$$\left|\left(\frac{\partial P}{\partial \xi}\right)_{T,\rho}\right| >> \left|\frac{\beta B_T T_o}{c_V} \left(\frac{\partial S}{\partial \xi}\right)_{T,\rho}\right| \quad , \tag{63}$$

or

$$B_T^\infty - B_T \approx B_S^\infty - B_S \tag{64}$$

for volume or density induced processes. We may note that eqs. (62) and (54) are essentially equivalent, as they should be. However, eqs. (64) and (57) are, in general, not equivalent.

§3.4 Representation of Bulk and Shear Viscosities

For the case of a fluid system in which the only cause of sound absorption is a relaxation process with a single relaxation time, the sound absorption and sound velocity can be calculated from Eq. (41) together with the hydrodynamical equations (2-3) and (2-5). For δP and $\delta\rho$ proportional to $e^{i(\omega t-\vec{k}.\vec{r})}$, (2-3) and (2-5) give

$$\frac{\delta P}{\delta\rho} = \frac{\omega^2}{k^2} \quad . \tag{65}$$

Eq. (65) is obtained from Euler's equation, which has been derived for force-free fluid. We wish to make a remark here: If $\frac{\delta P}{\delta\rho}$ in (65) is real and is equal to B_S/ρ, then eq. (65) cannot describe sound absorption. To obtain sound absorption, the Euler's equation has to be replaced by Navier-Stokes equation or other modified force density equation. An alternative way is what we are doing. The Euler's equation is used but $\frac{\delta P}{\delta\rho}$ in (65) is complex, so that sound absorption is automatically taken into account in the thermodynamics in terms of an ordering parameter ξ, which is what we have discussed in this chapter. The first way of doing things requires a hydrodynamic equation involving the bulk and shear viscosities, which is not applicable at high frequencies. It is interesting to see how the bulk viscosity arises in the thermodynamic theory of relaxation. Substituting (41) into (65), one gets

$$k^2 = \frac{1+i\omega\tau_{SV}}{B_S+B_S^{\infty}i\omega\tau_{SV}} \; \frac{\omega^2 B_S}{v_o^2} \quad . \tag{66}$$

Now the description of sound absorption in terms of a bulk viscosity b gives, if one puts $\eta=0$ in (2-13),

$$k^2 = \frac{\omega^2 \rho}{B_S + i\omega b} \quad . \tag{67}$$

Substituting (67) into (66), we have

$$b = \frac{(B_S^\infty - B_S)\tau_{SV}}{1+i\omega\tau_{SV}} \quad . \tag{68}$$

Actually from the manner b is introduced in (2-10), it cannot be frequency dependent; which is precisely why the hydrodynamical equation of Navier-Stokes breaks down at high frequencies. Hence strictly speaking, one cannot substitute (67) into (66) to obtain (68). The proper way should be to compare the low frequency limit of (67) with that of (66), because it is in this limit that description in terms of the hydrodynamical equation is meaningful. Doing this, one obtains b as the low frequency limit of the relaxation process

$$b = (B_S^\infty - B_S)\ \tau_{SV} \quad . \tag{69}$$

However, (68) provides us a way to describe a relaxing, or frequency-dependent bulk viscosity.

In a similar way, one can describe the shear viscosity η as the low frequency limit of a shear relaxation process

$$\eta = (G_S^\infty - G_S)\ \tau_\eta , \tag{70}$$

where τ_η is the shear relaxation time and G_S, G_S^∞ are the shear modulus at zero and infinite frequencies respectively. In liquids, $G_S = 0$ and $G_S^\infty = G_T^\infty$. Hence (70) becomes

$$\eta = G^\infty \tau_\eta \tag{71}$$

A relaxing shear viscosity then can be written as

$$\eta(i\omega) = \frac{G^\infty \tau_\eta}{1+i\omega\tau_\eta} \quad . \tag{72}$$

As it is well known that the frequency dependence of a quantity can be considered as resulting from the Fourier transform of a time-dependent quantity, one can assume that there exists a function b'(t) for the bulk viscosity of the following form

$$b'(t) = (B_S^\infty - B_S)\, e^{-t/\tau_{SV}} \tag{73}$$

Then

$$b(i\omega) = \int_0^\infty e^{-i\omega t'}\, b'(t')dt'$$

$$= \frac{(B_S^\infty - B_S)\tau_{SV}}{1+i\omega\tau_{SV}} \quad \text{as in (68)} \quad .$$

Similarly the time dependent function for shear viscosity is

$$\eta'(t) = G^\infty e^{-t/\tau_\eta} \tag{74}$$

Thus in describing a thermodynamic relaxation process, one can either employ an ordering parameter

ξ, which adds a new degree of freedom to the thermodynamics of the system, or one can use (68). If one prefers the latter way, one has to find a suitable way to introduce the relaxing bulk viscosity into the hydrodynamical equation. We recall that for the unrelaxed case, the term in the hydrodynamical equation involving b is, from (2-9), b grad(div $\vec{u}$). Therefore an integral representation of a time dependent function of the following form is suitable

$$c(t) = \int_0^t b'(t-t') \text{ grad } (\text{div } \vec{u}(t'))\, dt' \;, \tag{75}$$

where b'(t) is given by (73). For, the frequency dependence of c(t) can be obtained by a Laplace transform

$$\int_0^\infty e^{-i\omega t}\, c(t)dt = \int_0^\infty dt \int_0^\infty e^{-i\omega t}\, b'(t-t')\text{grad div } \vec{u}(t')dt'$$

$$= \int_0^\infty dt'' b'(t'')e^{-i\omega t''} \int_0^\infty e^{-i\omega t'}\text{grad div } \vec{u}(t')\, dt' \;. \tag{76}$$

The first factor in (76) gives the correct frequency dependence as in (68).

We shall in a later chapter discuss the difference between the two ways of representing the relaxing bulk viscosity.

Since the shearing processes do not involve changes in volume or temperature of the fluid, a relaxing shear visocity is most conveniently described by an integral representation similar to the one outlined above for the bulk viscosity.

Chapter 4

MICROSCOPIC FORMULATION OF THE SCATTERING PROBLEM

The early formulations of the light scattering problem, described in Chapter 1, do not allow one to calculate readily the spectral distribution of the scattered light. Recently Kamarov and Fisher [20] and Pecora [21] have adapted Van Hove's correlation function technique (developed in connection with neutron scattering) to this problem. In this chapter we first briefly describe Van Hove's theory and then show how it is translated from the language of neutron scattering to that of light scattering.

§4.1 Van Hove's Theory of Neutron Scattering [22]

Consider a target system S containing N atoms, the position of the ith atom being denoted by $\vec{r}_i$. Let the incident neutron of mass m have momentum $\hbar\vec{k}_1$. It is scattered by S into a state with momentum $\hbar\vec{k}_2$, while S changes from the initial state $|I\rangle$ with energy E_I to the final state $|F\rangle$ with energy E_F. The transition probability per unit time is

$$W(k,\omega) = \frac{2\pi}{\hbar}|\langle F,k_2|\mathrm{Hint}|I,k_1\rangle|^2\rho(\varepsilon_F)\delta(\hbar\omega-E_F+E_I) , \qquad (1)$$ H(ω)

where Hint $(\vec{r})$ is the interaction potential; $\varepsilon_F=E_F+\frac{\hbar^2k_2^2}{2m}$

is the energy of the final state; $\frac{\hbar^2 k^2}{2m} = \hbar\omega = E_F - E_I$ is the change in energy of the neutron; $\delta(\hbar\omega - E_F + E_I)$ expresses conservation of energy and $\rho(\varepsilon_F)$ is the density per unit energy range of the final state.

Passing into continuum for the k_2 space, we have

$$\rho(\varepsilon_F) = \frac{m\ V\ k_2}{(2\pi)^3 \hbar^2}\ d\Omega \quad . \tag{2}$$

The differential scattering cross-section per unit solid angle per unit energy range is

$$\frac{d^2\sigma}{d\Omega d\varepsilon} = \frac{k_2}{k_1}\left(\frac{m}{2\pi\hbar^2}\right)^2 V^2 \left|\langle F, k_2 | \mathrm{Hint}(\vec{r}) | I, k_1 \rangle\right|^2 \delta(\hbar\omega - E_F + E_I) \tag{3}$$

Now in general there is a statistical distribution of initial target states $|I\rangle$, each with a probability $P(I)$, and will end up in a certain $|F\rangle$. Therefore, we have

$$\frac{d^2\sigma}{d\Omega d\varepsilon} = V^2\left(\frac{k_2}{k_1}\right)\left(\frac{m}{2\pi\hbar^2}\right)^2 \sum_{I,F} P(I) \left|\langle F, k_2 | \mathrm{Hint}(\vec{r}) | I, k_1 \rangle\right|^2 \delta(\hbar\omega - E_F + E_I) . \tag{4}$$

Usually, Hint $(\vec{r})$ can be written in the form

$$\mathrm{Hint}\ (\vec{r}) = \frac{2\pi\hbar^2}{m} \sum_i a_i\ \delta(\vec{r} - \vec{r}_i)\ , \tag{5}$$

where a_i is an operator depending on the spin of ith particle. Therefore,

$$\langle k_2 | \mathrm{Hint}(\vec{r}) | k_1 \rangle = \frac{1}{V} \int d^3\vec{r} \sum_i a_i \frac{2\pi\hbar^2}{m} \delta(\vec{r} - \vec{r}_i) e^{i(\vec{k}_1 - \vec{k}_2)\cdot\vec{r}}$$

$$= \frac{2\pi\hbar^2}{mV} \sum_i a_i\ e^{i\vec{k}\cdot\vec{r}_i} \quad . \tag{6}$$

We now replace the δ-function in (4) by the integral $\frac{1}{2\pi\hbar} \int e^{-i(\omega - \frac{E_F - E_I}{\hbar})t}\, dt$, and substitute (6) into (4) to obtain

$$\frac{d^2\sigma}{d\Omega d\varepsilon} = \frac{1}{2\pi\hbar} (\frac{k_2}{k_1}) \int dt\, e^{-i\omega t} \sum_{I,F} \sum_{i,j} P(I)$$
$$\times < F|e^{\frac{iH_o t}{\hbar}}\, a_i\, e^{i\vec{k}.\vec{r}_i(o)}\, e^{-\frac{iH_o t}{\hbar}}\, |I>$$
$$\times < I|a_j\, e^{-i\vec{k}.\vec{r}_j(o)}|F> , \qquad (7)$$

where we have used the equation $H_o|I> = E_I|I>$, H_o being the unperturbed Hamiltonian, and we have also chosen our initial time as the origin. We now denote $\sum_I P(I) <I|....|I>$ by the ensemble average <....>. Since $\sum_F |F><F| = 1$, (7) can be written as

$$\frac{d^2\sigma}{d\Omega d\varepsilon} = \frac{1}{2\pi\hbar} (\frac{k_2}{k_1}) \sum_{i,j} \int e^{-i\omega t} < a_i\, e^{-i\vec{k}.\vec{r}_i(o)} a_j(t) e^{i\vec{k}.\vec{r}_j(t)} > dt , \qquad (8)$$

where $\vec{r}_j(t)$ and $a_j(t)$ are now Heisenberg operators, i.e.,

$$\vec{r}_j(t) = e^{\frac{iH_o t}{\hbar}}\, \vec{r}_j(o)\, e^{-\frac{iH_o t}{\hbar}} ,$$

with similar expression for $a_j(t)$.

Consider now the expression

$$\int d^3\vec{x}\; d^3\vec{x}'\; e^{i\vec{k}.(\vec{x}-\vec{x}')} < \delta(\vec{x}'-\vec{r}_i(o))\delta(\vec{x}-\vec{r}_j(t))>$$

$$= < \int d^3\vec{x}'\; e^{-i\vec{k}.\vec{x}'}\delta(\vec{x}'-\vec{r}_i(o))\int d^3\vec{x}\;\delta(\vec{x}-\vec{r}_j(t))e^{i\vec{k}.\vec{x}}>$$

$$= < e^{-i\vec{k}.\vec{r}_i(o)}\; e^{i\vec{k}.\vec{r}_j(t)}> \quad . \tag{9}$$

Therefore, (8) becomes

$$\frac{d^2\sigma}{d\Omega d\varepsilon} = \frac{1}{2\pi\hbar}\left(\frac{k_2}{k_1}\right)\int d^3\vec{x}\; d^3\vec{x}'\; e^{i\vec{k}.(\vec{x}-\vec{x}')}\int dt\; e^{-i\omega t}$$

$$\times < \sum_{i,j} a_i(o)\delta(\vec{x}'-\vec{r}_i(o))a_j(t)\delta(\vec{x}-\vec{r}_j(t)) > . \tag{10}$$

If we make the transformation $\vec{x}-\vec{x}'=\vec{r}$, $\vec{x}=\vec{r}'$, and use the even property of the δ-function, we obtain

$$\frac{d^2\sigma}{d\Omega d\varepsilon} = \frac{1}{2\pi\hbar}\left(\frac{k_2}{k_1}\right)\int d^3\vec{r}\; d^3\vec{r}'\; dt\; e^{i(\vec{k}.\vec{r}-\omega t)}$$

$$\times < \sum_{i,j} a_i(o)\delta(\vec{r}+\vec{r}_i(o)-\vec{r}')a_j(t)\delta(\vec{r}'-\vec{r}_j(t)) >. \tag{11}$$

Define now the pair correlation function

$$\Gamma(\vec{r},t) = N^{-1} < \sum_{i,j}\int d^3\vec{r}'\; a_i(o)\delta(\vec{r}+\vec{r}_i(o)-\vec{r}')a_j(t)\delta(\vec{r}'-\vec{r}_j(t))>. \tag{12}$$

Therefore (11) becomes

$$\frac{d^2\sigma}{d\Omega d\varepsilon} = \frac{N}{2\pi\hbar}\left(\frac{k_2}{k_1}\right)\int e^{i(\vec{k}.\vec{r}-\omega t)}\;\Gamma(\vec{r},t)\; d^3\vec{r}\; dt\; . \tag{13}$$

One can define another pair correlation function $G(\vec{r},t)$

$$G(\vec{r},t) = N^{-1} < \sum_{i,j} \int d^3\vec{r}\,' \delta(\vec{r}+\vec{r}_i(o)-\vec{r}\,')\delta(\vec{r}\,'-\vec{r}_j(t))>. \tag{14}$$

In general, $\Gamma(\vec{r},t)$ can be studied in terms of the properties of $G(\vec{r},t)$. The latter is more familiarly known as Van Hove's pair correlation function. In fact if one makes the approximation $a_i=a_j=a$, then

$$\Gamma(\vec{r},t) \rightarrow a^2 G(\vec{r},t) \quad .$$

§4.2 Application to Light Scattering

The following derivation is due to Komarov and Fisher [20].

Consider a plane polarized monochromatic beam of light with electric vector

$$\vec{E}_o(\vec{r},t) = \vec{E}_1 \; e^{i(\Omega_o t-\vec{\kappa}_o . r)} \quad , \tag{15}$$

which is incident on a fluid. As we are only interested in dipole scattering, the interaction of the incident light and the fluid molecules will result in the induction of a dipole moment density given by

$$\vec{p}(\vec{r},t) = \alpha_e \; \vec{E}_o(\vec{r},t) \sum_i \delta(\vec{r}-\vec{r}_i(t)) \quad , \tag{16}$$

where α_e is the effective polarizability of each molecule, and $\vec{r}_i(t)$ is the position vector of the ith molecule at time t. The Hertz vector is then given by

$$\nabla^2\vec{\Pi}\;(\vec{r},t) - \frac{1}{c^2}\frac{\partial^2}{\partial t^2}\,\vec{\Pi}(\vec{r},t) = -4\pi\vec{p}(\vec{r},t) \tag{17}$$

and the scattered wave has an electric vector $\vec{E}'(\vec{r},t)$ given by

$$\vec{E}'(\vec{r},t) = \text{grad div }\vec{\Pi} - \nabla^2\,\vec{\Pi}. \tag{18}$$

In the wave zone (i.e. for large R), (18) becomes

$$\vec{E}'(\vec{R}.t) = \text{grad div }\vec{\Pi} - \frac{1}{c^2}\frac{\partial^2}{\partial t^2}\,\vec{\Pi}\;. \tag{19}$$

Now the solution of (17) is readily obtained in terms of the retarded potential as

$$\vec{\Pi}(\vec{R},t) = \int d^3\vec{r}'\int_{-\infty}^{\infty}dt'\,\frac{\vec{p}(\vec{r}',t')}{|\vec{r}'-\vec{R}|}\,\delta\Big(t'-t+\frac{|\vec{r}'-\vec{R}|}{c}\Big)\;. \tag{20}$$

Using (16) and the integral representation of the δ-function in (20), we have

$$\vec{\Pi}(\vec{R},t) = \frac{\alpha_e}{2\pi}\int d^3\vec{r}'dt'd\Omega'\,\frac{\vec{E}_0}{|\vec{r}'-\vec{R}|}\,e^{i(\Omega_0 t'-\vec{\kappa}_0\cdot\vec{r}')}$$

$$\times\; e^{i\Omega'(t'-t+\frac{|\vec{r}'-\vec{R}|}{c})}\;\sum_i\delta(\vec{r}-\vec{r}_i(t))\;. \tag{21}$$

For large R,

$$\Big(\text{grad div} - \frac{1}{c^2}\frac{\partial^2}{\partial t^2}\Big)\,\frac{\vec{E}_0}{|\vec{r}'-\vec{R}|}\,e^{i\Omega'(t'-t+\frac{|\vec{r}'-\vec{R}|}{c})}$$

$$\simeq \frac{1}{c^2R}\Big(\vec{E}_1 - \frac{\vec{E}_1\cdot\vec{R}}{R^2}\,\vec{R}\Big)\,e^{i\Omega'(t'-t+\frac{R}{c}-\frac{\vec{R}\cdot\vec{r}'}{cR})}\;. \tag{22}$$

Hence (19) gives

$$\vec{E}'(\vec{R},t) = \frac{\alpha_e}{2\pi c^2 R}\left(\vec{E}_1 - \frac{\vec{E}_1.\vec{R}}{R^2}\vec{R}\right)\int d^3\vec{r}'dt'd\Omega'^2 e^{i(\Omega_o t' - \vec{\kappa}_o.\vec{r})}$$

$$\times\ e^{i\Omega'(t' - t + \frac{R}{c} - \frac{\vec{R}.\vec{r}'}{cR})} \sum_i \delta(\vec{r}' - \vec{r}_i(t))\ . \qquad (23)$$

The Fourier transform of $\vec{E}'(\vec{R},t)$ is defined by

$$\vec{E}'(\vec{R},t) = \int_{-\infty}^{\infty} d\Omega'\ e^{i\Omega' t}\ \vec{E}'(\vec{R},\Omega')\ . \qquad (24)$$

Hence

$$\vec{E}'(\vec{R},\Omega) = \frac{\alpha_e \Omega^2}{2\pi c^2 R}\left(\vec{E}_1 - \frac{\vec{E}_1.\vec{R}}{R^2}\vec{R}\right)\int d^3\vec{r}'dt' e^{i(\Omega_o t' - \vec{\kappa}_o.\vec{r}')}$$

$$\times\ e^{-i\Omega(t' + \frac{R}{c} - \frac{\vec{R}.\vec{r}'}{cR})} \sum_i \delta(\vec{r}' - \vec{r}_i(t)) \qquad (25)$$

$$\vec{E}'^{*}(\vec{R},\Omega) = \frac{\alpha_e \Omega^2}{2\pi c^2 R}\left(\vec{E}_1 - \frac{\vec{E}_1.\vec{R}}{R^2}\vec{R}\right)\int d^3 r'' dt'' e^{-i(\Omega_o t'' + \vec{\kappa}_o.\vec{r}'')}$$

$\vec{E}'^{*}$

$$\times\ e^{i\Omega(t'' + \frac{R}{c} + \frac{\vec{R}.\vec{r}''}{cR})} \sum_j \delta(\vec{r}'' + \vec{r}_j(t''))\ . \qquad (26)$$

Therefore,

$$<|\vec{E}(\vec{R},\Omega)|^2> = \frac{\alpha_e^2 \Omega^4 N}{4\pi^2 c^4 R^2} E_o^2\ \sin^2\phi \int d^3\vec{r} d^3\vec{r}' dt dt''$$

$$\times\ e^{-i\left[(\vec{\kappa}_o - \frac{\Omega\vec{R}}{cR}).\vec{r} + (\Omega - \Omega_o)t\right]}$$

$$\times\ N^{-1} \sum_{i,j} < \delta(\vec{r}' - \vec{r}_i(t+t''))\delta(\vec{r} - \vec{r}' + \vec{r}_j(t''))>\ , \qquad (27)$$

where we have written $\vec{r}=\vec{r}'+\vec{r}''$ and $t=t'-t''$, and

$$\phi = \cos^{-1} \frac{\vec{E}_1 . \vec{R}}{|\vec{E}_1| R} \quad .$$

The last factor with the double summation is the Van Hove's two-particle correlation function $G(\vec{r},t)$ given in (14). Hence we have, for the intensity,

$$I(\vec{R},\Omega) = \frac{N\alpha_e^2\Omega^4}{2\pi c^2 R^2} I_o \sin^2\phi \int d^3r \int dt \; e^{-i[(\kappa_o - \frac{\Omega\vec{R}}{cR}).\vec{r}+(\Omega-\Omega_o)t]} \; G(\vec{r},t) \ , \tag{28}$$

where we have made use of the relation

$$I(\vec{R},\Omega)=\lim_{T\to\infty} \frac{\pi}{T} < |E(\vec{R},\Omega)|^2 > \ . \tag{29}$$

We now define $\omega=\Omega-\Omega_o$

$$\vec{k} = \frac{\Omega\vec{R}}{cR} - \vec{\kappa}_o = \vec{\kappa} - \vec{\kappa}_o \quad , \tag{30}$$

where $\vec{\kappa} = \frac{\Omega\vec{R}}{cR}$ is the wave vector of the scattered wave. Therefore, (28) becomes

$$I(\vec{R},\Omega) \equiv I(\vec{R},\omega) \approx \frac{N\alpha_e^2\Omega_o^4}{2\pi c^4 R^2} I_o \sin\phi \; S(\vec{k},\omega) \ , \tag{31}$$

where

$$S(\vec{k},\omega) = \int_V d^3\vec{r} \int dt \; e^{-i(\omega t-\vec{k}.\vec{r})} \; G(\vec{r},t) \ , \tag{32}$$

and where we have written Ω_o for Ω because for light scattering in fluids, $\omega \ll \Omega_o$.

Now for the light scattering problem, since $\omega << \Omega_o$, the time constants and lengths characterizing density fluctuations are much larger than those characteristic of molecular scattering processes. Therefore, only the relatively long time and large r limit of $G(\vec{r},t)$ is relevant. For this case $G(\vec{r},t)$ is reduced to the autocorrelated density function

$$G(\vec{r},t) = N^{-1} \int d^3\vec{r}\,' < n(\vec{r}\,'-\vec{r},o)n(\vec{r}\,',t)> , \tag{33}$$

where $n(\vec{r},t)$ is the number density at $\vec{r}$ and t. Also from symmetry of isotropic fluids,

$$G(\vec{r},t) = G(|\vec{r}|, t) . \tag{34}$$

We now let

$$n(\vec{r},t) - n_o = \sum_{k'} n(\vec{k}', t)\, e^{-i\vec{k}'.\vec{r}}$$

$$n(\vec{k},o) \equiv n(\vec{k}) , \tag{35}$$

where n_o is the mean number density of the molecules. The n_o part does not contribute to scattering. Substituting (35) and (33) into (32), and making use of

$$\frac{1}{V} \int e^{i(\vec{k}'-\vec{k}'').\vec{r}}\, d^3\vec{r} = \delta_{\vec{k}',\vec{k}''} , \tag{36}$$

we have

$$S(k,\omega) = V^2\, N^{-1} \int_{-\infty}^{\infty} e^{-i\omega t} < n(-\vec{k})n(\vec{k},t)>dt . \tag{37}$$

From (35), the inverse transform is

$$n(\vec{k},t) = \frac{1}{V} \int d^3\vec{r}\; e^{i\vec{k}.\vec{r}} |n(\vec{r},t) - n_o| \quad . \tag{38}$$

If we also define the Fourier transform in time,

$$n(\vec{k},\omega) = \int_{-\infty}^{\infty} dt'\; e^{-i\omega t'}\; n(\vec{k},t') \ , \tag{39}$$

(37) becomes

$$S(k,\omega) = V^2\; N^{-1} < n(-\vec{k}) n(\vec{k},\omega) > \quad . \tag{40}$$

The integrated intensity from (31), (39) and (40) is

$$I = \int I(\vec{R},\omega) d\omega = \frac{N\alpha_e^2 \Omega_o^4 I_o V^2}{R^2 c^4} \sin^2\phi < n(-\vec{k}) n(\vec{k}) > \ . \tag{41}$$

In light scattering, typically k ~ 10^5 cm^{-1}, so that k^{-1} >> intermolecular distance. For small k and except near the critical point of a fluid,

$$< n(-\vec{k}) n(\vec{k}) > = \frac{n_o^2 k_B T_o}{V\; B_T} \quad . \tag{42}$$

Substituting (42) into (41), we see that (41) is identical with Einstein's expression (1-19) provided we identify

$$4\pi\alpha_e n_o = \left[\rho\left(\frac{\partial \varepsilon}{\partial \rho}\right)_T\right]_{\rho=\rho_o} = \left[n\left(\frac{\partial \varepsilon}{\partial n}\right)_T\right]_{n=n_o} \ , \tag{43}$$

which is the same as (1-20).

Chapter 5

SPECTRAL DISTRIBUTION OF SCATTERED LIGHT IN RELAXING LIQUIDS

§5.1 Introduction

In this chapter we shall use the formalism outlined in Chapter 4 to calculate the spectral distribution of light scattered by a relaxing liquid. Such calculations both for a non-relaxing and relaxing liquids have been made previously by Mountain [23,24].

In a non-relaxing liquid the only mechanisms for the decay of density fluctuations are thermal conductivity and the static shear and bulk viscosities. Mountain [23] showed that in the limit of low frequencies $(\omega(b + \frac{4}{3}\eta)/\rho_o v^2 \ll 1)$, the spectrum consists of three Lorentzians, one for the Rayleigh line whose width depends on the thermal conductivity, and the other two for the two Brillouin components. The intensity ratio satisfies the Landau Placzek formula, as it should.

In a relaxing liquid the density fluctuations can decay in other modes than described above because of the existence of internal degrees of freedom. For the relaxing liquid Mountain [24] chose a model, in which there is essentially a frequency independent (static) shear viscosity and a frequency dependent or relaxing bulk viscosity, corresponding to the existence of a single relaxation time[†]. This gives rise to a fourth component. Mountain's model is applicable as long as η is such that $\omega\eta/\rho_o v^2 \ll 1$. If this is not the case, then, as is well known from ultrasonic data on liquids of high viscosity [13,16], shear viscosity must also be considered as a frequency dependent or relaxing quantity. Indeed, if one solves Mountain's equations for $\omega\eta/\rho_o v^2 > 1$, one finds that there are no Brillouin peaks in the scattered spectrum, contrary to observation in liquids like glycerine [see Refs. 35, 36].

In the present work we calculate the spectral distribution of scattered light for the following model of a relaxing liquid. We assume (1) that the ordinary shear viscosity is the low frequency limit of a shear relaxation process having a single relaxation time, and (2) that the same is true for bulk relaxation. For the latter we explicitly introduce an ordering parameter and use thermodynamic theory

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[†] Mountain actually considered a non-relaxing bulk viscosity also; this merely amounts to replacing η by $\eta + \frac{3}{4}b$ in the relevant equations.

of relaxation processes to calculate $\rho(\vec{k},t)$, instead of using the time integral representation of bulk viscosity as done by Mountain. We shall see later that our treatment, though somewhat lengthier, gives better insight into the type of bulk relaxation processes implied in Mountain's work. Anticipating our analysis we may mention that Mountain's representation for the bulk viscosity is appropriate for a density induced relaxation process, rather than the thermal relaxation process as stated by Mountain [24]†.

In Sec. 5.2 the exact expression for the spectral intensity of light scattered by our model of the liquid is derived. In Sec. 5.3, this spectral distribution is approximately expressed as a sum of five Lorentzians plus two other terms which are usually

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† In a recent paper, which came to hand after the work described in this chapter had been submitted for publication [25,26], Mountain [27] has treated the relaxing bulk viscosity by introducing a thermodynamic ordering parameter just as we do in the present work. Our formulation, however, is different from his. Our work differs from Mountain's also in that we consider a relaxing shear viscosity rather than a static shear viscosity.

small. The expressions for the heights and widths of the Lorentzians take particularly simple forms for certain limiting values of the shear and bulk relaxation times; these cases are discussed in subsequent sections of this chapter.

§5.2 Equations for Calculating $n(\vec{k},t)$ or $\rho(\vec{k},t)$ and $S(k,\omega)$

We have seen in Chapter 4 that the expression for the spectral intensity $S(k,\omega)$ involves the calculation of $n(\vec{k},t)$ or $\rho(\vec{k},t)$: this calculation proceeds along the same general lines as in the work of Kadanoff and Martin [28] and Mountain [24]. It is based on the suggestion, due to Landau and Placzek [11], that for a non-relaxing liquid the decay of density fluctuations is determined by the linearized hydrodynamic equations and the heat diffusion equation. In our work we have to start with a generalized form of the former equations to incorporate a relaxing shear viscosity, and to combine it with the thermodynamic equations appropriate for a fluid containing an ordering or relaxing parameter. The procedure is to first calculate $\rho(\vec{k},t)$ in terms of an initial fluctuation $\rho(\vec{k})$ and then to take the average over initial states indicated by $<\ldots>$ in the expression for $S(k,\omega)$.

The relevant equations for the calculation of $\rho(\vec{k},t)$ for our model are

$$\frac{\partial \rho}{\partial t} + \rho_o \operatorname{div} \vec{u} = 0 \tag{1}$$

$$\rho_o \frac{\partial \vec{u}}{\partial t} = -\operatorname{grad} P + \frac{4}{3} \int_0^t \eta'(t-t') \operatorname{grad} \operatorname{div} \vec{u}(t') dt' \tag{2}$$

$$\eta'(t) = G^{\infty} e^{-t/\tau_\eta} \tag{3}$$

$$\rho_o T_o \frac{\partial S}{\partial t} = \chi \quad \nabla^2 T \tag{4}$$

$$\frac{\partial \xi}{\partial t} = - L \, \delta \, Z \quad , \tag{5}$$

where the last equation is from (3-6). We shall take ρ, T and Z to be the independent variables. This set has the advantage of simplifying our calculations since the thermodynamic fluctuations in density are independent of those in T and Z.

Eq. (5) then can be rewritten as

$$\left(\frac{\partial Z}{\partial \xi}\right)_{T,\rho} \left[\left(\frac{\partial \xi}{\partial \rho}\right)_{T,Z} \left(\frac{\partial \rho}{\partial t}\right) + \left(\frac{\partial \xi}{\partial T}\right)_{\rho,Z} \left(\frac{\partial T}{\partial t}\right)\right] = -\left[\frac{\partial}{\partial t} + \frac{1}{\tau_{TV}}\right] \delta Z \tag{6}$$

where

$$\tau_{TV}^{-1} = L \left(\frac{\partial Z}{\partial \xi}\right)_{T,\rho} \quad . \tag{7}$$

We shall now make plentiful use of the thermodynamics relations which we derived in Chapter 3. Writing

$$\nabla P = \frac{B_T}{\rho_o} \nabla \rho + \beta B_T \nabla T + \left(\frac{\partial P}{\partial Z}\right)_{T,\rho} \nabla Z \tag{8}$$

and eliminating $\vec{u}$ between (1) and (2), we have

$$\frac{\partial^2 \rho}{\partial t^2} = \frac{B_T}{\rho_o} \nabla^2 \rho + \beta B_T \nabla^2 T + \left(\frac{\partial P}{\partial Z}\right)_{T,\rho} \nabla^2 Z + \frac{4}{3\rho_o} \int_o^t \eta'(t-t') \times \nabla^2 \left(\frac{\partial \rho}{\partial t'}\right) dt' \quad . \tag{9}$$

The equation of heat flow (4) can be written as

$$\frac{\chi}{\rho_o T_o} \nabla^2 T = - \frac{1}{\rho_o^2} \beta B_T \frac{\partial \rho}{\partial t} + \frac{c_V}{T_o} \frac{\partial T}{\partial t} + \left(\frac{\partial S}{\partial Z}\right)_{T,\rho} \left(\frac{\partial Z}{\partial t}\right) \quad . \tag{10}$$

The procedure now is to obtain the Fourier (space) and Laplace (time) transforms of (6), (9) and (10). Then the resulting equations can be solved for $\rho(\vec{k},S)$, which is the Fourier-Laplace transform of $\delta\rho(\vec{r},t)$. Thus $\rho(\vec{k},t)$ or $n(\vec{k},t)$ can be obtained as the inverse Laplace transform of $\rho(\vec{k},S)$. Accordingly, we define

$$\rho(\vec{k},S) = V^{-1} \int_0^\infty dt \int_V d^3\vec{r} [\rho(\vec{r},t)-\rho_o] e^{i\vec{k}.\vec{r}-St}, \quad \text{Re } S > 0 \ . \tag{11}$$

$$\rho(\vec{k}) = V^{-1} \int_V [\rho(\vec{r},0)-\rho_o] \ e^{i\vec{k}.\vec{r}} \ d^3\vec{r} \tag{12}$$

and similar formulae for $T(k,S)$, $T(k)$ and $Z(k,S)$, $Z(k)$.

Now we note that in the expression for the scattered spectrum given by (4-37), $n(\vec{k},t)$ occurs in $< \vec{n}(-\vec{k})n(\vec{k},t)>$, where the symbol <....> denotes statistical average, which is equivalent to time averaging. Owing to the arbitrariness of the time origin, we have

$$\phi(t) \equiv \langle n(-\vec{k})n(\vec{k},t)\rangle = \langle n(-\vec{k},t')n(\vec{k},t+t')\rangle \ . \qquad (13)$$

Since the liquid is, on the average, isotropic, therefore $\langle n(-\vec{k})n(\vec{k},t)\rangle = \langle n(\vec{k})n(-\vec{k},t)\rangle$. It is clear then that by a change of time variables in (13), we have

$$\phi(t) = \phi(-t) \ . \qquad (14)$$

The even property of $\phi(t)$ also requires that $\frac{d\phi}{dt} = 0$ at $t = 0$. Anticipating that $n(\vec{k},t)$ or $\rho(\vec{k},t)$ is to be used inside $\langle\ \rangle$, one can require $\rho(\vec{k},t)$ to satisfy

$$\rho(\vec{k},t) = \rho(\vec{k},-t), \left[\frac{\partial \rho(\vec{k},t)}{\partial t}\right]_{t=0} = 0 \ , \qquad (15)$$

which is the usual boundary condition used in such calculations [29]. Hence one may obtain the following results

$$V^{-1}\int d^3\vec{r}\int e^{i\vec{k}.\vec{r}-St}\,\frac{\partial \rho}{\partial t}\,dt = S\rho(\vec{k},S) - \rho(\vec{k})$$

$$V^{-1}\int d^3\vec{r}\int e^{i\vec{k}.\vec{r}-St}\,\frac{\partial^2 \rho}{\partial t^2}\,dt = S^2\rho(\vec{k},S) - S\rho\,(\vec{k})$$

$$V^{-1}\int dt\int e^{i\vec{k}.\vec{r}-St}\,\nabla^2\rho d^3\vec{r} = -k^2\rho(\vec{k},S) \ , \qquad (16)$$

with similar results for T and Z.

We now multiply (6), (9) and (10) by $V^{-1}e^{i\vec{k}.\vec{r}-St}$ and integrate. One obtains the following three equations:

$$\rho(\vec{k},S)\left[S\left(\frac{\partial Z}{\partial \xi}\right)_{T,\rho}\left(\frac{\partial \xi}{\partial \rho}\right)_{T,Z}\right] + T(\vec{k},S)\left[S\left(\frac{\partial Z}{\partial \xi}\right)_{T,\rho}\left(\frac{\partial \xi}{\partial T}\right)_{\rho,Z}\right]$$
$$+ (S + \tau_{TV}^{-1})Z(\vec{k},S) = \left(\frac{\partial Z}{\partial \xi}\right)_{T,\rho}\left(\frac{\partial \xi}{\partial \rho}\right)_{T,Z}\rho(\vec{k})$$
$$+ \left(\frac{\partial Z}{\partial \xi}\right)_{T,\rho}\left(\frac{\partial \xi}{\partial T}\right)_{\rho,Z} T(\vec{k}) + Z(\vec{k}) \tag{17}$$

$$\rho(\vec{k},S)\left[S^2 + \frac{4}{3\rho_o}\frac{k^2 S G^{\infty}\tau_\eta}{1+S\tau_\eta} + \frac{B_T k^2}{\rho_o}\right] + k^2\beta B_T T(\vec{k},S)$$
$$+ \left(\frac{\partial P}{\partial Z}\right)_{T,\rho} k^2 Z(\vec{k},S) = \left[S + \frac{4}{3\rho_o}\frac{k^2 G^{\infty}\tau_\eta}{1+S\tau_\eta}\right]\rho(\vec{k}) \tag{18}$$

$$\rho(\vec{k},S)\left[\frac{S\beta B_T}{\rho_o}\right] - \left[\frac{\lambda k^2}{\rho_o T_o} + \frac{S c_V}{T_o}\right] T(\vec{k},S) - S\left(\frac{\partial S}{\partial Z}\right)_{T,\rho} Z(\vec{k},S)$$
$$= \frac{\beta B_T}{\rho_o}\rho(\vec{k}) - \frac{c_V}{T_o}T(\vec{k}) - \left(\frac{\partial S}{\partial Z}\right)_{T,\rho} Z(\vec{k}) \ . \tag{19}$$

Eliminating $T(\vec{k},S)$ and $Z(\vec{k},S)$ and making use of thermodynamic relations in Chapter 3, we have

$$\rho(\vec{k},S) = (v_o k)^{-1}\frac{F(y)}{G(y)}\rho(\vec{k}) \ , \tag{20}$$

where we have neglected terms containing $T(\vec{k})$ and $Z(\vec{k})$ because from fluctuation theory, $<\rho(-\vec{k})T(\vec{k})> = <\rho(-\vec{k})Z(\vec{k})> = 0$. Hence

$$<\rho(-\vec{k})\rho(\vec{k},S)> = <\rho(-\vec{k})\rho(\vec{k})>\frac{F(y)}{v_o k G(y)} \tag{21}$$

or

$$<n(-\vec{k})n(\vec{k},S)> = <n(-\vec{k})n(\vec{k})>\sigma(k,S), \tag{22}$$

where

$$\sigma(k,S) = (v_o k)^{-1} \frac{F(y)}{G(y)} \qquad (23)$$

$$F(y) = y^4 x_1 x_2 + y^3 [x_1 + \frac{c_V}{c_V^\infty} x_2 + \alpha x_1 x_2] + y^2 \Big[\frac{B_S^\infty - B_T}{B_S} x_1 x_2$$

$$+ \frac{4}{3} \frac{G^\infty}{B_S} x_1 x_2 + \frac{c_V}{c_V^\infty} + \alpha(x_1 + x_2) \Big] + y \Big[\frac{B_S^\infty - B_T}{B_S}$$

$$+ \frac{B_S - B_T + \frac{4}{3} G^\infty}{B_S} \frac{c_V}{c_V^\infty} x_2 + \alpha + \alpha x_1 x_2 \frac{(B_T^\infty + \frac{4}{3} G^\infty - B_T)}{B_S} \Big]$$

$$+ \frac{c_V}{c_V^\infty} (1 - \frac{1}{\gamma}) + \alpha x_1 \frac{(B_T^\infty - B_T)}{B_S} + \frac{4}{3} \frac{G^\infty}{B_S} \alpha x_2 \qquad (24)$$

$$G(y) = y^5 x_1 x_2 + y^4 [x_1 + \frac{c_V}{c_V^\infty} x_2 + \alpha x_1 x_2] \; y^3 \Big[\frac{c_V}{c_V^\infty} + \frac{{v^\infty}^2}{v_o^2} x_1 x_2$$

$$+ \alpha(x_1 + x_2) \Big] + y^2 \Big[\frac{B_S^\infty}{B_S} x_1 + \frac{c_V}{c_V^\infty} \frac{(B_S + \frac{4}{3} G^\infty)}{B_S} x_2 + \alpha$$

$$+ \alpha x_1 x_2 \frac{(B_T^\infty + \frac{4}{3} G^\infty)}{B_S} \Big] + y \Big[\frac{c_V}{c_V^\infty} + \frac{B_T^\infty}{B_S} \alpha x_1$$

$$+ \frac{B_T + \frac{4}{3} G^\infty}{B_S} \alpha x_2 \Big] + \frac{\alpha}{\gamma} \quad . \qquad (25)$$

Here v^∞ is the sound velocity at infinite frequency.

$$v^\infty = \left[\frac{(B_S^\infty + \frac{4}{3} G^\infty)}{\rho_o} \right]^{\frac{1}{2}} , \qquad y = \frac{S}{v_o k}$$

$$x_1 = v_o k \tau_{TV} \qquad , \quad x_2 = v_o k \tau_\eta$$

$$\alpha = \chi k / (\rho_o v_o c_V^\infty) \qquad (26)$$

Now from (22),

$$\sigma(k,S) = \frac{\langle n(-\vec{k})n(\vec{k},S)\rangle}{\langle n(-\vec{k})n(\vec{k})\rangle} = \frac{F(y)}{v_o kG(y)}$$

Therefore

$$\sigma(k,t) = \frac{\langle n(-\vec{k})n(\vec{k},t)\rangle}{\langle n(-\vec{k})n(\vec{k})\rangle} \quad , \tag{27}$$

$$\sigma(k,S) = \int_0^\infty \sigma(\vec{k},t)\, e^{-St} dt \quad , \tag{28}$$

$$\sigma(k,\omega) = \frac{\langle n(-\vec{k})n(\vec{k},\omega)\rangle}{\langle n(-\vec{k})n(\vec{k})\rangle}$$

$$= \int_{-\infty}^{\infty} e^{-i\omega t}\, \sigma(k,t)dt \ . \tag{29}$$

Since from (27), we have

$$\sigma(k,t) = \sigma(k, -t) \ , \tag{30}$$

therefore

$$\sigma(k,\omega) = 2 \text{ Re } \sigma(k, S=i\omega)$$

$$= 2 \text{ Re } \frac{F(\frac{i\omega}{v_o k})^{\dagger}}{v_o kG(\frac{i\omega}{v_o k})} \quad , \tag{31}$$

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† Strictly speaking, one should write (31) as

$$\sigma(k,\omega) = \lim_{\delta\to 0} 2 \text{ Re } \frac{F(\frac{i\omega+\delta}{v_o k})}{v_o kG(\frac{i\omega+\delta}{v_o k})} \ , \ \delta > 0 \quad , \tag{32}$$

which satisfies the requirement on S that Re S > 0. (32) has to be used, for example, in the case of an idealized fluid having no sound absorption. (The spectral distribution for this case consists of just three δ-functions.)

and

$$S(k,\omega) = V^2N^{-1} < n(-\vec{k})n(\vec{k}) > \sigma(k,\omega) \quad , \tag{33}$$

where

$$< n(-\vec{k})n(\vec{k}) > = \frac{n_o^2 k_B T_o}{V\ B_T} \tag{34}$$

from Appendix

We shall for simplicity consider the spectral distribution to be given by $\sigma(k,\omega)$ of Eq. (31). The total integrated intensity is

$$\int_{-\infty}^{\infty}\sigma(k,\omega)d\omega = \int_{-\infty}^{\infty} dt\ \sigma(k,t) \int_{-\infty}^{\infty} e^{-i\omega t}\ d\omega$$

$$= 2\pi\int_{-\infty}^{\infty}\sigma(k,t)\delta(t)dt = 2\pi\sigma(k,o) = 2\pi \quad , \tag{35}$$

where we make use of $\sigma(k,o) = 1$ from (31)

§5.3 Approximate Determination of the Spectral Intensity

Eq. (31) is the exact expression for our model. Since F(y) and G(y) are quite complicated, it is not easy to visualize from (31) the variation of $\sigma(k,\omega)$ with ω and other parameters defined in F(y) and G(y). A more convenient, though necessarily approximate, form of $\sigma(k,\omega)$ can be obtained which separates out the various components. The method is as follows:

The inverse Laplace transform, $\sigma(k,t)$, of $\sigma(k,S)$ is first obtained by writing $\sigma(k,S)$ as partial fractions.

Then $\sigma(k,\omega)$ can be evaluated from $\sigma(k,t)$. We have

$$\sigma(k,t) = \int_{-\infty}^{\infty} \sigma(k,t')\delta(t-t')\,dt'$$

$$= \frac{1}{2\pi}\int_{-\infty}^{\infty} dt' \int_{-\infty}^{\infty} d\omega'\sigma(k,t')\, e^{i\omega'(t-t')}$$

$$= \frac{1}{2\pi}\int_{-\infty}^{\infty} d\omega' e^{i\omega' t}\{\int_{0}^{\infty}\sigma(k,t')e^{-i\omega' t'}dt' + \int_{0}^{\infty}\sigma(k,t')e^{i\omega' t'}dt'\}$$

$$= \frac{1}{\pi}\int_{-\infty}^{\infty} d\omega'\, e^{i\omega' t}\, \mathrm{Re}\,\sigma(k,i\omega') \; . \qquad (36)$$

In evaluating (36) by contour integration, one needs to know the poles of $\sigma(k,S)$, hence the roots of $G(y)=0$ and this can be done only approximately.

We shall assume that $\alpha(= \frac{\chi k}{\rho_o v_o c_V^\infty}) \ll 1$. This is true for almost all nonmetallic liquids for the value of k ($\sim 10^5$) relevant to the problem of light scattering. For example, for glycerine $\alpha \simeq 5 \times 10^{-9}k$, and from (1-32), k is at most $3 \times 10^5 \text{cm}^{-1}$ for scattering of visible light*.

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* Throughout this paper we consider this case ($\alpha \ll 1$) only. It may be mentioned that if $\alpha \gtrsim 1$, then Eq. (19) no longer adequately represents the energy transport and one should add on the left-hand side of it a term $\tau\frac{\partial}{\partial t}\left|\rho_o T\frac{dS}{dt}\right|$ where τ is a relaxation time characteristic of phonon-phonon collisions. For solids at low temperatures or for liquid helium this term may have to be taken into consideration; see, M. Chester, Phys. Rev. <u>131</u>, 2013 (1963).

Let us further assume, for the moment, that $\alpha x_1 \ll 1$, $\alpha x_2 \ll 1$. This covers most of the interesting relaxation region $x_1, x_2 \lesssim 1$. One then readily sees from (25) that there is one root $-y_o$ of $G(y) = 0$, which is much smaller than unity and is approximately given by

$$y_o \simeq \frac{\alpha c_V}{\gamma c_V^\infty} = \frac{\chi k}{\rho_o v_o c_P} \quad , \qquad y_o \ll 1 \quad . \tag{37}$$

To determine the other roots we try to factorize $G(y)$ in the form

$$\frac{G(y)}{x_1 x_2} = (y+\theta+\frac{iv}{v_o})(y+\theta-\frac{iv}{v_o})(y+q_1+q_2)(y+q_1-q_2)(y+y_o) \tag{38}$$

where v, θ, q_1 and q_2 are as yet unknowns, and where v can be interpreted as the velocity of the two propagating modes and $v_o k\theta$ their absorption per second. $2\pi(\frac{v_o}{v})\theta$ is the absorption per cycle. This will be obvious from the expression for $\sigma(k,t)$ which we shall obtain later.

Now θ is usually small compared with unity as absorption data from ultrasonic show. Hence in the following we shall neglect θ^2 compared to unity. Expanding (38), we obtain

$$\frac{G(y)}{x_1x_2} \simeq y^5+y^4(2q_1+2\theta+y_o)+y^3(q_1^2-q_2^2+\frac{v^2}{v_o^2}+4\theta q_1+y_o(2q_1+2\theta))$$

$$+y^2\left[2\theta(q_1^2-q_2^2) + 2q_1\frac{v^2}{v_o^2} + y_o(q_1^2-q_2^2+ \frac{v^2}{v_o^2})\right]$$

$$+y\left[(q_1^2-q_2^2)\frac{v^2}{v_o^2} +y_o(2\theta(q_1^2-q_2^2)+2q_1 \frac{v^2}{v_o^2})\right]+y_o(q_1^2-q_2^2)\frac{v^2}{v_o^2} \ . \qquad (39)$$

On the other hand, from (25)

$$\frac{G(y)}{x_1x_2} = y^5+y^4\left[\frac{1}{x_d} + \frac{1}{x_2} + \alpha\right]+y^3\left[\frac{1}{x_dx_2} + \frac{{v^\infty}^2}{v_o^2} +\alpha(\frac{1}{x_2} + \frac{c_V^\infty}{c_Vx_d})\right]$$

$$+ y^2 \left[\frac{B_S^\infty}{B_S}\frac{1}{x_2} + \frac{B_S+\frac{4}{3}G^\infty}{B_Sx_d} + \frac{\alpha c_V^\infty}{x_2x_dc_V} + \frac{\alpha(B_T^\infty+\frac{4}{3}G^\infty)}{B_S}\right]$$

$$+ y \left[\frac{1}{x_dx_2} + \frac{B_T^\infty\alpha}{B_Sx_2} + \frac{B_T+\frac{4}{3}G^\infty}{B_S}\frac{\alpha c_V^\infty}{c_Vx_d}\right] + \frac{\alpha c_V^\infty}{c_V\gamma x_2x_d} \qquad (40)$$

where we have used (3-34) to define

$$x_d \equiv v_o\ k\ \tau_{TV} = \frac{c_V^\infty}{c_V}x_1 \ . \qquad (41)$$

Comparing now terms independent of y and the coefficients of y^4 in (39) and (40), we have

$$q_1^2 - q_2^2 = (x_2x_d)^{-1}\frac{v_o^2}{v^2} \qquad (42)$$

$$2q_1 = x_2^{-1} + x_d^{-1} - 2\theta + \alpha(1 - \frac{c_V^\infty}{c_V\gamma})$$

$$\simeq x_2^{-1} + x_d^{-1} - 2\theta \ . \qquad (43)$$

Hence

$$2q_2 \approx \left[(x_2^{-1} + x_d^{-1} - 2\theta)^2 - 4(x_2 x_d)^{-1} \frac{v_o^2}{v^2}\right]^{\frac{1}{2}} \tag{44}$$

Next equating coefficients of y^2 in (39) and (40), making use of (42) and (43), and retaining only the linear terms in α, we have

$$\begin{aligned} 2\theta = {} & \left[x_2 x_d \left(\frac{v}{v_o}\right)^4 - 1\right]^{-1} \Big\{ x_2 \left(\frac{v}{v_o}\right)^2 \left[\left(\frac{v}{v_o}\right)^2 - \frac{(B_S + \frac{4}{3}G^\infty)}{B_S}\right] \\ & + x_d \left(\frac{v}{v_o}\right)^2 \left[\left(\frac{v}{v_o}\right)^2 - \frac{B_S^\infty}{B_S}\right] + \alpha(\frac{c_V^\infty}{c_V} \left[\frac{1}{\gamma} - \left(\frac{v}{v_o}\right)^2\right] \\ & + \alpha x_2 x_d \left(\frac{v}{v_o}\right)^2 \left[\left(\frac{v}{v_o}\right)^2 - \frac{(B_T^\infty + \frac{4}{3}G^\infty)}{B_S}\right] \Big\} . \end{aligned} \tag{45}$$

The only unknown left now is v/v_o. This we determine approximately by comparing the coefficients of y^3 in (39) and (40). Eliminating q_1 and q_2 from (42) and (43), neglecting terms containing α and terms proportional to θ^2, one obtains for v^2 the equation

$$\begin{aligned} & \left(\frac{v}{v_o}\right)^8 (x_2 x_d)^2 + \left(\frac{v}{v_o}\right)^6 \left[x_2^2 + x_d^2 + x_2 x_d - (x_2 x_d)^2 \frac{(B_S^\infty + \frac{4}{3}G^\infty)}{B_S}\right] \\ & - \left(\frac{v}{v_o}\right)^4 (x_2 + x_d) \left[x_2 (B_S + \frac{4}{3} G^\infty)/B_S + x_d B_S^\infty / B_S\right] \\ & + \left(\frac{v}{v_o}\right)^2 \left[x_2 x_d (B_S^\infty + \frac{4}{3} G^\infty)/B_S + 1\right] - 1 = 0 . \end{aligned} \tag{46}$$

We are interested in that solution of (46) which gives $v^2 = v_o^2$ when $x_2 = x_d = 0$. A particularly simple, though approximate, expression for v^2 is obtained if one sets $(\frac{v}{v_o})^2 = 1 + \Delta$, and assumes that $\Delta << 1$. Then, retaining only the linear terms in Δ and in $\frac{B_S^\infty - B_S}{B_S}$ and $\frac{\frac{4}{3}G^\infty}{B_S}$ one may readily obtain

$$\frac{v^2}{v_o^2} \simeq 1 + \Delta = 1 + \frac{\frac{4}{3}G^\infty}{B_S} \frac{x_2^2}{1+x_2^2} + \frac{B_S^\infty - B_S}{B_S} \frac{x_d^2}{1+x_d^2} \quad . \qquad (47)$$

Eq. (47) gives correct values for the velocities in the various limits, namely $v \to v_o$ for x_2, $x_d \to 0$ and $v \to v^\infty = [\frac{B_S^\infty + \frac{4}{3}G^\infty}{B_S}]^{\frac{1}{2}}$ for $x_2, x_d \to \infty$; $v \to (\frac{B_S}{\rho_o})^{\frac{1}{2}}$ for $x_2 \to 0$, $x_d \to \infty$ and $v \to (\frac{4}{3}\frac{G^\infty}{\rho_o})^{\frac{1}{2}}$ for $x_d \to 0$, $x_2 \to \infty$.

For intermediate values of x_2 and x_d, it is only approximate. If on the other hand we determine the velocity without neglecting the terms proportional to θ^2, we find, on ignoring terms proportional to α and retaining terms only up to quadratic powers in x_2 and x_d that

$$\frac{v^2}{v_o^2} \simeq 1 + \frac{B_S^\infty - B_S}{B_S}\left(1 - \frac{1}{4}\frac{B_S^\infty - B_S}{B_S}\right)x_d^2 + \frac{\frac{4}{3}G^\infty}{B_S}\left(1 - \frac{1}{3}\frac{G^\infty}{B_S}\right)$$
$$- \frac{2}{3}\frac{G^\infty}{B_S}\frac{(B_S^\infty - B_S)}{B_S} x_2 x_d + \ldots\ldots\ldots \qquad (48)$$

Finally, to complete the term by term comparison of (39) and (40), we note that the coefficients of y in them are equal if terms proportional to α are neglected.

Having determined the roots of $G(y)=0$ approximately, we are now in a position to calculate $\sigma(k,t)$. We first write $\sigma(k,S)$ as partial fractions

$$\sigma(k,S) = \sum_{m=0}^{2} \frac{\sigma_m}{S+S_m} + \frac{\sigma_B+ig}{S+\Gamma+ivk} + \frac{\sigma_B-ig}{S+\Gamma-ivk} \quad , \tag{49}$$

where

$$\Gamma = v_o k\,\theta \;, \qquad S_o = v_o k y_o \simeq \frac{\chi k^2}{\rho_o c_P} \;,$$

$$S_1 = v_o k\,(q_1+q_2), \qquad S_2 = v_o k\,(q_1 - q_2) \tag{50}$$

where σ_o, σ_1, σ_B and g are real constants (independent of S), which are to be determined. Now using (36) and (49), we have

$$\sigma(k,t) = \sum_{m=0}^{2} \sigma_m\, e^{-S_m|t|} + 2e^{-\Gamma|t|}(\sigma_B \cos vkt + g \sin vk|t|). \tag{51}$$

In the above equation, the interpretations we have given to v and Γ become clear.

In the calculation of $\sigma(k,t)$ by contour integration the singularities which are connected with the roots of $G(y)=0$ all lie in the upper complex plane. The quantities σ_m, σ_B and g are given by

$$\sigma_m = \lim_{S\to -S_m} (S + S_m)\, \frac{F(\frac{-S_m}{v_o k})}{v_o k G(\frac{-S_m}{v_o k})} \tag{52}$$

$$\sigma_B = \mathrm{Re} \lim_{S \to -\Gamma - ivk} (S+\Gamma+ivk) \frac{F(\frac{-\Gamma-ivk}{v_o k})}{v_o k G(\frac{-\Gamma-ivk}{v_o k})} \tag{53}$$

$$g = \mathrm{Im} \lim_{S \to -\Gamma - ivk} (S+\Gamma+ivk) \frac{F(\frac{-\Gamma-ivk}{v_o k})}{v_o k G(\frac{-\Gamma-ivk}{v_o k})} . \tag{54}$$

These expressions then give

$$\sigma_o = 1 - \frac{1}{\gamma} , \qquad \sigma_1 = f(q_1,q_2), \qquad \sigma_2 = f(q_1,-q_2) ,$$

$$\sigma_B = \frac{a_1 b_1 + a_2 b_2}{b_1^2 + b_2^2} , \qquad g = \frac{a_1 b_2 - a_2 b_1}{b_1^2 + b_2^2} , \tag{55}$$

where

$$f(q_1,q_2) = \{(1-x_2(q_1+q_2))[1 - \frac{1}{\gamma} + (\frac{1}{\gamma} - \frac{B_S^\infty}{B_S})(q_1+q_2)x_d]$$

$$+(q_1+q_2)(1-x_d(q_1+q_2)[q_1+q_2-x_2(q_1+q_2)^2 - \frac{4}{3}\frac{G^\infty}{B_S} x_2]\}$$

$$\{2q_2(q_1+q_2)x_d x_2[(q_1+q_2)^2 - 2\theta(q_1+q_2) + \frac{v^2}{v_o^2}]\}^{-1} \tag{56}$$

$$a_1 = 1 - \frac{1}{\gamma} - \frac{v^2}{v_o^2} + x_2 x_d (\frac{v}{v_o})^2 [\frac{(v^2 - v^{\infty 2})}{v_o^2} + \frac{1}{\gamma}] + \theta[x_d(\frac{3v^2}{v_o^2} - \frac{B_S^\infty}{B_S} + \frac{1}{\gamma})$$

$$+ x_2(\frac{3v^2}{v_o^2} - \frac{4}{3}\frac{G^\infty}{B_S} - 1 + \frac{1}{\gamma})] + \theta^2 x_2 x_d [(\frac{v^\infty}{v_o})^2 - 6(\frac{v}{v_o})^2 - \frac{1}{\gamma}] \tag{57}$$

$$a_2 = \frac{v}{v_o} \{x_d(\frac{B_S^\infty}{B_S} - \frac{1}{\gamma} - \frac{v^2}{v_o^2}) + x_2(1 - \frac{1}{\gamma} - \frac{v^2}{v_o^2} + \frac{4}{3}\frac{G^\infty}{B_S})$$

$$+ 2\theta[-1 + x_2 x_d(\frac{1}{\gamma} + \frac{2v^2 - v^{\infty 2}}{v_o^2})] + 3\theta^2(x_2+x_d)\} \tag{58}$$

$$b_1 = -2x_2 x_d (\frac{v}{v_o})^2 [(\frac{v_o}{v})^2 (\frac{1}{x_2 x_d}) - \frac{v^2}{v_o^2} - 4q_1\theta] \tag{59}$$

$$b_2 = -2x_2x_d\left(\frac{v}{v_o}\right)\left\{\theta\left[\left(\frac{v_o}{v}\right)^2 \frac{1}{x_2x_d} - \frac{3v^2}{v_o^2}\right] + \frac{2v^2q_1}{v_o^2}\right\} \tag{60}$$

From Eq. (29) and Eq. (51), one then has

$$\sigma(k,\omega) \simeq \sum_{m=0}^{2} \frac{\sigma_m 2S_m}{\omega^2+S_m^2} + \sigma_B\left[\frac{2\Gamma}{(\omega+vk)^2+\Gamma^2} + \frac{2\Gamma}{(\omega-vk)^2+\Gamma^2}\right]$$

$$+ 2g\left[\frac{\omega + vk}{(\omega+vk)^2+\Gamma^2} - \frac{\omega - vk}{(\omega-vk)^2+\Gamma^2}\right] . \tag{61}$$

§5.4 General Discussion

Eq. (61) is an approximate formula for the spectral distribution $\sigma(k,\omega)$. It is correct as long as the sound absorption is small enough so that $\theta^2 \ll 1$ is justified, and that x_2, x_d are not too large so that $\alpha x_2, \alpha x_d \ll 1$ hold.

The first three terms in (61) each has a peak at $\omega=0$, i.e. at the incident light frequency. Thus the central or Rayleigh component for our model consists in general of the sum of three Lorentzians. The width of the first of these is determined by the thermal conductivity, whereas the widths of the other two depend on the relaxation times τ_d and τ_η, in a way showing that the shear and bulk relaxation processes are mixed together. The next two terms in (61) have a peak at $\omega=-vk$ and $\omega=+vk$ respectively and represent Brillouin components. The width Γ of each of them is the sound absorption per second.

Thus if the last two terms in (61) could be ignored, the spectral distribution would consist of a sum of five Lorentzians, three peaked at the incident frequency and the other two at $\omega = \pm vk$ respectively.

We observe that the last two terms in (61) contribute nothing to the integrated intensity. Also, as may be readily verified, their effect on intensity distribution may be neglected so long as $\theta (= \Gamma/vk) \ll 1$. If, however, $\theta \gtrsim 1$, they affect markedly the position and shape of the Brillouin peaks. It may be mentioned that these asymmetric terms would occur also in the corresponding expressions in the works of previous authors [24, 28], although they did not write them explicitly*. The origin of these terms can be traced to the requirement that any solution for $\sigma(k,t)$ must satisfy the boundary conditions similar to (19), viz.

$$\sigma(k,t) = \sigma(k,-t) \text{ and } \left.\frac{\partial \sigma(k,t)}{\partial t}\right|_{t=0} = 0 . \tag{62}$$

The second of these conditions can be satisfied only if g is not approximated to zero in eqns. (49) and (51). Using (62) into (51) one obtains a consistency relation for the solution

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* The existence of these terms has been recently noted also by Montrose et al. [30].

$$2gvk = \sum_{m=0}^{2} \sigma_m S_m + 2\sigma_B \Gamma \quad . \tag{63}$$

The importance of the asymmetric terms in the spectral distribution is probably best illustrated by considering a model in which the effect of thermal conductivity can be ignored and the only cause of sound absorption is due to non-relaxing viscosities. One can obtain a simple exact expression for $\sigma(k,\omega)$ for this case which we shall discuss at the next section.

For the total integrated intensity, we have from (35) that $\int_{-\infty}^{\infty} \sigma(,\omega)\, d\omega = 2\pi$. If we perform this integration on Eq. (61), we obtain the relation

$$\sigma_o + \sigma_1 + \sigma_2 + 2\sigma_B = 1 \; . \tag{64}$$

The intensity ratio is then given by

$$R = \frac{I_R}{2I_B} = \frac{\sigma_o+\sigma_1+\sigma_2}{2\sigma_B} = \frac{1}{2\sigma_B} - 1 \; . \tag{65}$$

This quantity is in general very complicated and differs from the value of $\gamma-1$ of Landau Placzek.

We shall now study some special cases for which the various complicated expressions simplify somewhat or very much. Moreover we shall show that for some cases our results can be reduced to those obtained by previous workers.

§5.5 Special Cases

(a) Unrelaxed viscosities as the only loss mechanisms

This case is obtained if we put $\alpha=0$, $x_d, x_2 \rightarrow 0$, but $(B_S^{\infty} - B_S)x_d = v_o k b$, $G^{\infty}x_2 = v_o k \eta$ are finite. Then for small dispersion, $\Gamma \rightarrow \frac{1}{2\rho_o}(\frac{4}{3}\eta + b)k^2$, $\sigma_o=\sigma_1=\sigma_2=0$, $\sigma_B \rightarrow \frac{1}{2}$, $g \rightarrow \frac{1}{2}\Gamma/v_o k$. However, one can easily carry out an exact analysis for this case. The factorization of $G(y)$ can be done without approximation. From (23), (24) and (25), we have

$$\sigma(k,S) = \frac{1}{v_o k}\,\frac{F(y)}{G(y)} \quad ,$$

$$F(y) = y + a$$

$$G(y) = y^2 + ay + 1$$

$$a = \frac{k(b + \frac{4}{3}\eta)}{\rho_o v_k} \quad . \qquad (66)$$

Then

$$G(y) = (y + \theta + \frac{iv}{v_o})(y + \theta - \frac{iv}{v_o})$$

with

$$\frac{v}{v_o} = (1 - \frac{1}{4}a^2)^{\frac{1}{2}}$$

$$\theta = \tfrac{1}{2}a, \qquad \text{or } \Gamma = \frac{1}{2}\,\frac{(b + \frac{4}{3}\eta)k^2}{\rho_o} \quad . \qquad (67)$$

From these one determines easily that

$$\sigma_o=\sigma_1=\sigma_2= 0 \;, \qquad \sigma_B = \tfrac{1}{2}$$

$$g = \tfrac{1}{2}\,\Gamma/vk \quad . \qquad (68)$$

All these are exact results. We see that g is not zero, so that the Brillouin peaks do not occur at $\omega=\pm vk$. Their position can be obtained by finding the maxima of the spectral distribution

$$\sigma(k,\omega) = \tfrac{1}{2}\left[\frac{2\Gamma}{(\omega+vk)^2+\Gamma^2} + \frac{2\Gamma}{(\omega-vk)^2+\Gamma^2}\right] + \frac{\Gamma}{vk}\left[\frac{\omega+vk}{(\omega+vk)^2+\Gamma^2} - \frac{\omega-vk}{(\omega-vk)^2+\Gamma^2}\right] . \tag{69}$$

From (31), this is also equal to

$$\sigma(k,\omega) = \frac{2a\,v_o^3\,k^3}{a^2\omega^2v_o^2k^2+(\omega^2-v_o^2k^2)^2} . \tag{70}$$

Then $\frac{\partial\,\sigma(k,\omega)}{\partial\,\omega} = 0$ gives two maxima at

$$\omega = \omega_B = \pm v_o k\,[1 - \tfrac{1}{2}a^2]^{\frac{1}{2}} \tag{71}$$

and a minimum at $\omega=0$. So in general, $\omega_B \neq v_o k$. We also see in Eq. (71) that if the viscosities are so large that $a^2 > 2$ or

$$\frac{(b+\frac{4}{3}\eta)k}{\rho_o v_o} > \sqrt{2} \tag{72}$$

then there are no Brillouin peaks.

(b) <u>$x_2 << 1$, $\alpha x_d << 1$</u>

This case is relevant to the study of a relaxing bulk viscosity and we should then be in a position to compare our model with that of Mountain's.

In this case, since $\alpha \ll 1$, we have also $\alpha x_2 \ll 1$. (50) and (55) then reduce to

$$S_o \simeq \frac{\chi k^2}{\rho_o c_P} \quad , \quad S_1 \simeq \frac{1}{\tau_\eta} \quad , \quad S_2 \simeq \frac{v_o^2}{v^2 \tau_d} \quad ,$$

$$\sigma_o = 1 - \frac{1}{\gamma} \quad , \quad \sigma_1 \sim 0(x_2^4) \sim 0 \quad ,$$

$$\sigma_2 \simeq \left\{ \frac{(B_S^\infty - B_S)k^2}{\rho_o} - \left(\frac{v^2}{v_o^2} - 1\right)\left[\frac{v_o^4}{v^4 \tau_d^2} + v_o^2 k^2 \left(1 - \frac{1}{\gamma}\right)\right] \right\} \times \left\{ v^2 k^2 + \frac{v_o^4}{v^4 \tau_d^2} \right\}^{-1}$$

$$2\sigma_B = 1 - \sigma_o - \sigma_1 - \sigma_2 \quad . \tag{73}$$

From (45), we have

$$2\theta \simeq \frac{v^2}{v_o^2} x_d \left(\frac{B_S^\infty}{B_S} - \frac{v^2}{v_o^2}\right) + \frac{\alpha c_V^\infty}{c_V} \left(\frac{v^2}{v_o^2} - \frac{1}{\gamma}\right) \quad . \tag{74}$$

We have neglected any static viscosities in our model. If one wants to include the static shear viscosity also , one can do this by taking $x_2 \to 0$ while $G^\infty \to \infty$ and $G^\infty x_2 = \frac{4}{3}\eta \, v_o k$. Thus (45) becomes[†]

[†] The frequency independent part of the bulk viscosity, b_o, as considered also by Mountain, can be included easily by replacing η in (75) by $\eta + \frac{3}{4} b_o$.

$$2\theta \simeq \frac{v^2}{v_o^2}\, x_d\Big(\frac{B_S^\infty}{B_S} - \frac{v^2}{v_o^2}\Big) + \frac{\alpha c_V^\infty}{c_V}\Big(\frac{v^2}{v_\rho^2} - \frac{1}{\gamma}\Big) + \frac{\frac{4}{3}\eta k v^2}{\rho_o v_o^3}(1 + \alpha x_d). \quad (75)$$

For the special case $\tau_d \to 0$, it can be verified easily that $\sigma_2 \to 0$ and $2\sigma_B = \frac{1}{\gamma}$. (76)

Hence there is just one mode for the central component, and the intensity ratio

$$R = \frac{I_R}{2I_B} = \gamma - 1 \quad (77)$$

corresponds to the Landau-Placzek value. The sound absorption per cycle is from (75) given by

$$2\Gamma = [(v'^{\infty 2} - v_o^2)]k^2\, \tau_d + \frac{4}{3}\frac{\eta k^2}{\rho_o} + (\gamma - 1)\frac{\chi k^2}{\rho_o c_P}, \quad (78)$$

where $v'^\infty = (B_S^\infty/\rho_o)^{\frac{1}{2}}$ is the velocity of sound waves at frequencies such that $x_2 << 1$ and $x_d >> 1$.

For the case $x_d >> 1$, we have

$$\sigma_2 \simeq \frac{1}{\gamma}\Big(1 - \frac{v_o^2}{v'^{\infty 2}}\Big),$$

$$2\sigma_B = 1 - \sigma_o - \sigma_2 = \frac{1}{\gamma}\frac{v_o^2}{v'^{\infty 2}} = \frac{B_T}{B_S^\infty}. \quad (79)$$

Therefore

$$R = \frac{I_R}{2I_B} = \gamma\frac{v'^{\infty 2}}{v_o^2} - 1 \quad (80)$$

Eq. (80) was first obtained by Rytov [31]. For a purely temperature-induced relaxation process, $B_T = B_T^\infty$ [see

Sec. 3-3c], and Eq. (80) may be written in the alternative form

$$R = \frac{I_R}{2I_B} = \gamma^{\infty} - 1 \tag{81}$$

Let us now compare our results with those obtained by Mountain [24]. The expressions (61) with g=0 (which Mountain assumed) and S_o, S_1, σ_o, σ_1 etc. given by (73) agrees with the expressions (43) in Mountain's work provided we identify his τ with our $\tau_d \equiv \tau_{SV}$. In Sec.3-2, we have discussed and given the transformations of the various types of relaxation times. We wish to point out that it is important to remember which relaxation time is determined from the light scattering data, if it is to be compared with that obtained from ultrasonic data.

Now Mountain in his work represented the relaxing bulk viscosity by a time integral. As we remarked before, this representation does not take into account properly the interaction between effects of heat flow and relaxation. In fact, if αx_d is not small compared with unity, then our expression for $\sigma(k,\omega)$ would be different from his. This is best illustrated by neglecting in our exact expressions (24) and (25) for F(y) and G(y) the terms due to shear processes (i.e. $G^{\infty}=0$, $x_2=0$) and comparing the $\sigma(k,S)$ so obtained with the corresponding expression for $\sigma(k,S)$ obtained from Mountain's paper [Eqs. (28) and (29) of Ref. 24 with $b_o = 0$]. We find that the two expressions differ from each other wherever the product αx_d occurs. The two become identical only if

$$c_V = c_V^\infty \quad , \tag{82}$$

or equivalently,

$$B_S^\infty - B_S = B_T^\infty - B_T \quad , \tag{83}$$

that is, for a density induced relaxation process.

We shall not give here the expression for $\sigma(k,\omega)$ valid when $x_2 \ll 1$ and $\alpha x_d > 1$, because it is only in liquids of high viscosity that the second condition can usually be satisfied for values of k relevant to light scattering, and in these liquids then $\alpha x_2 > 1$ also [13, 16]. For the case $G^\infty = 0$ (i.e. no shear viscosity) and $\alpha x_d \gg 1$, one may obtain $\sigma(k,\omega)$ from the expressions given under case (d) below by putting $G^\infty = 0$.

(c) <u>$x_2, x_d \gg 1,\ \alpha x_2, \alpha x_d \ll 1$</u>

This represents the high frequency limit of the expression (61) for $\sigma(k,\omega)$, for it is by assuming the second condition that (61) was derived.

For this case, Eqs. (50), (55)-(60) give

$$2q_1 \simeq \frac{B_S + \frac{4}{3}G^\infty}{\rho_o v^{\infty 2}} \, \frac{1}{v_o k \tau_d} + \frac{B_S^\infty}{\rho_o v^{\infty 2}} \, \frac{1}{v_o k \tau_\eta} \quad ,$$

$$q_2 \approx \left[q_1^2 - \frac{B_S/(\rho_o v^{\infty^2})}{v_o^2 k^2 \tau_d \tau_\eta}\right]^{\frac{1}{2}}$$

$$\sigma_1 = f(q_1, q_2) \approx [2q_2(q_1+q_2)v_o^2 k^2 \tau_d \tau_\eta]^{-1}$$

$$\times \ \{[1 - v_o k \tau_\eta (q_1+q_2)]\,[(B_S - B_T)/(\rho_o v^{\infty^2})$$

$$- (q_1+q_2) v_o k \tau_d \frac{(B_S^\infty - B_T)}{\rho_o v^{\infty 2}}]$$

$$- \frac{4}{3} \frac{G^\infty}{\rho_o v^{\infty 2}} v_o k \tau_\eta (q_1+q_2) \ [1 - v_o k \tau_d (q_1+q_2)]\}$$

$$\sigma_2 = f(q_1, -q_2), \qquad \sigma_o = 1 - \frac{1}{\gamma} \quad , \qquad 2\sigma_B = \frac{B_T}{\rho_o v^{\infty 2}} \ ,$$

$$2\Gamma = \frac{B_S^\infty - B_S}{\rho_o v^{\infty^2} \tau_d} + \frac{\frac{4}{3} G^\infty}{\rho_o v^{\infty^2} \tau_\eta} + (\gamma^\infty - 1) \frac{B_S^\infty}{\rho_o v^{\infty^2}} \frac{\chi k^2}{\rho_o c_P^\infty} \tag{84}$$

Of course, v in the formula (61) is now v^∞. The intensity ratio is

$$R = \frac{\sigma_o + \sigma_1 + \sigma_2}{2\sigma_B} = \frac{1}{2\sigma_B} - 1 = \gamma\left(\frac{v^\infty}{v_o}\right)^2 - 1 \ , \tag{85}$$

which has the same form as (80), except that $v'^\infty = (B_S^\infty/\rho_o)^{\frac{1}{2}}$ is replaced by $v^\infty = \left[\frac{B_S^\infty + \frac{4}{3} G^\infty}{\rho_o}\right]^{\frac{1}{2}}$.

The expression for σ_1, σ_2, S_1, S_2 also take simple forms if one of the relaxation times is much greater than the other.

For $\tau_d >> \tau_\eta$,

$$S_1 \simeq \frac{B_S^\infty}{\rho_o {v^\infty}^2 \tau_\eta} \quad , \quad \sigma_1 \simeq \frac{B_T \frac{4}{3} G^\infty}{B_S^\infty \rho_o {v^\infty}^2} \quad ,$$

$$S_2 \simeq \frac{B_S}{B_S^\infty \tau_d} \quad , \quad \sigma_2 \simeq \frac{B_S^\infty - B_S}{\gamma\ B_S^\infty} \quad . \tag{86}$$

On the other hand, for $\tau_\eta >> \tau_d$,

$$S_1 \simeq \frac{B_S}{(B_S + \frac{4}{3} G^\infty)\tau_\eta} \quad , \quad \sigma_1 \simeq \frac{\frac{4}{3} G^\infty}{\gamma (B_S + \frac{4}{3} G^\infty)} \quad ,$$

$$S_2 \simeq \frac{B_S + \frac{4}{3} G^\infty}{\rho_o {v^\infty}^2 \tau_d} \quad , \quad \sigma_2 \simeq \frac{B_T (B_S^\infty - B_S)}{\rho_o {v^\infty}^2 (B_S + \frac{4}{3} G^\infty)} \quad . \tag{87}$$

(d) $\underline{x_2, x_d >> 1, \quad \alpha x_2, \alpha x_d >> 1}$

We still assume, however, that $\alpha << 1$. For this case the results obtained in (61) etc. no longer hold, and one has to factorize G(y) again. It can be verified easily that the small root $-y_o'$ of the equation $G(y) = 0$ is given by

$$y_o' \simeq \frac{B_T^\infty + \frac{4}{3} G^\infty}{\rho_o {v^\infty}^2} \alpha = \frac{B_T^\infty + \frac{4}{3} G^\infty}{\rho_o {v^\infty}^2} \quad \frac{\chi k}{\rho_o c_V^\infty v_o} \tag{88}$$

instead of y_o given by (37). Then writing G(y), analogously to (38), in the form

$$\frac{G(y)}{x_1 x_2} = \left(y+\theta+\frac{iv}{v_o}\right)\left(y+\theta-\frac{iv}{v_o}\right)(y+q_1'+q_2')(y+q_1'-q_2')(y+y_o') \tag{89}$$

and following the procedure similar to that in obtaining (61), we have

$$2q_1' \simeq \left(B_T^\infty + \tfrac{4}{3}G^\infty\right)^{-1}\left[\frac{(B_T+\frac{4}{3}G^\infty)}{v_o k\tau_1} + \frac{B_T^\infty}{v_o k\tau_\eta}\right],$$

$$q_2' \simeq \left[q_1'^2 - \frac{B_T}{v_o^2 k^2 \tau_1 \tau_\eta}\left(B_T^\infty + \frac{4}{3}G^\infty\right)\right]^{\frac{1}{2}}, \tag{90}$$

$$\sigma(k,\omega) \simeq \sum_{m=0}^{2} \sigma_m' \frac{2S_m'}{\omega^2+S_m'^2} + \sigma_B'\left[\frac{2\Gamma}{(\omega+v^\infty k)^2+\Gamma^2} + \frac{2\Gamma}{(\omega-v^\infty k)^2+\Gamma^2}\right], \tag{91}$$

where $\tau_1 \equiv \tau_{TV}$, and we have neglected g, which is of the order α; Γ is again given by (84), and

$$S_o' = v_o k y_o' , \quad S_1' = v_o k(q_1'+q_2') , \quad S_2' = v_o k(q_1'-q_2')$$

$$2\sigma_B' = \frac{B_T}{\rho_o v^{\infty 2}} , \quad \sigma_o' = \frac{(\gamma^\infty-1)B_T B_T^\infty}{\rho_o v^{\infty 2}(B_T^\infty+\frac{4}{3}G^\infty)} , \quad \sigma_1' = f(q_1',q_2') ,$$

$\sigma_2' = f(q_1', -q_2')$, with

$$f(q_1',q_2') = -(2q_2' v_o^2 k^2 \tau_1 \tau_\eta)^{-1}\left\{[1-v_o k\tau_\eta(q_1'+q_2')]\frac{v_o k\tau_1(B_T^\infty-B_T)}{B_T^\infty+\frac{4}{3}G^\infty} + \frac{\frac{4}{3}G^\infty v_o k\tau_\eta}{B_T^\infty+\frac{4}{3}G^\infty}[1 - v_o k\tau_1(q_1'+q_2')]\right\} . \tag{92}$$

The intensity ratio is $\gamma(\frac{v^\infty}{v_o})^2 - 1$ as in (85). For the case $\tau_d \gg \tau_\eta$,

$$S_1' \approx \frac{B_T^\infty}{B_T^\infty+\frac{4}{3}G^\infty}\,\frac{1}{\tau_\eta}\;, \qquad \sigma_1' \approx \frac{B_T\frac{4}{3}G^\infty}{B_T^\infty(B_T^\infty+\frac{4}{3}G^\infty)}\;,$$

$$S_2' \approx \frac{B_T}{B_T^\infty\tau_1}\;, \qquad \sigma_2' \approx \frac{B_T^\infty-B_T}{B_T^\infty}\;. \tag{93}$$

and for $\tau_\eta >> \tau_d$,

$$S_1' \approx \frac{B_T}{B_T+\frac{4}{3}G^\infty}\,\frac{1}{\tau_\eta}\;, \qquad \sigma_1' \approx \frac{\frac{4}{3}G^\infty}{B_T+\frac{4}{3}G^\infty}\;,$$

$$S_2' \approx \frac{B_T+\frac{4}{3}G^\infty}{B_T^\infty+\frac{4}{3}G^\infty}\,\frac{1}{\tau_1}\;, \qquad \sigma_2' \approx \frac{B_T(B_T^\infty-B_T)}{(B_T^\infty+\frac{4}{3}G^\infty)(B_T+\frac{4}{3}G^\infty)}\;. \tag{94}$$

A comparison of (91)-(94) with the expression for $\sigma(k,\omega)$ for the case (c) shows that both the intensity distribution and the integrated intensity in the Brillouin components are the same for case (d) as for case (c). There is, however, a redistribution of intensity amongst the three Lorentzians which contribute to the central peak as one goes from the case $\alpha x_2, \alpha x_d << 1$ to $\alpha x_2, \alpha x_d >> 1$. However, since the total integrated intensity of the Rayleigh component remains the same, it would probably be hard experimentally to distinguish the two cases. Another remark we wish to make is that the intensity distributions in the Lorentzians associated with the relaxation processes are simply related for the two cases (c) and (d). For example, Eqs. (93) and (94) may be obtained from the corresponding Eqs. (86) and (87) by replacing in the latter, $B_S \rightarrow B_T$, $B_S^\infty \rightarrow B_T^\infty$ and $\tau_d(=\tau_{SV}) \rightarrow \tau_1(=\tau_{TV})$, showing that the relaxation modes are now decaying isothermally, in accordance with the condition $\alpha x_2, \alpha x_d >> 1$. The Brillouin components, on the other hand, remain unaffected, since we have still retained the condition $\alpha << 1$.

§5.6 Intensity Distribution calculated from Thermodynamic Fluctuation Theory

The total integrated intensity for the scattered light from liquids by density fluctuations has been shown in Chapter 1 to be proportional to $< \delta\rho^2 >$. From thermodynamic theory of fluctuations [see Appendix], we have

$$< \delta\rho^2 > = \frac{\rho_o^3 k_B T_o}{B_T} \quad . \tag{95}$$

This value is independent of the possible kinds of loss mechanisms which are responsible for sound absorption in the liquids. The latter only have to do with the distribution of intensity amongst the different components of the spectrum. For a model of fluid for which the only source of sound absorption is thermal conductivity, the distribution of the integrated intensity between the different components can be calculated using the theory of thermodynamic fluctuations. This was done in Chapter 1, Sec. 1-3D. In this case, the central nonoscillatory Rayleigh line has a value of intensity proportional to $1-\frac{1}{\gamma}$ and the oscillatory Brillouin components have together a value proportional to $\frac{1}{\gamma}$.

When there is an additional cause of sound absorption arising from a relaxing bulk viscosity, if one represents it by a time integral, it is not built into the thermodynamics of the system; hence one cannot use the thermodynamic theory of fluctuations to investigate the spectral composition of the scattered light. In our model we have used the thermodynamic ordering parameter instead. We have also developed in the Appendix a thermodynamic fluctuation theory to include an ordering process. Hence we can use such a fluctuation theory to calculate the spectral composition. However, since the shear relaxation process is not described in the thermodynamic theory, our calculation will correspond to the case $G^{\infty} = x_2 = 0$. We shall now give such a calculation.

First, taking S, P and Z and independent variables, we have

$$< \delta\rho^2 > = \left(\frac{\partial \rho}{\partial S}\right)^2_{P,Z} < \delta S^2 > + \left(\frac{\partial \rho}{\partial P}\right)^2_{S,Z} < \delta P^2 > + \left(\frac{\partial \rho}{\partial Z}\right)^2_{S,P} < \delta Z^2 >$$

$$+ 2\left(\frac{\partial \rho}{\partial P}\right)_{S,Z} \left(\frac{\partial \rho}{\partial Z}\right)_{S,P} < \delta P \; \delta Z >$$

$$\equiv < \delta\rho^2 >_S + < \delta\rho^2 >_P + < \delta\rho^2 >_Z + < \delta\rho^2 >_{PZ} \quad . \tag{96}$$

From Appendix

$$< \delta S^2 > = k_B \, c_P \quad , \qquad < \delta Z^2 > = k_B T_o \left(\frac{\partial Z}{\partial \xi}\right)_{S,\rho}$$

$$< \delta P^2 > = \rho_o k_B T_o B_S^\infty \quad , \quad < \delta P \delta Z > = - \frac{k_B T_o B_S^\infty}{\rho_o} \left(\frac{\partial \rho}{\partial \xi}\right)_{S,P} \quad . \tag{97}$$

Therefore using thermodynamic relations derived in 3-2, it can be verified easily that

$$< \delta\rho^2 >_S / < \delta\rho^2 > = 1 - \frac{1}{\gamma} \tag{98}$$

$$< \delta\rho^2 >_P / < \delta\rho^2 > = \frac{1}{\gamma} \frac{B_S^\infty}{B_S} \tag{99}$$

$$< \delta\rho^2 >_Z / < \delta\rho^2 > = \frac{1}{\gamma} \frac{B_S^\infty - B_S}{B_S} \tag{100}$$

$$< \delta\rho^2 >_{PZ} / < \delta\rho^2 > = - \frac{2}{\gamma} \frac{B_S^\infty - B_S}{B_S} \tag{101}$$

The sum of (98) to (101) is unity, in accordance with Eq. (64).

If we take S, P and ξ as independent variables, we have

$$< \delta\rho^2> = (\frac{\partial\rho}{\partial S})^2 < \delta S^2> + (\frac{\partial\rho}{\partial P})^2_{S,\xi} <\delta P^2> + (\frac{\partial\rho}{\partial\xi})^2_{S,P} < \delta\xi^2>$$

$$+ 2(\frac{\partial\rho}{\partial\xi})_{S,P} (\frac{\partial\rho}{\partial S})_{P,\xi} <\delta S\delta\xi>$$

$$\equiv <\delta\rho >'_S + <\delta\rho^2>'_P + <\delta\rho^2>'_\xi + <\delta\rho^2>'_{S\xi} \qquad (102)$$

where we have used $< >'$ to denote average of $\delta\rho^2$ using a different set of variables i.e. S,P and ξ. From Appendix, we have

$$< \delta\xi^2> = k_B T_o (\frac{\partial\xi}{\partial Z})_{T,P}$$

$$< \delta S\delta\xi> = - k_B c_P (\frac{\partial T}{\partial Z})_{S,P} \qquad (103)$$

Hence

$$< \delta\rho^2>'_S / <\delta\rho^2> = \frac{(\gamma^\infty-1)B_T c_P}{B_S^\infty c_P^\infty} \qquad (104)$$

$$< \delta\rho^2>'_P / <\delta\rho^2> = \frac{1}{\gamma}\frac{B_S}{B_S^\infty} \qquad (105)$$

$$< \delta\rho^2>'_\xi / <\delta\rho^2> = \frac{1}{\gamma}\frac{B_S^\infty-B_S}{B_S^\infty}\frac{c_P}{c_P^\infty} \qquad (106)$$

$$< \delta\rho^2>'_{S\xi} / <\delta\rho^2> = 2\{\frac{1}{\gamma}\frac{c_P}{c_P^\infty}\frac{B_S}{B_S^\infty} - \frac{c_P}{2\gamma c_P^\infty}\frac{B_S}{B_T^\infty} - \frac{1}{2\gamma}\frac{B_S}{B_S^\infty} + \frac{1}{2} - \frac{c_P}{2\gamma c_P^\infty}\} \qquad (107)$$

In the last equation, we have made use of the relations

$$(\frac{\partial\rho}{\partial S})_{P,\xi} = - \frac{\beta^\infty B_T^\infty T_o\rho_o}{B_S^\infty c_V^\infty}$$

and $(\frac{\partial \rho}{\partial S})_{P,Z} = (\frac{\partial \rho}{\partial S})_{P,\xi} - (\frac{\partial \rho}{\partial \xi})_{S,P} (\frac{\partial T}{\partial Z})_{S,P}$.

Again it can be easily verified that the sum of (104)-(107) is unity.

In Brillouin scattering we are interested in separating out the various contributions into oscillatory and nonoscillatory modes, that is, we want to write

$$< \delta\rho^2 > = <\delta\rho^2>_{nonosc.} + <\delta\rho^2>_{osc.} \tag{108}$$

We shall now study Eqs. (96) and (102) in the light of such a separation.

For the study of not very high frequency case, i.e. for $\alpha x_d << 1$, Eq. (96) is the more appropriate one to consider, because the relaxation process is not coupled to the entropy mode, so that the contribution to the total integrated intensity normalized to unity from the entropy mode is given by $<\delta\rho^2>_S = 1 - \frac{1}{\gamma}$. [From now on we shall for convenience assume that $< \delta\rho^2>$ is normalized, i.e. $\frac{\rho_o^3 k_B T_o}{B_T}$ is put equal to unity.] In the low frequency limit, i.e. for $v_o k\tau_d << 1$, energy transfer can easily occur so that the relaxation process is completely coupled to the oscillatory mode. Therefore

$$< \delta\rho^2>_{osc} \equiv 2\sigma_B = <\delta\rho^2>_P + <\delta\rho^2>_Z + <\delta\rho^2>_{PZ} = \frac{1}{\gamma} . \tag{109}$$

These correspond to the Brillouin components and the results agree with those of Eq. (78). For high frequency limit (while still retaining $\alpha x_1 << 1$), (109) is no longer true because energy transfer cannot occur easily, and $<\delta\rho^2>_{osc}$ has to be evaluated at constant ξ and S. However, because of $\alpha x_d << 1$, we still have $<\delta\rho^2>_S = 1 - \frac{1}{\gamma}$ as contribution from the entropy mode. The oscillatory component can be extracted from the sum $<\delta\rho^2>_P + <\delta\rho^2>_Z + <\delta\rho^2>_{PZ}$ as follows:

We write δZ as

$$\delta Z = (\frac{\partial Z}{\partial S})_{P,\xi}\delta S + (\frac{\partial Z}{\partial P})_{S,\xi}\delta P + (\frac{\partial Z}{\partial \xi})_{P,S}\,\delta\xi \ , \tag{110}$$

and then take $\delta S=\delta\xi=0$ so that $\delta Z = (\frac{\partial Z}{\partial P})_{S,\xi}\delta P$. Hence we have

$$< \delta Z^2> = (\frac{\partial Z}{\partial P})^2_{S,\xi} <\delta P^2> = \frac{1}{\rho_o^4}\,(\frac{\partial \rho}{\partial \xi})^2_{S,P} < \delta P^2>$$

$$<\delta P\delta Z> = (\frac{\partial Z}{\partial P})_{S,\xi} <\delta P^2> = -\frac{1}{\rho_o^2}\,(\frac{\partial \rho}{\partial \xi})_{S,P} <\delta P^2>. \tag{111}$$

Using (3-26), (97) and (111), we have, in the high frequency limit,

$$< \delta\rho^2>_{osc} = [<\delta\rho^2>_P + <\delta\rho^2>_Z + <\delta\rho^2>_{PZ}]_{S,\xi}$$

$$= \frac{B_T}{B_S^\infty} = \frac{1}{\gamma}\frac{B_S}{B_S^\infty} = 2\sigma_B \quad . \tag{112}$$

To conserve the total intensity, we get an amount of contribution equal to $\frac{1}{\gamma}(1 - \frac{B_S}{B_S^\infty})$ for the nonoscillatory mode due to the relaxation process. These results agree with those of Eq. (79).

For very high frequency (i.e. $\alpha x_d >> 1$), the entropy mode is coupled to the relaxation process, hence its contribution to the intensity is no longer given by $< \delta\rho^2>_S = 1 - \frac{1}{\gamma}$. The contribution from the oscillatory mode is still given by (112), as expected. There is, however, a redistribution of intensity between the entropy mode and the relaxation mode. In this case, it is more convenient for us to consider Eq. (102) instead of Eq. (96). Putting $\delta S=\delta\xi=0$ in that equation, we have

$$2\sigma_B = <\delta\rho^2>_{osc} = <\delta\rho^2>'_P = \frac{1}{\gamma} \frac{B_S}{B_S^\infty} \quad ,$$

which is the same as (112).

The contribution from the entropy mode at this high frequency limit can be obtained easily by taking $\delta\xi=0$ in the sum $<\delta\rho^2>'_S + <\delta\rho^2>'_\xi + <\delta\rho^2>'_{S\xi}$. From fluctuation theory [see Appendix], this is equivalent to replacing the value of $<\delta\rho^2> = k_B c_P$ by $k_B c_P^\infty$. Doing this, it can be obtained from (104) that

$$< \delta\rho^2>'_S \rightarrow \frac{(\gamma^\infty-1)B_T}{B_S^\infty} \quad . \qquad (113)$$

This value is then σ_o'. Again to conserve intensity, the relaxation mode has a contribution to the intensity equal to $1 - \frac{1}{\gamma}\frac{B_S}{B_S^\infty} - \frac{(\gamma^\infty-1)B_T}{B_S^\infty} = 1 - \frac{B_T}{B_T^\infty}$. The results agree with those of (92) with $G^\infty = 0$.

Chapter 6

VELOCITY DISPERSION FOR A SINGLE RELAXATION PROCESS[†]

As we discussed in Chapter 1, the Brillouin components in the spectrum of light scattered from liquids can be interpreted in terms of a Doppler shift effect, due to the motion of the two sound waves moving in opposite directions. The shift in the frequency, ω, is then related to the sound velocity v, according to (1-32) and (1-38), by

$$v = \omega/k \quad . \tag{1}$$

However, this is only true in the ideal case when there is no absorption of sound [see (1-49)], in which case the hypersonic waves are plane waves of undiminished amplitude. In general loss mechanisms are always present in liquids and Eq. (1) will have to be modified. It seems that this has not been generally recognized except until only very recently [30,26], in the sense that the positions of the experimentally determined Brillouin peaks are taken to give the sound velocity. This has not generally given rise to difficulties because sound absorption is small in most cases and the resolving power of detection devices always gives some uncertainty in the measured values.

[†] This work was published in Bhatia and Tong, Can. J.Phys. 47, No. 3, 361 (1969).

From the theory and calculations which we developed in the last chapter, it becomes obvious that Eq. (1) is equivaleny to neglecting the g terms in $\sigma(k,\omega)$, which is small only if $\frac{\Gamma}{vk} << 1$.

In terms of the frequency shift of the Brillouin components, which we denote by ω_B, one can certainly define a 'sound velocity', v_B, by

$$v_B = \omega_B/k \ . \tag{2}$$

The quantities v and v_B are, therefore, not the same thing in general.

In a recent paper by Mountain and Litovitz [32], negative velocity dispersion in Brillouin scattering was discussed. By using a perturbation procedure about $k \sim 0$, they stated the result that the velocity dispersion graph (i.e. v versus k) for a single relaxation process will show a negative slope for

$$\frac{v_\infty^2}{v_o^2} > 3 \quad . \tag{3}$$

In this chapter, we wish to discuss the fact with its consequences that v and v_B satisfy different dispersion relations so that when one talks about velocity dispersion, one has to mention explicitly which quantity one is talking about. In fact, from Eq. (5-48), one obtains, for a single relaxation process (i.e. putting $G^\infty = 0$), the dispersion relation

$$\frac{v^2}{v_o^2} \simeq 1 + \frac{B_S^\infty - B_S}{B_S}\left[1 - \frac{1}{4}\,\frac{B_S^\infty - B_S}{B_S}\right] x_d^2 \quad , \qquad (4)$$

which yields a condition for negative dispersion

$$\frac{v^{\infty 2}}{v_o^2} > 5 \quad , \qquad (5)$$

and this condition is different from that in (3).

There is yet another possibility of defining a sound velocity. As is well-known, the velocity dispersion of sound waves in a medium depends on whether the absorption is spatial or temporal [33,34], corresponding to whether one makes k or ω complex. The definitions of the velocities v and v' for the temporally and spatially, absorbed waves are thus, respectively,

$$v = \mathrm{Re}\ \omega/k, \quad k \text{ real}, \ \omega \text{ complex} \qquad (6)$$

and

$$v' = \omega[\mathrm{Re}\ k]^{-1} \ , \quad k \text{ complex}, \quad \omega \text{ real}^\dagger \ . \qquad (7)$$

The difference between v and v' is particularly significant if the absorption is due to nonrelaxing viscosities alone, the dispersion being negative for v and positive for v', as can be readily verified. The spatial absorption

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† Ultrasonic measurements usually refer to v'.

is relevant to progressive waves whereas the temporal absorption refers to the decay of standing waves with time in a medium. The latter is appropriate to Brillouin scattering of light in liquids, and Eq.(6) defines the same velocity as that in Eq. (4).

We shall now study the different dispersion relations which arise owing to the different ways of defining the sound velocity. For simplicity we shall consider a single relaxation process. In particular, we shall show that the conditions in (3) and (5) are exact results.

§6.1 Velocity dispersion for v

The relevant dispersion equation for determining v is, from (3-41) or (3-66),

$$\tau\omega^3 - i\omega^2 - \frac{B_S^\infty}{\rho_o} k^2 \omega\tau_d + \frac{iB_S}{\rho_o} k^2 = 0 \ . \qquad (8)$$

Eq. (8) can also be obtained from (5-25). We recall that the imaginary part of the complex roots in G(y)=0 gives the velocity of the temporally absorbed hypersonic waves. For a single relaxation process, the dispersion equation (5-25) reduces to

$$y^3 + \frac{1}{x} y^2 + \frac{B_S^\infty}{B_S} y + \frac{1}{x} = 0 \qquad (9)$$

where $x=v_o k\tau_d$. Putting $y = \frac{i\omega}{v_o k}$, (9) reduces to (8). We assume that B_S^∞ is a noninfinite positive number so that if $\tau_d \to 0$, $B_S^\infty\tau_d \to 0$ also. Writing now $\omega=\omega_1+i\omega_2$ in (8) and eliminating ω_2, one obtains for v the equation

$$x^4(z-z_\infty)(4z-z_\infty)^2+ x^2\left[8z^2-6zz_\infty+\tfrac{1}{4}(z_\infty^2+18z_\infty-27)\right]+z-1 = 0 \;, \tag{10}$$

where we have written

$$z = \frac{v^2}{v_o^2} \quad , \qquad z_\infty = \frac{B_S^\infty}{B_S} = \frac{v^{\infty 2}}{v_o^2} \quad . \tag{11}$$

Eq. (10) can be more simply obtained if one defines $y=y' - \frac{1}{3x}$ to transform (9) to

$$y'^3 + \left(\frac{B_S^\infty}{B_S} - \frac{1}{3x^2}\right)y' + \left[\frac{2}{27x^3} - \frac{B_S^\infty}{3xB_S} + \frac{1}{x}\right] = 0 \tag{12}$$

and then write $y' = y_1' + iy_2'$, eliminate y_1' and define $\frac{v^2}{v_1^2} = y_2'^2 = z$. One obtains an alternative form of (10) as

$$\left[z - z_\infty + \frac{1}{3x^2}\right]\left[4z - z_\infty+ \frac{1}{3x^2}\right]^2 = \frac{27}{4}\left[\frac{2}{27x^3} - \frac{z_\infty}{3x} + \frac{1}{x}\right]^2 \tag{13}$$

Hence,

$$\frac{\partial z}{\partial x} = \frac{4}{3x^5}\left\{\frac{x^2\left[4z^2-3zz_\infty+\frac{1}{8}(z_\infty^2+18z_\infty-27)\right]+z-1}{\left(4z-z_\infty+\frac{1}{3x^2}\right)\left(4z-3z_\infty+ \frac{1}{x^2}\right)}\right\} \tag{14}$$

$$\frac{\partial^2 z}{\partial x^2} = -\frac{5}{x}\frac{\partial z}{\partial x} + \frac{4}{3x^4}\{2[4z^2-3z_\infty z+\frac{1}{8}(z_\infty^2+18z_\infty-27)]$$

$$+\frac{1}{x}\frac{\partial z}{\partial x} + 8xz\frac{\partial z}{\partial x} - 3z_\infty x\frac{\partial z}{\partial x}\}/\{(4z-z_\infty+\frac{1}{3x^2})(4z-3z_\infty+\frac{1}{x^2})\}$$

$$-\frac{\partial z}{\partial x}[(4z-3z_\infty+\frac{1}{x^2})(4\frac{\partial z}{\partial x} - \frac{2}{3x^2})+(4\frac{\partial z}{\partial x} - \frac{2}{x^3})(4z-z_\infty+\frac{1}{3x^2})]\}$$

$$\cdot\{(4z-z_\infty+\frac{1}{3x})(4z - 3z_\infty+\frac{1}{x^2})\}^{-1} . \tag{15}$$

From Eqs. (10), (13), (14) and (15), we can draw the following conclusions:

(i) For x → 0, (10) gives

$$\frac{v^2}{v_o^2} = z \simeq 1 - \frac{1}{4}x^2(z_\infty - 1)(z_\infty - 5) \to 1 \tag{16}$$

$$\frac{\partial z}{\partial x} \to -\tfrac{1}{2}x(z_\infty - 1)(z_\infty - 5) \to 0 \text{ for all } z_\infty \tag{17}$$

$$\lim_{x\to 0}\frac{\partial^2 z}{\partial x^2} = -\tfrac{1}{2}(z_\infty - 1)(z_\infty - 5) . \tag{18}$$

$$\text{Hence } \lim_{x\to 0}\frac{\partial^2 z}{\partial x^2} \begin{smallmatrix}\le\\=\\>\end{smallmatrix} 0 \quad \text{if} \quad z \begin{smallmatrix}\ge\\=\\<\end{smallmatrix} 5 \tag{19}$$

(ii) For x → ∞, (9) gives

$$z \to z_\infty \qquad \text{or } v \to v_\infty \tag{20}$$

$$\frac{\partial z}{\partial x} \to \frac{1}{2z_\infty^2 x^3}(z_\infty + 3)(z_\infty - 1) \to 0 . \tag{21}$$

Since from general thermodynamic considerations, $B_S^\infty \geqslant B_S$, we have

$$z_\infty \geqslant 1 \quad . \tag{22}$$

Hence for large x

$$\frac{\partial z}{\partial x} > 0 \ . \tag{23}$$

(iii) The condition for nontrivial stationary points (i.e. $\frac{\partial z}{\partial x} = 0$) can be obtained by combining (10) and (14) to give

$$x^4 = \frac{z - 1}{(4z - z_\infty)^2 (z - z_\infty)} \quad . \tag{24}$$

Hence there are no stationary points for z if $1 < z < z_\infty$. That is, for this range of values of z, $\frac{\partial z}{\partial x}$ is never negative.

Furthermore, from Eq. (10), because the equation is quadratic in x^2, one can see that for every value of z there can be at most two values of x, since $x > 0$.

One may may conclude then that negative dispersion (decrease of z with increasing x) must start from the origin, and this occurs when $z_\infty > 5$. Figure 1 sketches the variation of z with x for different values of z_∞.

For $x \ll 1$, one has the expansion given by Eq.(16) which is identical with Eq. (4).

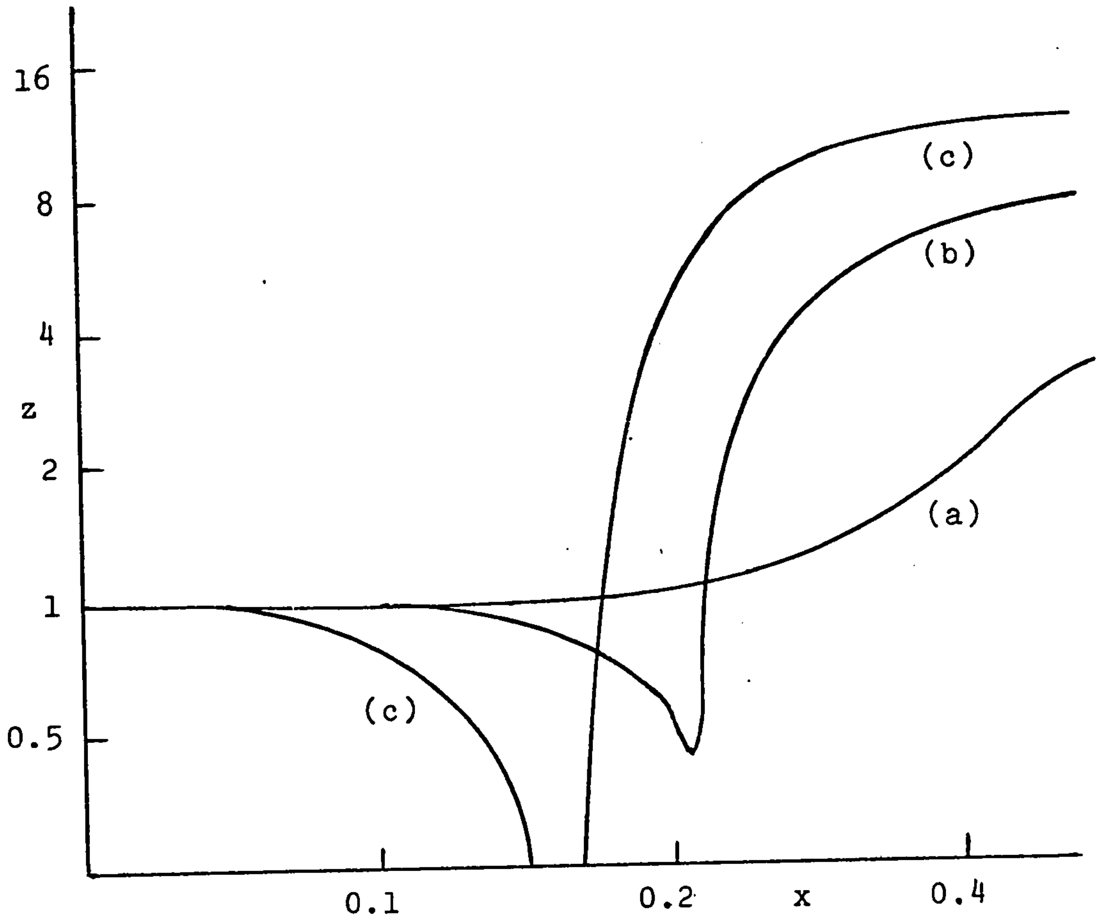

Fig. 1. Schematic variation of $z(=v^2/v_o^2)$ with x on log log plot for different values of z_∞. (a): $1<z_\infty<5$; (b): $5<z_\infty<9$; (c): $z_\infty>9$. For $z_\infty=9$, the minimum in curve (b) occurs at $x=(27)^{-\frac{1}{2}}$ and $z_{min}=0$. As shown in curve (c) for $z_\infty>9$, there is a range of values of x for which eq. (10) has no real positive roots.

§6.2 Velocity dispersion for v'

This velocity is defined by Eq. (7). The relevant equation to consider is also Eq. (8). Writing $k=k_1-ik_2$, one can eliminate k_2 to obtain an equation in k_1 and ω. This equation can be rewritten, by defining $z' = \frac{v'^2}{v_o^2}$, $z_\infty = \frac{B_S^\infty}{B_S}$, to give

$$z'^3x^2\{(z_\infty-1)^2+4z_\infty^3x^2\}+4z_\infty x^2z'^2\{1+z_\infty-z_\infty^3x^2\}$$

$$+4z'(1-2z_\infty^2x^2)-4=0\ . \tag{25}$$

From (25), it can be seen easily that for $x \to 0$, $z' \to 1$, or

$$\lim_{x\to 0}\ v' \to v_o\quad . \tag{26}$$

For small x, $z' = \frac{v'^2}{v_o^2} \simeq 1 + \frac{1}{4}\,x^2(3z_\infty+1)(z_\infty-1)$. (27)

Since $z_\infty > 1$, $\frac{\partial z'}{\partial x}$ is always nonnegative near the origin. For $x \to \infty$, $z' \to \frac{v_\infty'^2}{v_o^2} = \frac{B_S^\infty}{B_S} = z_\infty$,

or

$$v_\infty' = v_\infty\ . \tag{28}$$

For large x, $z' \simeq z_\infty - \frac{1}{4z_\infty^2x^2}(z_\infty+3)(z_\infty-1)$ (29)

and $\frac{\partial z'}{\partial x}$ is positive for all values of $z_\infty > 1$. Again, since (25) is quadratic in x^2, by similar argument as we had for z in (1-(iii)), we conclude that z' is a monotonically increasing function of x for all x and for all z_∞. Figure 2 sketches the variation of z' with x.

§6.3 Velocity dispersion for v_B

To calculate the velocity v_B defined by (2) we need the expression for the spectral distribution. This is obtained from (5-24), (5-25) and (5-31) by taking the limits $\alpha=0$, $G^\infty=x_2=0$. We get

$$\sigma(k,\omega) = 2\,\mathrm{Re}\,\frac{1}{v_o k}\lim_{y=\frac{i\omega}{v_o k}}\frac{y^2x+y+(\frac{B_S^\infty}{B_S}-1)\,x}{y^3x+y^2+\frac{B_S^\infty}{B_S}xy+1}$$

$$= \frac{2}{v_o k}\,\frac{(z_\infty-1)\,x}{\left[1-\frac{\omega^2}{v_o^2k^2}\right]^2+\frac{\omega^2x^2}{v_o^2k^2}\left[z_\infty-\frac{\omega^2}{v_o^2k^2}\right]^2}\,. \qquad (30)$$

Hence

$$\frac{\partial\sigma}{\partial\omega} = -\frac{4(z_\infty-1)\,\omega x}{v_o^3k^3\left[(1-\frac{\omega^2}{v_o^2k^2})^2+\frac{\omega^2x^2}{v_o^2k^2}(z_\infty-\frac{\omega^2}{v_o^2k^2})^2\right]^2}$$

$$\times\ \{x^2(z_\infty-\frac{\omega^2}{v_o^2k^2})^2-2(1-\frac{\omega^2}{v_o^2k^2})-\frac{2x^2\omega^2}{v_o^2k^2}(z_\infty-\frac{\omega^2}{v_o^2k^2})\}. \qquad (31)$$

The maxima and minima in the σ versus ω curve are given by

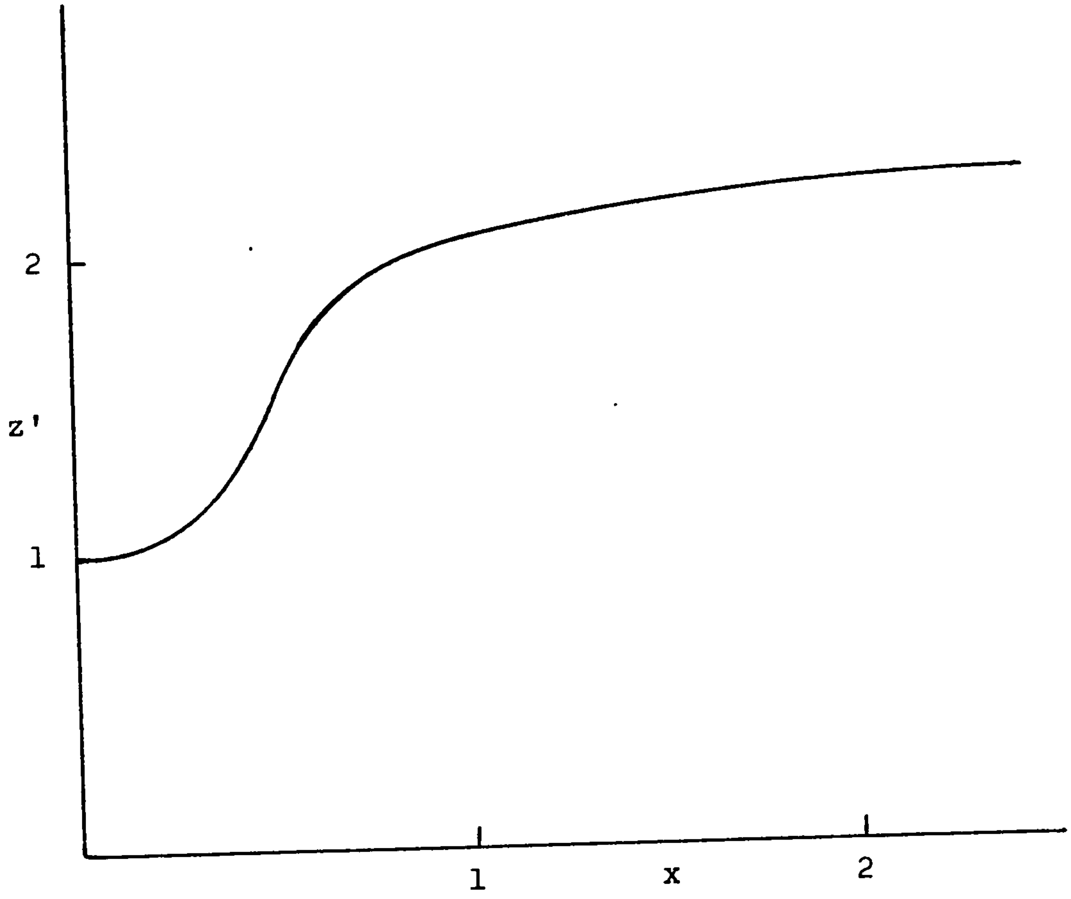

Fig. 2. Schematic variation of $z'(=v'^2/v_0^2)$ with x. z' is a monotonically increasing function of x for all x and for all z_∞.

$$\frac{\partial\,\sigma(k,\omega)}{\partial\,\omega} = 0 \quad . \tag{32}$$

The solutions of (32) are

$$\omega = 0$$
$$\omega_{\pm}^2 = \left(\frac{v_o^2 k^2}{3x^2}\right) \left[2z_{\infty}x^2 - 1 \pm A^{\frac{1}{2}}\right] , \tag{33}$$

where $A = z_{\infty}^2 x^4 - 4z_{\infty}x^2 + 6x^2 + 1$. By evaluating $\frac{\partial^2\sigma}{\partial\,\omega^2}$, it can be verified easily that

$$\left.\frac{\partial^2\sigma}{\partial\,\omega^2}\right|_{\omega\to\omega_{\pm}} = -\frac{16(z_{\infty}-1)x}{v_o^4 k^4}\,\omega_{\pm}^2 \left\{\frac{3x^2\omega_{\pm}^2}{v_o^2 k^2} - 2z_{\infty}x^2 + 1\right\}$$
$$= \mp \frac{16(z_{\infty}-1)x\;\omega_{\pm}^2}{v_o^4 k^4}\, A^{\frac{1}{2}} \quad . \tag{34}$$

The discriminant of A is $12(z_{\infty}-1)(z_{\infty}-3)$. If $z_{\infty} < 3$, A is always positive. If $z_{\infty} > 3$, there is always a range of x for which A is negative so that ω_{+} and ω_{-} are complex. One can also verify that

$$\left.\frac{\partial^2\sigma}{\partial\,\omega^2}\right|_{\omega\to 0} = -(z_{\infty}^2 x^2 - 2) \ . \tag{35}$$

From the above, we can say the following:

(i) At $\omega=0$, $\sigma(k,\omega)$ has a maximum or a minimum according to whether $z_{\infty}x^2-2 > 0$ or < 0.

(ii) Provided ω_{+} is real, nonzero and distinct from ω_{-}, $\sigma(k,\omega)$ has a maximum at ω_{+}. For $x^2 \geqslant (2z_{\infty})^{-1}$, ω_{+} satisfies these conditions if $A > 0$. For $x^2 < (2z_{\infty})^{-1}$, the corresponding requirement is that $A > (2z_\infty x^2-1)^2$, which is equivalent to the inequality $z_\infty^2 x^2-2 < 0$, i.e. a minimum at $\omega=0$ according to (35). For $z_\infty < 3$, $\sigma(k,\omega)$ has a maximum at $\omega_+(\neq 0)$ for all x. For $z_\infty > 3$, however, there is a range of values of x for which ω_+ is complex.

(iii) Provided ω_- is real, nonzero and distinct from ω_+, $\sigma(k,\omega)$ has a minimum at ω_-. From (33), it can be seen that these conditions on ω_- are satisfied only if (a) $A > 0$ and (b) x^2 is greater than both $(2z_\infty)^{-1}$ and $(2/z_\infty^2)$.

Taking together (i), (ii) and (iii) imply that if $\sigma(k,\omega)$ has a maximum at $\omega_+(\neq 0)$, then it has a minimum either at $\omega=\omega_-$ or at $\omega=0$; in the former case it has another maximum at $\omega=0$.

(iv) For $x \to 0$,

$$\frac{\omega_+^2}{v_o^2k^2} \to 1 - \tfrac{1}{2}x^2(z_\infty - 1)(z_\infty - 3) \to 1 \qquad (36)$$

For large x,

$$\frac{\omega_+^2}{v_o^2k^2} \to z_\infty - \frac{(z_\infty-1)}{z_\infty x^2} \to z_\infty \quad , \qquad (37)$$

and

$$\frac{\partial}{\partial x}\left[\frac{\omega_+^2}{v_o^2k^2}\right] > 0 \quad . \qquad (38)$$

Also,

$$\frac{\omega_-^2}{v_o^2k^2} \rightarrow \frac{1}{3}\,(z_\infty + \frac{z_\infty-3}{z_\infty x^2}\,)$$

$$\rightarrow \frac{1}{3}\,z_\infty \quad . \tag{39}$$

(v) $\omega_+ = \omega_o$ if A=0. If $z_\infty < 3$, this is never satisfied. For $z_\infty > 3$, ω_+ and ω_- are equal to each other for two values of x, which are roots of the equation A=0. At these points it can be easily verified that

$$\frac{\partial\,\omega_+}{\partial\,x} = \frac{\partial\,\omega_-}{\partial\,x} = \infty \quad , \tag{40}$$

except for $z_\infty = 3$. At $x^2= 2/z_\infty^2$, $\omega_-=0$, $\omega_+\neq0$ for $z_\infty < 4$ and $\omega_+=0$, ω_- is complex for $z_\infty > 4$. If $z_\infty = 4$, then $\omega_+=\omega_-=0$ at this point.

The foregoing discussions show that we can identify ω_+ with ω_B, and enable us to make schematic plots of $z_B \equiv \omega_B^2/v_o^2k^2$ versus x. Such plots for certain values of z_∞ lying in certain ranges are given in Figure 3. We see that if $z_\infty < 3$, z_B shows negative dispersion which starts at the origin. Also there is a range of values of x for which there are no Brillouin peaks.

The difference between v and v_B is particularly marked if $z_\infty \geqslant 3$. Unfortunately no liquid is known at the present time for which $z_\infty > 3$. However, even for

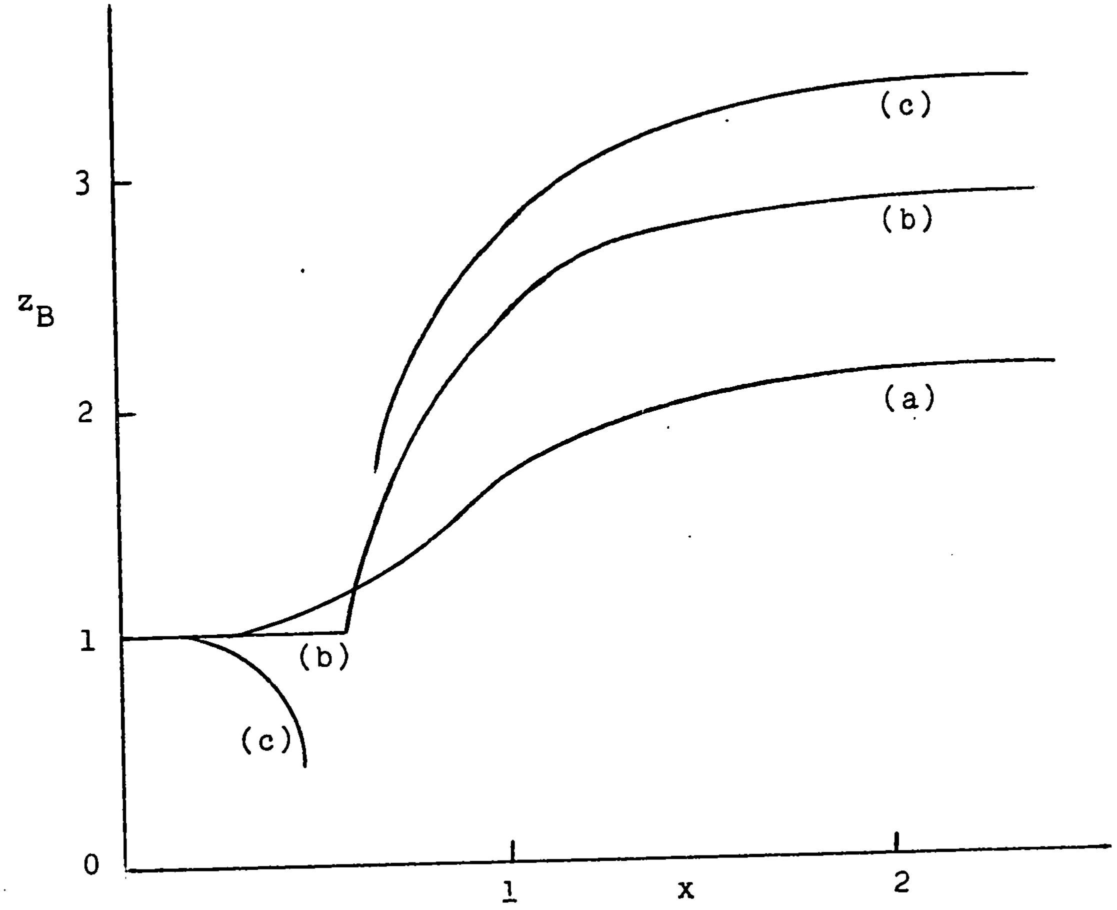

Fig. 3. Schematic variation of $z_B(=v_B^2/v_o^2)$ with x for different values of z_∞. (a): $1 < z_\infty < 3$; (b): $z_\infty=3$; (c): $3 < z_\infty < 4$. For $z_\infty \geqslant 4$, the branch showing negative dispersion in (c) meets the abscissa at $x=\sqrt{2}/z_\infty$; the branch showing positive dispersion in (c) remains qualitatively unaltered.

$z_\infty < 3$, the difference between v and v_B (and v') can be significant in the region $x \sim 1$. Table I gives a comparison of the variation of v, v_B and v' with x for $z_\infty = 2.24$, which is the value appropriate to glycerol. It is only when $z_\infty - 1 \ll 1$ or sound absorption per cycle is much smaller than unity that $v' \simeq v \simeq v_B$.

Table I. Values of v_B, v and v' for several values of $v_o k\tau_{SV}$, assuming $z_\infty = 2.24$

x	$(v_B/v_o)^2$	$(v/v_o)^2$	$(v'/v_o)^2$
0	1	1	1
0.2	1.020	1.037	1.096
0.5	1.170	1.327	1.506
1.0	1.743	1.928	1.960
1.5	2.003	2.098	2.105
2.5	2.153	2.188	2.189
∞	2.24	2.24	2.24

Chapter 7

SPECTRAL DISTRIBUTION FOR LIQUIDS HAVING DISTRIBUTION OF RELAXATION TIMES

In Chapter 5 we calculated the spectral distribution of light scattered by a relaxing liquid in which both the bulk and shear relaxation processes were each characterized by a single relaxation time. There are many liquids, however, in which there may be more than one relaxation time for the bulk relaxation - for example, for thermal relaxation in polyatomic liquids. A specially interesting case is that of liquids of high viscosity in which both the shear and bulk relaxation processes have to be characterized by a distribution of relaxation times [13,16]. In this chapter we generalize the treatment of Chapter 5 to cover these cases.

§7.1 Basic Equations

Following the same procedure as in Chapter 5, the modified linearized hydrodynamic equations are

$$\frac{\partial \rho}{\partial t} = -\rho_o \operatorname{div} \vec{u} \qquad (1)$$

$$\rho\frac{\partial \vec{u}}{\partial t} = -\nabla P + \frac{4}{3} \int_0^t \eta'(t-t') \operatorname{grad} \operatorname{div} \vec{u}(t') \, dt' \,, \qquad (2)$$

and the energy transport equation is

$$\rho_o \; T_o \; \frac{\partial S}{\partial t} = \chi \; \nabla^2 \; T \; , \tag{3}$$

where we assume the following:

(i) There is a distribution of shear relaxation times $g_\eta(\tau)$ such that

$$\int_0^\infty g_\eta(\tau) \; d\tau = 1 \tag{4}$$

$$\eta'(t) = G^\infty \int_0^\infty g_\eta(\tau) \; e^{-t/\tau} \; d\tau \; . \tag{5}$$

(ii) There are n ordering processes each being characterized by an ordering parameter ξ_i corresponding to an ordering force Z_i. The relaxation equations are

$$\frac{\partial \xi_i}{\partial t} = - \sum_{j=1}^{n} L_{ij} \; \delta Z_j \quad , \; i = 1, \; \ldots \; n \; . \tag{6}$$

Thus (1), (2), (3) and (6) are to be solved together to give $\rho(\vec{k},t)$ for the calculation of $\sigma(k,\omega)$. For independent variables it is convenient to choose S, ρ and Z, where Z denotes Z_1, Z_2 .... Z_n. This will be apparent later when we discussed comparison with experimental data.

Making use of thermodynamic relations derived in §3.2, we can write

$$\nabla^2 P = \frac{T_o \beta B_T}{c_V} \; \nabla^2 S + \frac{B_S}{\rho_o} \; \nabla^2 \rho + \sum_{i=1}^{n} P'_{Z_i} \; \nabla^2 Z_i \tag{7}$$

$$\nabla^2 T = \frac{T_o}{c_V} \; \nabla^2 S + \frac{T_o \beta B_T}{\rho_o^2 c_V} \; \nabla^2 \rho + \sum_{i=1}^{n} T'_{Z_i} \; \nabla^2 Z_i \quad , \tag{8}$$

where $P'_{Z_i} = (\frac{\partial P}{\partial Z_i})_{S,\rho,Z'_i}$; $T'_{Z_i} = (\frac{\partial T}{\partial Z_i})_{S,\rho,Z'_i}$,

and Z'_i denotes $Z_1, Z_2, \ldots Z_{i-1}, Z_{i+1}, \ldots Z_n$.

Eq. (7-6) can be written as

$$(\frac{\partial \xi_i}{\partial S})_{\rho,Z} (\frac{\partial S}{\partial t}) + (\frac{\partial \xi_i}{\partial \rho})_{S,Z} \frac{\partial \rho}{\partial t} = - \sum_j [(\frac{\partial \xi_i}{\partial Z_j})_{\rho,S,Z'_j} \times \frac{\partial}{\partial t} + L_{ij}] \, \delta Z_j \quad . \qquad (9)$$

It can be shown by thermodynamics that

$$(\frac{\partial \xi_i}{\partial S})_{\rho,Z} = - T'_{Z_i}$$

$$(\frac{\partial \xi_i}{\partial \rho})_{S,Z} = - \frac{1}{\rho_o^2} P'_{Z_i} \quad . \qquad (10)$$

If we define

$$\phi_{ij}^{-1} = (\frac{\partial \xi_i}{\partial Z_j})_{S,\rho,Z'_j} \quad ; \quad \tau_{ij}^{-1} = L_{ij} \, \phi_{ij} \quad , \qquad (11)$$

then eq. (7-9) can be written as

$$T'_{Z_i} \frac{\partial S}{\partial t} + \frac{1}{\rho_o^2} P'_{Z_i} \frac{\partial \rho}{\partial t} = \sum_j \phi_{ij}^{-1} (\frac{\partial}{\partial t} + \frac{1}{\tau_{ij}}) \, \delta Z_j \quad . \qquad (12)$$

Eq. (1) and Eq. (2) can be combined to give

$$\frac{\partial^2 \rho}{\partial t^2} = \nabla^2 P + \frac{4}{3\rho_o} \int_0^t \eta'(t-t') \nabla^2 (\frac{\partial \rho}{\partial t'}) \, dt' \quad . \qquad (13)$$

§7.2 Calculation of $\sigma(k,\omega)$

As before, the Laplace transform $\sigma(k,S)$ has to be first obtained. This is done by multiplying (3), (12) and (13) by $V^{-1}\, e^{i\vec{k}.\vec{r}-St}$ and integrating, using (5-15) and (5-16). The results are the following n+2 equations

$$\rho(\vec{k},S)\ \{\frac{T_o\beta B_T k^2}{\rho_o^2 c_V}\} + S(\vec{k},S)\ \{\frac{\rho_o T_o S}{\chi} + \frac{T_o k^2}{c_V}\}$$

$$+ \sum_j k^2\, T'_{Z_j}\ Z_j(\vec{k},S) = \frac{\rho_o T_o}{\chi}\ S(\vec{k}) \tag{14}$$

$$\rho(\vec{k},S)\ \{\frac{SP'_{Z_i}}{\rho_o^2}\} + S(\vec{k},S)\ \{S\, T'_{Z_i}\} - \sum_j \frac{(1+S\tau_{ij})}{\phi_{ij}\tau_{ij}}\ Z_j(\vec{k},S)$$

$$= \rho(\vec{k})\, \{\frac{P'_{Z_i}}{\rho_o^2}\} + S(\vec{k})\, \{T'_{Z_i}\} - \sum_j \frac{Z_j(k)}{\phi_{ij}},\ i=1,\ldots n \tag{15}$$

$$\rho(\vec{k},S)\ \{S^2 + \frac{B_S k^2}{\rho_o} + \frac{4}{3\rho_o}\, G^\infty k^2 S \int \frac{g_\eta(\tau)\tau\, d\tau}{1+S\tau}$$

$$+ S(\vec{k},S)\ \{\frac{T_o\beta B_T k^2}{c_V}\} + \sum_j k^2\, P'_{Z_j}\ Z_j(\vec{k},S)$$

$$= \rho(\vec{k})\ \{S + \frac{4}{3\rho_o}\, G^\infty k^2 \int \frac{g_\eta(\tau)\tau\, d\tau}{1+S\tau}\}. \tag{16}$$

In general, Eqs. (14)-(16) can be solved for the n + 2 unknowns $\rho(\vec{k},S)$, $S(\vec{k},S)$ and $Z_i(\vec{k},S)$. For the light scattering problem, we are only interested in $\rho(\vec{k},S)$, as only $<\rho(-\vec{k})\rho(\vec{k},S)>$ contributes to the spectral intensity. Also from fluctuation theory [Appendix], we have $\langle\rho(-\vec{k})Z_i(\vec{k})\rangle = 0$ so that one can neglect all the $Z_i(\vec{k})$ terms.

Thus we can write our solution as

$$\rho(\vec{k},S) = \frac{\|A\|}{\|B\|}, \tag{17}$$

where $\|A\|$ and $\|B\|$ are 2 determinants of order n+2.

$$\|A\| = \left|\begin{array}{ccccc} \frac{\rho_o T_o}{\chi} S(\vec{k}) & \frac{\rho_o T_o S}{\chi} + \frac{T_o k^2}{c_V} & k^2 T'_{Z_1} & \cdots & k^2 T'_{Z_n} \\ A_{12}\,\rho(\vec{k}) & \frac{T_o \beta B_T k^2}{c_V} & k^2 P'_{Z_1} & \cdots & k^2 P'_{Z_n} \\ \frac{1}{\rho_o^2} P'_{Z_1}\rho(\vec{k}) + T'_{Z_1} S(\vec{k}) & S\,T'_{Z_1} & -\frac{(1+S\tau_{11})}{\phi_{11}\tau_{11}} & \cdots & -\frac{(1+S\tau_{1n})}{\phi_{1n}\tau_{1n}} \\ \vdots & \vdots & & & \\ \frac{1}{\rho_o^2} P'_{Z_n}\rho(\vec{k}) + T'_{Z_n} S(\vec{k}) & S\,T'_{Z_n} & -\frac{(1+S\tau_{n1})}{\phi_{n1}\tau_{n1}} & \cdots & -\frac{(1+S\tau_{nn})}{\phi_{nn}\tau_{nn}} \end{array}\right|$$

where $A_{12} = \left[S + \frac{4}{3}\frac{G^{\infty}k^2}{\rho_o}\int\frac{g_n(\tau)\tau\,d\tau}{1+S\tau}\right]$ (18)

$$\|B\| = \begin{vmatrix} \dfrac{T_o \beta B_T k^2}{\rho_o^2 c_V} & \dfrac{\rho_o T_o S}{\chi} + \dfrac{T_o k^2}{c_V} & k^2 T'_{Z_1} & \cdots\cdots & k^2 T'_{Z_n} \\ B_{12} & \dfrac{T_o \beta B_T k^2}{c_V} & k^2 P'_{Z_1} & \cdots\cdots & k^2 P'_{Z_n} \\ \dfrac{S}{\rho_o^2} P'_{Z_1} & S\, T'_{Z_1} & \dfrac{-(1+S\tau_{11})}{\phi_{11}\tau_{11}} & \cdots\cdots & \dfrac{-(1+S\tau_{11})}{\phi_{11}\tau_{1n}} \\ \vdots & \vdots & \vdots & & \vdots \\ \dfrac{S}{\rho_o^2} P'_{Z_n} & S\, T'_{Z_n} & \dfrac{-(1+S\tau_{11})}{\phi_{n1}\tau_{n1}} & & \dfrac{-(1+S\tau_{nn})}{\phi_{nn}\tau_{nn}} \end{vmatrix} \tag{19}$$

where $B_{12} = S^2 + \dfrac{B_S k^2}{\rho_o} + \dfrac{4}{3}\dfrac{G^\infty k^2 S}{\rho_o} \int \dfrac{g_n(\tau)\tau\, d\tau}{1+S\tau}$.

Anticipating that $\rho(k,S)$ is to be considered only in $< \rho(-\vec{k})\rho(\vec{k},S)>$, and that $< \rho(-\vec{k})S(\vec{k})> = -\dfrac{\beta B_T}{\rho_o^2} <\rho(\vec{k})\rho(-\vec{k})>$ [see Appendix], we can replace $S(\vec{k})$ in (17) by $-\dfrac{\beta B_T}{\rho_o^2}\rho(\vec{k})$.

We now try to simplify $\|A\|$ and $\|B\|$ by applying some elementary operations on them.

We multiply the 1st column of $\|A\|$ by $\dfrac{\rho_o^2 k^2}{\rho(\vec{k})}$ and the 2nd column by k^2/S. This will increase the determinant by the factor $\rho_o^2 k^4/S\rho(\vec{k})$. Then we add to the 1st column

βB_T times the 2nd column. This will not change the value of the determinant. Finally we interchange the 1st and the 2nd columns. This will change the sign of the determinant.

For the determinant $\|B\|$, we shall multiply the 1st column by $\rho_o^2 k^2/S$ and the 2nd column by k^2/S, and then interchange them.

The results of such operations yield

$$\|A\| = -\frac{S\rho(\vec{k})}{\rho_o^2\,k^4}\begin{vmatrix} \frac{k^2}{S}\left(\frac{\rho_o T_o S}{\chi} + \frac{T_o k^2}{c_V}\right) & \frac{T_o\beta B_T k^4}{S c_V} & k^2 T'_{Z_1} & \cdots\cdots & k^2 T'_{Z_n} \\ \frac{T_o\beta B_T k^4}{S c_V} & \rho_o^2 k^2\left[A_{12} + \frac{T_o\beta^2 B_T^2 k^2}{S\rho_o^2 c_V}\right] & k^2 P'_{Z_1} & \cdots\cdots & k^2 P'_{Z_n} \\ k^2 T'_{Z_1} & k^2 P'_{Z_1} & \frac{-(1+S\tau_{11})}{\phi_{11}\tau_{11}} & \cdots & \frac{-(1+S\tau_{1n})}{\phi_{1n}\tau_{1n}} \\ \vdots & \vdots & \vdots & & \\ k^2 T'_{Z_n} & k^2 P'_{Z_n} & \frac{-(1+S\tau_{n1})}{\phi_{n1}\tau_{n1}} & \cdots & \frac{-(1+S\tau_{nn})}{\phi_{nn}\tau_{nn}} \end{vmatrix} \tag{20}$$

$$||B|| = -\frac{S^2}{\rho_o^2\, k^4} \begin{vmatrix} \frac{k^2}{S}\left(\frac{\rho_o T_o S}{\chi} + \frac{T_o k^2}{c_V}\right) & \frac{T_o \beta B_T k^4}{S c_V} & k^2 T'_{Z_1} & \cdots\cdots & k^2 T'_{Z_n} \\ \frac{T_o \beta B_T k^4}{S c_V} & \frac{\rho_o^2 k^2}{S}\, B_{12} & k^2 P'_{Z_1} & \cdots\cdots & k^2 P'_{Z_n} \\ k^2 T'_{Z_1} & k^2 P'_{Z_1} & \frac{-(1+S\tau_{11})}{\phi_{11}\tau_{11}} & \cdots\cdots & \frac{-(1+S\tau_{1n})}{\phi_{1n}\tau_{1n}} \\ \vdots & \vdots & \vdots & & \\ k^2 T'_{Z_n} & k^2 P'_{Z_n} & \frac{-(1+S\tau_{n1})}{\phi_{n1}\tau_{n1}} & \cdots\cdots & \frac{-(1+S\tau_{nn})}{\phi_{nn}\tau_{nn}} \end{vmatrix} \tag{21}$$

We recall that $\phi_{ij}=\phi_{ji}$. Further it is reasonable to assume that $L_{ij}=L_{ji}$, then (20) and (21) are symmetrical, which simplifies the expressions considerably.

Consider

$$\delta\xi_i = \left(\frac{\partial \xi_i}{\partial S}\right)_{\rho,Z} \delta S + \left(\frac{\partial \xi_i}{\partial \rho}\right)_{S,Z} \delta\rho + \sum_j \left(\frac{\partial \xi_i}{\partial Z_j}\right)_{\rho,S,Z'_j} \delta Z_j \ ,$$

$$i=1 \ \ldots\ldots\ n \tag{22}$$

This can be written as

$$[\delta\xi] = \delta S\left[\frac{\partial \xi}{\partial S}\right] + \delta\rho\left[\frac{\partial \xi}{\partial P}\right] + \left|\left|\frac{\partial \xi_i}{\partial Z_j}\right|\right| [\delta Z] \tag{23}$$

where $[\delta\xi]$, $\left[\frac{\partial\xi}{\partial S}\right]$, $\left[\frac{\partial\xi}{\partial\rho}\right]$ and $[\delta Z]$ are column vectors, i.e. $[\delta\xi] = \begin{pmatrix}\delta\xi_1\\ \delta\xi_2\\ \vdots\\ \delta\xi_n\end{pmatrix}$ etc., and $\left\|\frac{\partial\xi_i}{\partial Z_j}\right\|$ is an n × n symmetric matrix. Hence there exists a non singular similarity matrix D such that $D\left\|\frac{\partial\xi_i}{\partial Z_j}\right\|D^{-1}$ is diagonal. If we now define

$$[\delta\xi]' = D[\delta\xi]$$

$$[\delta Z]' = D[\delta Z] \quad , \tag{24}$$

then we have the result that

$$\left[\frac{\partial\xi_i}{\partial Z_j}\right]' = \left[\frac{\partial\xi_i}{\partial Z_i}\right]'\delta_{ij} \quad . \tag{25}$$

So, without loss of generality, one can assume that $\delta\xi_i$ depends only on ρ, S and the corresponding δZ_i †. Or,

$$\frac{\partial\xi_i}{\partial t} = -L_{ii}\,\delta Z_i \quad , \tag{26}$$

---

† This kind of relaxation where each parameter can be assumed to relax independently of the others is usually called relaxation in parallels. [13, 16]

with the understanding that any τ defined from (26) is at constant S and ρ, i.e. τ_{SV}.

We shall now write $\phi_i \equiv \phi_{ii}$, $\tau_i \equiv \tau_{ii}$, and again apply elementary operations on $\left|\left|A\right|\right|$ and $\left|\left|B\right|\right|$ to evaluate these determinants, remembering that now $\left|\left|\frac{(1+S\tau_{ij})}{\phi_{ij}\tau_{ij}}\right|\right|$ is diagonal. Let c_i and R_i denote the ith column and ith row respectively. We now apply the following:

(i) $c_2 + \sum_i \frac{\phi_i\tau_i}{1+S\tau_i} k^2 P'_{Z_i} \; c_{2+i}$, followed by similar operations on R_2.

(ii) $c_1 + \sum_i \frac{\phi_i\tau_i}{1+S{\rightarrow}_i} k^2 T'_{Z_i} \; c_{2+i}$, followed by similar operations on R_1.

The determinants $\left|\left|A\right|\right|$ and $\left|\left|B\right|\right|$ then become

$$\left|\left|A\right|\right| = -\frac{\chi}{\rho_o^5 k^8 T_o}\, \rho(\vec{k})\; F(S)\; (-1)^n \prod_i \frac{(1+S\tau_i)}{\phi_i\tau_i}$$

$$\left|\left|B\right|\right| = -\frac{\chi}{\rho_o^5 k^8 T_o}\, G(S)(-1)^n \prod_i \frac{(1+S\tau_i)}{\phi_i\tau_i} \quad .$$

Hence Eq. (17) becomes

$$\rho(\vec{k},S) = \frac{F(S)}{G(S)}\, \rho(\vec{k}) = \sigma(k,S)\rho(\vec{k}) \tag{27}$$

$$\sigma(k,S) = \frac{F(S)}{G(S)} \quad , \tag{28}$$

$$\begin{aligned}
F(S) = {} & S^2 \{1 + \frac{\chi k^2}{\rho_o T_o} \sum_i \frac{\phi_i T'^2_{Z_i} \tau_i}{1+S\tau_i}\} \\
& + S \{\frac{\chi k^2}{\rho_o c_V} + \frac{4}{3\rho_o} G^\infty k^2 \int \frac{g_\eta(\tau)\tau \, d\tau}{1+S\tau}(1 + \frac{\chi k^2}{\rho_o T_o} \sum_i \frac{\phi_i T'^2_{Z_i} \tau_i}{1+S\tau_i}) \\
& + \frac{k^2}{\rho_o^2} \sum_i \frac{\phi_i P'^2_{Z_i} \tau_i}{1+S\tau_i} + \frac{\chi k^4}{\rho_o^3 T_o} \sum_{i,j} \frac{\phi_i \phi_j \tau_i \tau_j}{(1+S\tau_i)(1+S\tau_j)} \\
& \times (T'^2_{Z_i} P'^2_{Z_j} - T'_{Z_i} T'_{Z_j} P'_{Z_i} P'_{Z_j})\} + \frac{\chi k^4}{\rho_o^2 c_V} \{\frac{4}{3} G^\infty \int \frac{g_\eta(\tau)\tau \, d\tau}{1+S\tau} \\
& + \frac{1}{\rho_o} \sum_i \frac{\phi_i \tau_i}{1+S\tau_i} (P'^2_{Z_i} - 2\beta B_T T'_{Z_i} P'_{Z_i} + \beta^2 B_T^2 T'^2_{Z_i})\} + c_o^2 k^2 (1 - \frac{1}{\gamma})
\end{aligned} \tag{29}$$

$$\begin{aligned}
G(S) = {} & S^3 \{1 + \frac{\chi k^2}{\rho_o T_o} \sum_i \frac{\phi_i \tau_i T'^2_{Z_i}}{1+S\tau_i}\} + S^2 \{\frac{\chi k^2}{\rho_o c_V} + \frac{4}{3\rho_o} G^\infty k^2 \times \\
& \int \frac{g_\eta(\tau)\tau d\tau}{1+S\tau}(1 + \frac{\chi k^2}{\rho_o T_o} \sum_i \frac{\phi_i \tau_i T'^2_{Z_i}}{1+S\tau_i}) + \frac{k^2}{\rho_o} \sum_i \frac{\phi_i \tau_i P'^2_{Z_i}}{1+S\tau_i} \\
& + \frac{\chi k^4}{\rho_o^3 T_o} \sum_{i,j} \frac{\phi_i \phi_j \tau_i \tau_j}{(1+S\tau_i)(1+S\tau_j)} (T'^2_{Z_i} P'^2_{Z_j} - T'_{Z_i} T'_{Z_j} P'_{Z_i} P'_{Z_j})\} \\
& + S \{c_o^2 k^2 + \frac{k^4}{\rho_o^2 c_V} [\frac{4}{3} G^\infty \int \frac{g_\eta(\tau)\tau \, d\tau}{1+S\tau} + \frac{1}{\rho_o} \sum_i \frac{\phi_i \tau_i}{1+S\tau_i} \\
& \times (P'^2_{Z_i} - 2\beta B_T T'_{Z_i} P'_{Z_i} + \frac{B_S c_V}{T_o} T'^2_{Z_i})]\} + \frac{\chi k^2}{\rho_o c_P} c_o^2 k^2 \, .
\end{aligned} \tag{30}$$

We next write down some thermodynamic relations, for the case of multiple relaxation, which are generalizations of eqns. (17), (24) and (27) of Chapter 3. One may verify that

$$B_S^\infty - B_S = \rho_o^{-1} \sum_j \phi_j P_{Z_j}'^2 \quad , \qquad (31)$$

$$\frac{1}{c_V^\infty} - \frac{1}{c_V} = T_o^{-1} \sum_j \phi_j T_{Z_j}'^2 \quad , \qquad (32)$$

$$\frac{\beta^\infty B_T^\infty}{c_V^\infty} - \frac{\beta B_T}{c_V} = T_o^{-1} \sum_j \phi_j P_{Z_j}' T_{Z_j}' \quad . \qquad (33)$$

If we now go to the continuum limit, so that there are many relaxation times τ_i in a small range between τ_i and $\tau_i + d\tau_i$, we can define three distribution functions as follows:

$$g_d\ (\tau_i) = \frac{\phi_i P_{Z_i}'}{\sum_j \phi_j P_{Z_j}'^2} \quad , \quad g_d'(\tau_i) = \frac{\phi_i T_{Z_i}'^2}{\sum_j \phi_j T_{Z_j}'^2}$$

$$\text{and } g_d''(\tau_i) = \frac{\phi_i T_{Z_i}' P_{Z_i}'}{\sum_j \phi_j T_{Z_j}' P_{Z_j}'} \quad , \qquad (34)$$

which are each normalized to unity, i.e.

$$\int g_d(\tau_i)\, d\tau_i = 1 \quad .$$

We can then replace in (29) and (30)

$$\sum_i \rho_o^{-1} \phi_i P_{Z_i}'^2 f(\tau_i) \rightarrow (B_S^\infty - B_S) \int g_d(\tau) f(\tau) d\tau$$

$$\sum_i T_o^{-1} \phi_i T_{Z_i}'^2 f(\tau_i) \rightarrow \left(\frac{1}{c_V^\infty} - \frac{1}{c_V}\right) \int g_d'(\tau) f(\tau) d\tau$$

$$\sum_i T_o^{-1} \phi_i T_{Z_i}' P_{Z_i}' f(\tau_i) \rightarrow \left(\frac{\beta^\infty B_T^\infty}{c_V^\infty} - \frac{\beta B_T}{c_V}\right) \int g_d''(\tau) f(\tau) d\tau \ . \tag{35}$$

where $f(\tau)$ is any function of τ. It may be verified from (34) that only two of the three distribution functions are independent, since

$$g_d''(\tau) \ \alpha \ \sqrt{g_d(\tau) g_d'(\tau)} \quad . \tag{36}$$

With the substitution of (35) and (36) into (29) and (30), one sees that the expression for the spectral distribution will in general contain two distribution functions for bulk relaxation.

We next observe that if

$$\begin{aligned} T_{Z_i}' / P_{Z_i}' &= \text{constant (independent of i)} \\ &= A, \text{ say }, \end{aligned} \tag{37}$$

then it follows from (35) that

$$g_d(\tau) = g_d'(\tau) = g_d''(\tau) \ , \tag{38}$$

so that only one distribution function is sufficient for the description of bulk relaxation processes. When (37) is satisfied we shall say that all the individual bulk relaxation processes in the fluid are of the same type. It is interesting to note that condition (37) is satisfied if all the individual relaxation processes are either (1) density induced or (2) pressure induced or (3) temperature induced. The definition of these three types of relaxation processes was given in Chapter 3, and one may verify that for these cases $A=0$, $T_o\rho_o^{-1}\beta c_P^{-1}$, $(\beta B_T)^{-1}$, respectively.

In principle, there is, of course, no reason why in a given liquid all the relaxation processes be of the same type. However it is known that in highly associated liquids like water and glycerine, the relaxation processes are predominantly pressure induced, whereas in other liquids (Kneser type) they are primarily temperature induced [13, 16]. Since use of (37) simplifies the analysis considerably, we shall calculate here spectral distribution for this case only.

§7.3 Approximate Determination of Spectral Density

In the preceding section we obtained an expression for $\sigma(k,S) = F(S)/G(S)$ for the case where the relaxing bulk viscosity is characterized by a discrete set of relaxation times. Also we gave a prescription for going to the limit where these relaxation times lie in a continuous range. When the relaxation times form a discrete set, they are usually only few in number. In Chapter 5 we have already discussed the case of two relaxation times, and for this reason we shall not discuss the discrete case further here.

For the continuum case, expressions (29) and (30) can be written as, on using eqns. (35) and (38),

$$\begin{aligned}
F(S) = {} & S^2 \{1 + \frac{\chi k^2}{\rho_o c_V} (\frac{c_V}{c_V^\infty} - 1) \int \frac{g_d(\tau)\tau \, d\tau}{1+S\tau}\} \\
& + S\{\frac{\chi k^2}{\rho_o c_V} + \frac{4}{3} \frac{G^\infty}{\rho_o} k^2 \int \frac{g_\eta(\tau)\tau \, d\tau}{1+S\tau} [1 + \frac{\chi k^2}{\rho_o c_V}(\frac{c_V}{c_V^\infty} - 1) \times \\
& \int \frac{g_d(\tau)\tau \, d\tau}{1+S\tau}] + \frac{k^2}{\rho_o} (B_S^\infty - B_S) \int \frac{g_d(\tau)\tau \, d\tau}{1+S\tau}\} \\
& + \frac{\chi k^4}{\rho_o^2 c_V} \{\frac{4}{3} G^\infty \int \frac{g_\eta(\tau)\tau \, d\tau}{1+S\tau} + \frac{c_V}{c_V^\infty} (B_T^\infty - B_T) \int \frac{g_d(\tau)\tau \, d\tau}{1+S\tau} \\
& + c_o^2 k^2 (1 - \frac{1}{\gamma}) \\
= {} & S^2 + S\{\frac{\chi k^2}{\rho_o c_V} \int \frac{1+\frac{c_V}{c_V^\infty} S\tau}{1+S\tau} g_d(\tau) d\tau + \frac{4}{3} \frac{G^\infty}{\rho_o} \int \frac{g_\eta(\tau)\tau \, d\tau}{1+S\tau} \\
& + \frac{k^2(B_S^\infty - B_S)}{\rho_o} \int \frac{g_d(\tau)\tau \, d\tau}{1+S\tau}\} + \frac{\chi k^4}{\rho_o^2 c_V} \{\frac{4}{3} G^\infty \int \frac{g_\eta(\tau)\tau \, d\tau}{1+S\tau} \times \\
& \int \frac{1+\frac{c_V}{c_V^\infty} S\tau}{1+S\tau} g_d(\tau) d\tau + (B_T^\infty - B_T) \frac{c_V}{c_V^\infty} \int \frac{g_d(\tau)\tau \, d\tau}{1+S\tau}\} + c_o^2 k^2 (1 - \frac{1}{\gamma})
\end{aligned} \tag{39}$$

$$
\begin{aligned}
G(S) = {} & S^3\{(1 + \frac{\chi k^2}{\rho_o c_V}(\frac{c_V}{c_V^\infty} - 1) \int \frac{g_d(\tau)\tau \, d\tau}{1+S\tau}\} \\
& + S^2 \{\frac{\chi k^2}{\rho_o c_V} + \frac{4}{3}\frac{G^\infty k^2}{\rho_o} \int \frac{g_\eta(\tau)\tau \, d\tau}{1+S\tau} \Big[1 + \frac{\chi k^2}{\rho_o c_V}(\frac{c_V}{c_V^\infty} - 1) \times \\
& \int \frac{g_d(\tau)\tau \, d\tau}{1+S\tau}\Big] + \frac{k^2(B_S^\infty - B_S)}{\rho_o} \int \frac{g_d(\tau)\tau \, d\tau}{1+S\tau}\} + S\{c_o^2 k^2 + \frac{\chi k^4}{\rho_o^2 c_V} \\
& \times \Big[\frac{4}{3} G^\infty \int \frac{g_\eta(\tau)\tau \, d\tau}{1+S\tau} + (\frac{c_V B_T^\infty}{c_V^\infty} - B_T) \int \frac{g_d(\tau)\tau \, d\tau}{1+S\tau}\Big]\} \\
& + \frac{\chi k^2}{\rho_o c_P} c_o^2 \, k^2 \\
= {} & S^3 + S^2\{\frac{\chi k^2}{\rho_o c_V} \int \frac{1 + \frac{c_V}{c_V^\infty} S\tau}{1+S\tau} g_d(\tau) d\tau + \frac{4}{3}\frac{G^\infty k^2}{\rho_o} \times \\
& \int \frac{g_\eta(\tau)\tau \, d\tau}{1+S\tau} + \frac{B_S^\infty - B_S}{\rho_o} k^2 \int \frac{g_d(\tau)\tau \, d\tau}{1+S\tau}\} + S\{c_o^2 k^2 + \frac{\chi k^4}{\rho \rho_o^2 c_V} \\
& \times \Big[\frac{4}{3} G^\infty \int \frac{g_\eta(\tau)\tau \, d\tau}{1+S\tau} \int \frac{1 + \frac{c_V}{c_V^\infty} S\tau}{1+S\tau} g_d(\tau) d\tau + (B_T^\infty - B_T)\frac{c_V}{c_V^\infty} \times \\
& \int \frac{g_d(\tau)\tau}{1+S\tau} d\tau\Big]\} + \frac{\chi k^2}{\rho_o c_P} c_o^2 k^2 \int \frac{1 + \frac{c_V}{c_V^\infty} S\tau}{1+S\tau} g_d(\tau) d\tau \, . \qquad (40)
\end{aligned}
$$

We shall now proceed to factorize G(S) approximately. It is convenient to define the following dimensionless quantities:

$$
y = \frac{S}{v_o k} \quad ; \quad \alpha = \frac{\chi k}{\rho_o v_o c_V^\infty} \quad ; \quad x = v_o k \, \tau \quad ; \quad A = \frac{c_V}{c_V^\infty}
$$

$$
g_d(x) = \frac{1}{v_o k} g_d(\tau) \; ; \qquad g_\eta(x) = \frac{1}{v_o k} g_\eta(\tau) \, . \qquad (41)
$$

Hence Eq. (7-27) becomes

$$\sigma(k,S) = \frac{1}{v_o k} \frac{F(y)}{G(y)} \quad , \tag{42}$$

where

$$\begin{aligned} F(y) = {} & y^2 + y \left\{ \frac{\alpha}{A} \int \frac{1+Ayx}{1+yx} g_d(x)dx + \frac{4}{3} \frac{G^\infty}{B_S} \int \frac{x}{1+yx} g_\eta(x)dx \right. \\ & \left. + \frac{B_S^\infty - B_S}{B_S} \int \frac{x}{1+yx} g_d(x)dx \right\} + \frac{\alpha}{A} \frac{4}{3} \frac{G^\infty}{B_S} \int \frac{x}{1+yx} g_\eta(x) \int \frac{1+Ayx}{1+yx} \\ & \times g_d(x)dx + \frac{B_T^\infty - B_T}{B_S} \alpha \int \frac{x}{1+yx} g_d(x)dx + 1 - \frac{1}{\gamma} \end{aligned} \tag{43}$$

$$\begin{aligned} G(y) = {} & y^3 + y^2 \left\{ \frac{\alpha}{A} \int \frac{1+Ayx}{1+yx} g_d(x)dx + \frac{4}{3} \frac{G^\infty}{B_S} \int \frac{x}{1+yx} g_\eta(x)dx \right. \\ & \left. + \frac{B_S^\infty - B_S}{B_S} \int \frac{x}{1+yx} g_d(x)dx \right\} + y \left\{ 1 + \frac{\alpha}{A} \frac{4}{3} \frac{G^\infty}{B_S} \int \frac{x}{1+yx} g_\eta(x)dx \right. \\ & \times \int \frac{1+Ayx}{1+yx} g_d(x)dx + \frac{B_T^\infty - B_T}{B_S} \alpha \int \frac{x}{1+yx} g_d(x)dx + \frac{A-1}{\gamma A} \alpha \\ & \left. \times \int \frac{x}{1+yx} g_d(x)dx \right\} + \frac{\alpha}{\gamma A} \quad . \end{aligned} \tag{44}$$

The low and high frequency limits are then defined by $v_o k \bar{\tau} \to 0$ and $v_o k \bar{\tau} \to \infty$ respectively, where $\bar{\tau} = \int_0^\infty \tau g(\tau) d\tau$ is the mean relaxation time. This definition of the limits then agrees with the condition that the frequency dependent modulus

$$M(i\omega) = M_o + (M^\infty - M_o) \int_0^\infty \frac{i\omega\tau}{1+i\omega\tau} g(\tau)\, d\tau \tag{45}$$

has the value M_o and M^∞ respectively if one takes the low and high frequency limits.

We shall in the following analysis assume that $\alpha\bar{x}_d$ and $\alpha\bar{x}_\eta \ll 1$, where $\bar{x}_d = v_o k\, \bar{\tau}_d$; $\bar{x}_\eta = v_o k\, \bar{\tau}_\eta$. Writing (44) as

$$G(y) \equiv y^3 + c_2 y^2 + c_1 y + c_o = 0, \tag{46}$$

we see that the small root is

$$-y_o \simeq -\frac{\alpha}{\gamma A} \quad . \tag{47}$$

Therefore, $G(y) = (y + y_o)[y^2 + (c_2+\varepsilon_2)y + c_1 + \varepsilon_1]$, (48)

where ε_1 and ε_2 are of order α.

Expanding (48), and comparing coefficients, we get

$$\varepsilon_2 \simeq -y_o = -\frac{\alpha}{\gamma A}$$
$$\varepsilon_1 \simeq -\frac{\alpha}{\gamma A} \cdot \{\frac{B_S^\infty - B_S}{B_S} \int \frac{x}{1+yx}\, g_d(x)dx + \frac{4}{3}\,\frac{G^\infty}{B_S} \int \frac{x}{1+yx}\, g_\eta(x)dx\} \tag{49}$$

Define now

$$\begin{aligned} 2\delta &= c_2 + \varepsilon_2 \\ d &= c_1 + \varepsilon_1 \;. \end{aligned} \tag{50}$$

Therefore, $G(y) = (y + y_o)(y^2 + 2\delta y + d)$,

$$2\delta = \frac{B_S^{\infty}-B_S}{B_S} \int \frac{x}{1+yx}\, g_d(x)dx + \frac{4}{3}\frac{G^{\infty}}{B_S} \int \frac{x}{1+yx}\, g_\eta(x)dx$$

$$+ \frac{\alpha}{A}\left(1 - \frac{1}{\gamma}\right) - \frac{\alpha(A-1)}{A} \int \frac{yx}{1+yx}\, g_d(x)dx \qquad (52)$$

$$d = 1 + \frac{\alpha}{A}\frac{4}{3}\frac{G^{\infty}}{B_S}\left(1 - \frac{1}{\gamma}\right) \int \frac{x}{1+yx}\, g_\eta(x)dx + \frac{A-1}{A}\,\alpha\,\frac{4}{3}\frac{G^{\infty}}{B_S} \times$$

$$\int \frac{x}{1+yx}\, g_\eta(x)dx \int \frac{yx}{1+yx}\, g_d(x)dx + \frac{A-1}{A}\frac{\alpha}{\gamma} \int \frac{x}{1+yx}\, g_d(x)dx$$

$$+ \alpha\left[\frac{B_T^{\infty}-B_T}{B_S} - \frac{B_S^{\infty}-B_S}{B_S}\right] \int \frac{x}{1+yx}\, g_d(x)dx \ . \qquad (53)$$

We now write

$$\frac{F(y)}{G(y)} = \frac{\sigma_o}{y+y_o} + \frac{by+c}{y^2+2\delta y+d} \ . \qquad (54)$$

Comparing (54) with (43), we get

$$\sigma_o \simeq \left(1 - \frac{1}{\gamma}\right)$$

$$b \simeq \frac{1}{\gamma}$$

$$c \simeq \frac{2\delta}{\gamma}\{1 + \frac{A-1}{A}\,\alpha\left(1 - \frac{1}{\gamma}\right) \int \frac{x}{1+yx}\, g_d(x)dx - \frac{\alpha}{A}\frac{4}{3}\frac{G^{\infty}}{B_S} \int \frac{x}{1+yx}$$

$$\times\, g_\eta(x)dx \int \frac{1+Ayx}{1+yx}\, g_d(x)dx - \frac{\alpha(B_T-B_T)}{B_S} \int \frac{x}{1+yx}\, g_d(x)dx$$

$$+ \frac{2\alpha}{\gamma A}\, 2\delta - \frac{\alpha}{A}\, 2\delta \ . \qquad (55)$$

Now consider Eq. (54). The first term corresponds to a central component arising from thermal conductivity, just as in the case of single relaxation times. The second term contains other central components and the Brillouin components. In general it is very difficult to separate out these components. We shall use an approximate method, taking as our guideline that the results should reduce to those that we previously deduced for the case of single relaxation times. We first assume that the sound absorption is small ($\Gamma/vk \ll 1$) so that the Brillouin components and central components are well separated. Now from (54), consider

$$y^2 + 2\delta y + d \tag{56}$$

where we recall that δ and d are functions of y. Relevant to our problem, y is eventually to be considered complex and is equal to $\frac{i\omega}{v_o k}$. Hence δ and d are also complex.

For the description of the Brillouin components, we require a form of

$$(y + \theta + \frac{iv}{v_o})(y + \theta - \frac{iv}{v_o}) = y^2 + 2\theta y + \theta^2 + \frac{v^2}{v_o^2}, \tag{57}$$

which is to be extracted from (7-55).

Writing $y = iy'$, $y' = \frac{\omega}{v_o k}$, we can arrange (7-55) to give

$$y^2 + y\,(2\delta_1 + d_2') + 2\delta_2 y + d_1, \tag{58}$$

where
$$\begin{aligned} 2\delta &= 2\delta_1 + 2\delta_2 \\ d &= d_1 + d_2 \\ d_2 &= y d_2' \quad , \end{aligned} \tag{59}$$

d_1, d_2, δ_1 being real, and d_2, δ_2 being pure imaginary.

We shall now replace some of the y's in (58) by $\frac{iv}{v_o}$, while keeping others of the y's untouched. We do this in anticipation of reducing (58) to (57).

So we shall identify

$$2\theta = [2\delta_1 + d_2']_{\,y'=v/v_o}$$

$$\theta^2 + \frac{v^2}{v_o^2} = [2\delta_2 y + d_1]_{y'=v/v_o} \quad . \tag{60}$$

From (52) and (53), we have

$$\begin{aligned} 2\theta = {} & \frac{B_S^\infty - B_S}{B_S} \int \frac{x}{1+zx^2}\, g_d(x)dx + \frac{4}{3}\frac{G^\infty}{B_S} \int \frac{x}{1+zx^2}\, g_\eta(x)dx \\ & + \frac{\alpha}{A} \int \frac{1+Azx^2}{1+zx^2}\, g_d(x)dx - \frac{\alpha}{\gamma A} + \alpha\Big[\frac{B_S^\infty}{\gamma A B_S} - \frac{B_T^\infty}{B_S}\Big] \int \frac{x^2}{1+zx^2}\, g_d(x)dx \\ & - \frac{\alpha}{A}\,\frac{4}{3}\,\frac{G^\infty}{B_S}\Big(1 - \frac{1}{\gamma}\Big) \int \frac{x^2}{1+zx^2}\, g_\eta(x)dx + \frac{\alpha(A-1)}{A}\,\frac{4}{3}\,\frac{G^\infty}{B_S} \int \frac{x}{1+zx^2} \\ & \times g_\eta(x)dx \int \frac{x}{1+zx^2}\, g_d(x)dx - \frac{A-1}{A}\,\alpha\,\frac{4}{3}\,\frac{G^\infty}{B_S} \int \frac{x^2}{1+zx^2}\, g_\eta(x)dx \\ & \times \int \frac{zx^2}{1+zx^2}\, g_d(x)dx \end{aligned} \tag{61}$$

$$\simeq \frac{B_S^\infty - B_S}{B_S} \int \frac{x}{1+zx^2}\, g_d(x)dx + \frac{4}{3}\frac{G^\infty}{B_S} \int \frac{x}{1+zx^2}\, g_\eta(x)\, dx \ . \tag{62}$$

$$\frac{v^2}{v_o^2} \equiv z = \left[2\delta_2 y + d_1\right]_{y'=v/v_o} - \theta^2$$

$$\simeq 1 + \frac{B_S^\infty - B_S}{B_S} \left\{ \int \frac{x^2}{1+x^2} g_d(x)dx - \frac{1}{4} \frac{B_S^\infty - B_S}{B_S} \left[\int \frac{x}{1+x^2} g_d(x)dx \right]^2 \right\}$$

$$+ \frac{4}{3} \frac{G^\infty}{B_S} \left\{ \int \frac{x^2}{1+x^2} g_\eta(x)dx - \frac{1}{4} \frac{\frac{4}{3}G^\infty}{B_S} \left[\int \frac{x}{1+x^2} g_\eta(x)dx \right]^2 \right\}$$

$$- \frac{1}{2} \frac{B_S^\infty - B_S}{B_S} \frac{4}{3} \frac{G^\infty}{B_S} \int \frac{x}{1+x^2} g_\eta(x)dx \int \frac{x}{1+x^2} g_d(x)dx. \quad (63)$$

The Brillouin components are then given by

$$\frac{\sigma_B + ig}{y+\theta+\frac{iv}{v_o}} + \frac{\sigma_B - ig}{y+\theta-\frac{iv}{v_o}} \quad (64)$$

where σ_B and g are still to be determined. We shall find them by comparing (64) with the second term of (54). Writing

$$b = b_1 + b_2$$

$$c = c_1 + c_2$$

$$c_2 = y\, c_2' \quad , \quad (65)$$

where b_1, c_1, c_2' are real and b_2, c_2 are pure imaginary, we identify

$$2\sigma_B = \left[b_1 + c_2'\right]_{y'=v/v_o}$$

$$2\sigma_B\theta + 2g\frac{v}{v_o} \simeq \left[c_1 + b_2\, y\right]_{y'=v/v_o} . \quad (66)$$

Therefore,

$$2\sigma_B \simeq \frac{1}{\gamma}\left\{1 - \frac{B_S^\infty - B_S}{B_S}\int \frac{x^2}{1+zx^2}\, g_d(x)dx - \frac{4}{3}\frac{G^\infty}{B_S}\int \frac{x^2}{1+zx^2}\, g_\eta(x)dx\right\} \tag{67}$$

$$2g \simeq \frac{v_o}{2\gamma v}\left\{2\theta + 2\theta\left[\frac{B_S^\infty - B_S}{B_S}\int \frac{x^2}{1+zx^2}\, g_d(x)dx + \frac{4}{3}\frac{G^\infty}{B_S}\int \frac{x^2}{1+zx^2} \times g_\eta(x)dx\right]\right\} \quad . \tag{68}$$

Hence the spectral distribution is given by

$$\sigma(k,\omega) = \frac{2\sigma_o S_o}{\omega^2 + S_o} + \sigma_B\left[\frac{2\Gamma}{(\omega+vk)^2+\Gamma^2} \quad \frac{2\Gamma}{(\omega-vk)^2+\Gamma^2}\right]$$

$$+ 2g\left[\frac{\omega+vk}{(\omega+vk)^2+\Gamma^2} - \frac{\omega-vk}{(\omega-vk)^2+\Gamma^2}\right] + \text{central components}$$

due to relaxation processes. (69)

In the above, we have written

$$S_o = v_o k\, y_o = \frac{\chi k^2}{\rho_o c_P}\ , \quad \sigma_o = 1 - \frac{1}{\gamma}\ , \ \Gamma = v_o k\, \theta . \tag{70}$$

The intensity ratio is, as before, given by $R = I_R/2I_B = \frac{1}{2\sigma_B} - 1$.

The central components arising from the relaxation processes are in general quite mixed together and the resultant distribution is in general not Lorentzian. However, by virtue of conservation of intensity, their combined contribution is equal to

$$\sigma' = 1 - \sigma_o - 2\sigma_B . \tag{71}$$

One can obtain a very approximate expression for such a resultant distribution. Assuming that it is approximately Lorentzian, one can write down its contribution to $\sigma(k,S)$ as $\frac{\sigma'}{S+S'}$. Neglecting the contribution to the intensity at $\omega=0$ from Brillouin components we have

$$\frac{\sigma'}{S'} = \lim_{y\to 0} \frac{by + c}{y^2+2\delta y+d} \frac{1}{v_o k}$$

$$= \frac{1}{\gamma} \{\frac{B_S^\infty-B_S}{B_S} \bar{\tau}_d + \frac{4}{3} \frac{G^\infty}{B_S} \bar{\tau}_\eta\}. \tag{72}$$

Hence

$$S' = \sigma'\gamma / \{\frac{B_S^\infty-B_S}{B_S} \bar{\tau}_d + \frac{4}{3} \frac{G^\infty}{B_S} \bar{\tau}_\eta\} . \tag{73}$$

The contribution to $\sigma(k,\omega)$ is then given by

$$\frac{2\sigma'S'}{\omega^2+S'^2} . \tag{74}$$

It can be verified easily that in both low and high frequency limits, (61) and (67) both reduce in the case of single relaxation times to the expressions for 2Γ and $2\sigma_B$ given in §5.5. The expression for v^2/v_o^2 in (5-47) and (5-48) can also be obtained as such limits of (63).

Chapter 8

DISCUSSION AND SUMMARY

In the preceding chapters of this thesis we have given a formulation of the problem of calculating the spectral distribution of a liquid which possesses both a relaxing bulk and a relaxing shear viscosity. The former is ascribed to the relaxation of ordering parameters and the thermodynamic theory of relaxation processes has been applied to the calculation of the density correlation function, and hence of the spectral intensity. It was shown that such a treatment enables one to determine the extent to which the integral representation for the relaxing bulk viscosity is appropriate.

As for the shear viscosity, it must be taken as the low frequency limit of a shear relaxation process if the occurrence of Brillouin components is to be explained in liquids of high viscosity. In general, the use of a relaxing shear viscosity is necessary whenever $\omega\eta/B_S \gtrsim 1$. This condition is easily met in liquids of high viscosity for the values of ω involved in light scattering experiments. Parenthetically it may be mentioned that in neutron scattering this condition is met in other liquids also, and it is well known that the neutron scattering data requires that high frequency shear waves propagate in liquids without much absorption, indicating the necessity of using a relaxing shear viscosity.

In Chapter 5 we have calculated the spectral intensity for the case where both the bulk and shear relaxations are each characterized by a single relaxation time for many liquids (e.g., the so called normal liquids). However, one usually has $x_2(=v_o k\tau_\eta) << 1$, whereas x_d can have values such that $x_d \gtrsim 1$. As already mentioned in Chapter 5, this special case of our results has been discussed by previous workers in some detail [24, 27, 32]. We shall therefore confine our comments here mainly to liquids of high viscosity.

The viscous liquids have the property that their shear and bulk viscosities, and hence τ_η and τ_d, are of the same order of magnitude at a given temperature, and that both increase sharply as the temperature decreases. It is, therefore, possible by varying the temperature to obtain the spectral intensity of scattered light for different values of x_2 and x_d covering the range $x_2, x_d << 1$ to $x_2, x_d >> 1$, $\alpha x_2, \alpha x_d << 1$ to $\alpha x_2, \alpha x_d >> 1$. The expected qualitative behaviour of the spectral distribution as one goes from low frequency (high temperature) to high frequency (low temperature) limit is as follows:

(i) In the low frequency limit, $x_d << 1$, $x_2 << 1$, the central components due to the relaxing modes have very large half-widths but small total intensity, so that they form a weak background. The central line is predominantly due to thermal conductivity, and is very sharp. The Brillouin components are also very sharp and somewhat taller than the central components.

(ii) As temperature decreases so that $x_2, x_d \sim 1$, $\theta (=\Gamma / v_o k)$ is not very small compared with unity. The Brillouin components then become broader and shorter. Further because the g terms (see 5-61) have now become significant, the shape of the Brillouin components will deviate from the Lorentzian shape, with the maxima displaced towards the centre ($\omega=0$) of the spectrum. The central components due to the relaxing modes now have smaller half widths and greater heights.

(iii) As temperature decreases further so that $x_2, x_d >> 1$, the Brillouin components become very short compared with the central line which is now predominantly due to contributions from the relaxing modes.

The above behaviour is in qualitative agreement with the measurements of Knaap, Gornall and Stoicheff [36] and Pinnow, Candau et al. [35] on glycerine.

For a quantitative comparison one has to take into account the fact, which is well known from ultrasonic work, namely, that both the bulk and shear relaxations have each to be characterized by a multiplicity of closely spaced relaxation times. In ultrasonic work the only relevant quantity for bulk relaxation is the complex modulus $B_S(i\omega)$, so that it is sufficient to interpret ultrasonic data in terms of one distribution function for bulk relaxation and one for shear. These are the distribution functions $g_d(\tau)$ and $g_\eta(\tau)$ introduced in Chapter 7. In contrast to this we saw in Chapter 7 that the expression for spectral intensity, in general, contains two distribution functions $g_d(\tau)$ and $g_d'(\tau)$; only when all the bulk relaxa-processes are of the same type does the expression for the spectral intensity contain one distribution function ($g_d(\tau)$).

Montrose, Solovyev and Litovitz [30] have empirically generalized Mountain's expression for the case of single relaxation time to cover viscous liquids. Their expression[†] thus contains one distribution function.

[†] Like Mountain's expression in [24], it is thus strictly valid if all bulk relaxation processes in the liquid are density induced.

for bulk relaxation and one for shear relaxation. Pinnow, Candau, La Macchia and Litovitz [35] have used this expression to interpret their light scattering data in glycerine. They find that $g_d(\tau)$ which fits the light scattering data is substantially different from that required to fit the ultrasonic data, whereas as for shear relaxation, the two are practically the same.

Our work suggests two possible explanations for the discrepancy referred to above:

(1) all the relaxation processes are of the same type but they are not density induced;

(2) all the processes are not of the same type.

This is supported by the fact that it is experimentally found for glycerine that $\beta^{\infty} \neq \beta$, so that all the bulk relaxation processes, taken as a whole, are not purely density induced [see, for example, Ref. (13), p. 254].

The above discussion and summary refers to the work described in Chapters 5 and 7. In Chapter 6, we drew attention that one should, in general, distinguish between the velocity v of the temporally absorbed sound waves and the velocity v_B measured by the relation $v_B = \omega_B/k$, where ω_B is the shift in the frequency of the

Brillouin components. The difference between v_B and v is significant whenever the sound absorption per cycle is not small compared with unity. A numerical example shows that the difference could be as much as 10 to 15% in relaxing liquids.

APPENDIX

FLUCTUATIONS OF THERMODYNAMIC QUANTITIES

A.1 Method of Calculation

Let a physical quantity x deviate from its mean value $\bar{x}$ by a quantity δx. If the probability distribution for such a fluctuation is of the form

$$\omega(\delta x) \propto \exp \{- \frac{b(\delta x)^2}{2\ k_B}\} \tag{1}$$

where b and k_B are constants (for later purpose, k_B will be Boltzmann constant), then the distribution is Gaussian, and the mean square fluctuation is

$$< \delta x^2> = k_B/b \quad . \tag{2}$$

If there are simultaneous deviations of several physical quantities x_1, x_2 .... x_n, and if the probability distribution is

$$\omega(\delta x_1 \ldots \delta x_n) \propto \exp \{- \frac{1}{2k_B} \sum_{i,k} B_{ik} \delta x_i \delta x_k\} \ , \tag{3}$$

then it can be shown that [29]

$$< \delta x_i \delta x_k> = k_B\ B^{-1}_{ik} \quad , \tag{4}$$

where B^{-1} is the inverse matrix of $B = ||B_{ik}||$.

Let us now consider a volume element V_o of fluid embedded in a large fluid system. We assume that V_o is large enough to allow thermodynamic description. Although the fluid in V_o is at equilibrium, it will at any instant of time experience fluctuations of the various thermodynamic quantities. The probability of a fluctuation is related to the minimum work required to carry out reversibly such a fluctuation by [29]

$$\omega \propto e^{-R_{min}/k_B T_o} \quad , \tag{5}$$

$$R_{min} = \delta U - T\delta S + P\delta V - Z\delta\xi \ , \tag{6}$$

where δU, δS and $\delta\xi$ are the changes in energy, entropy and the ordering parameter of the fluid in V_o. Writing $U=U(S,V,\xi)$ and assuming that the fluctuations are small, we have from (6)

$$\begin{aligned} R_{min} &\simeq \tfrac{1}{2}\left[\frac{\partial^2 U}{\partial S^2}\delta S^2 + \frac{\partial^2 U}{\partial V^2}\delta V^2 + \frac{\partial^2 U}{\partial \xi^2}\delta\xi^2 + 2\frac{\partial^2 U}{\partial S\partial V}\delta S\ \delta V \right. \\ &\qquad \left. + 2\frac{\partial^2 U}{\partial S\partial \xi}\delta S\ \delta\xi + 2\frac{\partial^2 U}{\partial V\partial \xi}\delta V\ \delta\xi\right] \\ &= \tfrac{1}{2}\left[\delta S\ \delta\left(\frac{\partial U}{\partial S}\right)_{V,\xi} + \delta V\ \delta\left(\frac{\partial U}{\partial V}\right)_{S,\xi} + \delta\xi\ \delta\left(\frac{\partial U}{\partial \xi}\right)_{S,V}\right] \\ &= \tfrac{1}{2}\left(\delta S\ \delta T - \delta P\ \delta V + \delta Z\ \delta\xi\right) . \end{aligned} \tag{7}$$

If we substitute (7) into (6), choose three independent variables and expand the rest in terms of them, the probability distribution becomes Gaussian and the results of (3) and (4) can be used to calculate the mean square fluctuations of the various quantities.

A.2 Mean Square Fluctuations of the various thermodynamic Quantities

Eq. (7) can be written as

$$2\ R_{min} = \delta S\ \delta T + \frac{V}{\rho}\ \delta P\ \delta\rho + \delta Z \quad . \tag{8}$$

Taking ρ, T and Z as independent variables and making use of (3-14), we have

$$2\ R_{min} \simeq \frac{c_V}{T_o}\ \delta T^2 + \frac{V_o B_T}{\rho_o^2}\ \delta\rho^2 + \left(\frac{\partial\ \xi}{\partial\ Z}\right)_{T,\rho}\delta Z^2 + 2\left(\frac{\partial\ S}{\partial\ Z}\right)_{T,\rho}\delta T\delta Z \ . \tag{9}$$

In (9), $\delta\rho$ is independent of the others. Hence, using (2), we have

$$<\delta\rho^2> = \frac{\rho_o^2 k_B T_o}{V_o B_T} \tag{10}$$

$$<\delta\rho\delta T> = 0 \tag{11}$$

$$<\delta\rho\delta Z> = 0 \quad . \tag{12}$$

The other fluctuation quantities in (9) can be evaluated by defining

$$B_{11} = \frac{c_V}{T_o^2} \ , \quad B_{22} = \frac{1}{T_o}\left(\frac{\partial\ \xi}{\partial\ Z}\right)_{T,\rho} \quad B_{12} = B_{21} = \frac{1}{T_o}\left(\frac{\partial\ S}{\partial\ Z}\right)_{T,\rho} \ .$$

Hence

$$|B| = \frac{1}{T_o^2} \{ \frac{c_V}{T_o} (\frac{\partial \xi}{\partial Z})_{T,\rho} - (\frac{\partial S}{\partial Z})^2_{T,\rho} \}$$

$$= \frac{1}{T_o^3} (\frac{\partial \xi}{\partial Z})_{T,\rho} \, c_V^\infty \quad , \text{ using (3-22)}$$

therefore

$$< \delta T^2 > = \frac{k_B \; B_{22}}{|B|} = \frac{k_B \; T_o^2}{c_V^\infty} \tag{13}$$

$$< \delta Z^2 > = \frac{k_B \; B_{11}}{|B|} = k_B \; T_o \; \frac{c_V}{c_V^\infty} (\frac{\partial Z}{\partial \xi})_{T,\rho}$$

$$= k_B \; T_o \; (\frac{\partial Z}{\partial \xi})_{S,\rho} \quad \text{using (3-34)} \tag{14}$$

$$< \delta Z \; \delta T > = - \frac{k_B \; B_{12}}{|B|} = - \frac{k_B \; T_o^2}{c_V^\infty} (\frac{\partial S}{\partial \xi})_{T,\rho} \quad . \tag{15}$$

The mean square fluctuation of number density can be obtained from (10) as

$$< \delta n^2 > = \frac{n_o^2 \; k_B \; T_o}{V_o \; B_T} \quad . \tag{16}$$

The mean square fluctuation of the number of particles is

$$< \delta N^2 > = \frac{n_o^2 \; k_B \; T_o \; V_o}{B_T} \quad . \tag{17}$$

If we now take S, P and Z as independent variables, we have

$$2 \; R_{min} \simeq \frac{T_o}{c_P} \; \delta S^2 + \frac{V_o}{B_S} \delta P^2 + (\frac{\partial \xi}{\partial Z})_{S,P} \; \delta Z^2 + 2 (\frac{\partial \xi}{\partial P})_{S,Z} \; \delta P \delta Z \; . \tag{18}$$

From (18), we immediately have

$$< \delta S^2> = k_B \, c_P \quad . \tag{19}$$

The determinant required for the evaluation of the fluctuation in other variables is

$$\frac{1}{T_o^2} \left\{ \frac{V_o}{B_S} \left(\frac{\partial \xi}{\partial Z}\right)_{S,P} - \left(\frac{\partial \xi}{\partial P}\right)^2_{S,Z} \right\}$$

$$= \frac{1}{T_o^2} \left\{ \frac{V_o}{B_S} \left(\frac{\partial \xi}{\partial Z}\right)_{S,P} - \frac{V_o^2}{\rho_o^2} \left(\frac{\partial \rho}{\partial Z}\right)^2_{S,P} \right\}$$

$$= \frac{V_o}{T_o^2} \left(\frac{\partial \xi}{\partial Z}\right)_{S,P} \left\{ \frac{1}{B_S} - \frac{V_o}{\rho_o^2} \left(\frac{\partial \rho}{\partial Z}\right)_{S,P} \left(\frac{\partial \rho}{\partial \xi}\right)_{S,P} \right\}$$

$$= \frac{V_o}{T_o^2} \left(\frac{\partial \xi}{\partial Z}\right)_{S,P} \frac{1}{B_S^\infty} \quad \text{using (3-26) .}$$

Hence

$$< \delta P^2> = \frac{k_B \, T_o \, B_S^\infty}{V_o} \tag{20}$$

$$< \delta P \, \delta Z> = - \frac{k_B T_o \, B_S^\infty}{V_o} \left(\frac{\partial \xi}{\partial P}\right)_{S,Z} \left(\frac{\partial Z}{\partial \xi}\right)_{S,P}$$

$$= - \frac{k_B \, T_o \, B_S^\infty}{\rho_o} \left(\frac{\partial \rho}{\partial \xi}\right)_{S,P} \tag{21}$$

$$< \delta S \, \delta P> = 0 \tag{22}$$

$$< \delta S \, \delta Z> = 0 \; . \tag{23}$$

If we now take S, P and ξ as independent variables, we have

$$2\ R_{min} \simeq \frac{T_o}{c_P^{\infty}}\ \delta S^2 + \frac{V_o}{B_S^{\infty}}\ \delta P^2 + \left(\frac{\partial Z}{\partial \xi}\right)_{S,P} \delta\xi^2 + 2\left(\frac{\partial T}{\partial \xi}\right)_{S,P} \delta S \delta\xi . \tag{24}$$

The value of the determinant for S and ξ is

$$\frac{1}{T_o^2}\ \left\{\frac{T_o}{c_P^{\infty}}\ \left(\frac{\partial Z}{\partial \xi}\right)_{S,P} - \left(\frac{\partial T}{\partial \xi}\right)_{S,P}^2\right\}$$

$$= \frac{1}{T_o c_P}\ \left(\frac{\partial Z}{\partial \xi}\right)_{S,P} \quad \text{, using (3-24).}$$

Hence

$$<\delta\xi^2> = \frac{k_B\ T_o\ c_P}{c_P^{\infty}}\ \left(\frac{\partial \xi}{\partial Z}\right)_{S,P}$$

$$= k_B\ T_o\ \left(\frac{\partial \xi}{\partial Z}\right)_{T,P} \quad \text{, using (3-33)} \tag{25}$$

$$< \delta S \delta\xi> = -\ k_B\ c_P\left(\frac{\partial T}{\partial Z}\right)_{S,P} \tag{26}$$

$$< \delta P \delta\xi> = 0\ . \tag{27}$$

For ρ, T and ξ to be independent variables, we have

$$2\ R_{min} \simeq \frac{V_o}{\rho_o^2}\ B_T^{\infty}\ \delta\rho^2 + \frac{c_V^{\infty}}{T_o}\ \delta T^2 + \left(\frac{\partial Z}{\partial \xi}\right)_{T,\rho} \delta\xi^2 + \frac{2V_o}{\rho_o}\left(\frac{\partial P}{\partial \xi}\right)_{T,\rho} \delta\rho\delta\xi\ . \tag{28}$$

The value of the determinant for ρ and ξ is

$$\frac{V_o}{\rho_o^2 T_o^2}\left\{\ B_T^{\infty}\ \left(\frac{\partial Z}{\partial \xi}\right)_{T,\rho} - V_o\left(\frac{\partial P}{\partial \xi}\right)_{T,\rho}^2\right\}$$

$$= \frac{B_T\ V_o}{\rho_o^2 T_o^2}\ \left(\frac{\partial Z}{\partial \xi}\right)_{T,\rho} \quad \text{, using (3-16)}$$

Hence

$$< \delta\rho\delta\xi> = \frac{\rho_o\ k_B\ T_o}{B_T}\left(\frac{\partial\,\xi}{\partial\,Z}\right)_{T,\rho} \tag{29}$$

$$< \delta T\delta\xi> = 0\ . \tag{30}$$

Finally for ρ, S and Z as independent variables,

$$2\ R_{min} \simeq \frac{T_o}{c_V}\ \delta S^2 + \frac{V_o}{\rho_o^2}\ B_S\ \delta\rho^2 + 2\left(\frac{\partial\,T}{\partial\,\rho}\right)_{S,Z}\ \delta\rho\delta S + \left(\frac{\partial\,\xi}{\partial\,Z}\right)_{S,\rho}\delta Z^2\ . \tag{31}$$

Using (3-12) to evaluate the determinant for S, ρ, we have

$$< \delta\rho\delta S> = -\ \frac{k_B}{T_o}\ \left(\frac{\partial\,T}{\partial\,\rho}\right)_{S,Z}/(V_oB_T/T_oc_V\rho_o^2)\ .$$

Now

$$\left(\frac{\partial\,T}{\partial\,\rho}\right)_{S,Z} = \frac{V_o}{\rho_o}\ \left(\frac{\partial\,P}{\partial\,S}\right)_{\rho,Z} = -\ \frac{V_o}{\rho_o}\left(\frac{\partial\,\rho}{\partial\,S}\right)_{P,Z}\ \left(\frac{\partial\,P}{\partial\,\rho}\right)_{S,Z}$$

$$= -\ \frac{V_o}{\rho_o}\ \left(\frac{\partial\,\rho}{\partial\,T}\right)_{P,Z}\ \left(\frac{\partial\,T}{\partial\,S}\right)_{P,Z}\ \left(\frac{\partial\,P}{\partial\,\rho}\right)_{S,Z}$$

$$= V_o\ \beta\ T_o\ B_T/c_V\ \rho_o\ \ . \tag{32}$$

Hence

$$< \delta\rho\delta S> = -\rho_o k_B T_o \beta \tag{32}$$

$$< \delta\rho\delta Z> = 0\ \ . \tag{33}$$

If we now write

$$\delta P\ \delta T = \delta T\ \{\left(\frac{\partial\,P}{\partial\,\rho}\right)_{T,\xi}\delta\rho + \left(\frac{\partial\,P}{\partial\,T}\right)_{\rho,\xi}\delta T + \left(\frac{\partial\,P}{\partial\,\xi}\right)_{T,\rho}\ \delta\xi\},$$

and make use of (11), (13) and (30), we have

$$< \delta P \ \delta T> = (\frac{\partial P}{\partial T})_{\rho,\xi} < \delta \ T^2> = \frac{\beta^\infty B_T^\infty k_B T_o^2}{c_V^\infty} \qquad (34)$$

For

$$\delta P \delta \rho = \delta \rho \{ (\frac{\partial P}{\partial T})_{\rho,Z} \ \delta T + (\frac{\partial P}{\partial \rho})_{T,Z} \ \delta \rho + (\frac{\partial P}{\partial Z})_{T,\rho} \ \delta Z \} \ ,$$

and make use of (11), (12) and (10 to obtain

$$< \delta P \ \delta \rho> = (\frac{\partial P}{\partial \rho})_{T,Z} < \delta \rho^2> = \frac{\rho_o \ k_B \ T_o}{V_o} \qquad (35)$$

For

$$\delta Z \ \delta \xi = \delta \xi \{ (\frac{\partial Z}{\partial T})_{P,\xi} \ \delta T + (\frac{\partial Z}{\partial P})_{T,\xi} \delta P + (\frac{\partial Z}{\partial \xi})_{T,P} \ \delta \xi \},$$

we make use of (25), (27) and (30) to obtain

$$< \delta Z \ \delta \xi> = k_B \ T_o \quad . \qquad (36)$$

Similarly, we have

$$< \delta S \ \delta T> = (\frac{\partial S}{\partial T})_{\rho,\xi} < \delta T^2> = k_B \ T_o \quad . \qquad (37)$$

It is convenient to summarize the results as in Table 2.

A.3 Fluctuations of Fourier components of thermodynamic Quantities

For this purpose we write the minimum work as

$$R_{min} = \tfrac{1}{2} \int_{V_o} \rho_o \ (\delta U - T_o \delta S + P_o \delta V - Z \delta \xi) \ dV \ , \qquad (38)$$

where the extensive variables in the integrand refer to values per unit mass and the integrant then represents R_{min} per unit volume. By the same procedure as before, (8) becomes

Table 2. Mean square fluctuations in various thermodynamic quantities. (To obtain, say, $<\delta P\,\delta\rho>$, read the intersection of corresponding row and column.)

Mean fluctuations	δS	δT	δP	$\delta\rho$	δZ	$\delta\xi$
δS	$k_B c_P$	$k_B T_o$	0	$-\rho_o k_B T_o$ $\times\ \beta$	0	$-k_B c_P\ \times$ $(\frac{\partial T}{\partial Z})_{S,P}$
δT	$k_B T_o$	$\frac{k_B T_o^2}{c_V^\infty}$	$\frac{\beta^\infty B_T^\infty k_B T_o^2}{c_V^\infty}$	0	$-\frac{k_B T_o^2}{c_V^\infty}\ \times$ $(\frac{\partial S}{\partial \xi})_{T,\rho}$	0
δP	0	$\frac{\beta^\infty B_T^\infty k_B T_o^2}{c_V^\infty}$	$\frac{k_B T_o B_S^\infty}{V_o}$	$\frac{\rho_o k_B T_o}{V_o}$	$-\frac{k_B T_o B_S^\infty}{\rho_o}\times$ $(\frac{\partial \rho}{\partial \xi})_{S,P}$	0
$\delta\rho$	$-\rho_o k_B T_o$ $\times\ \beta$	0	$\frac{\rho_o k_B T_o}{V_o}$	$\frac{\rho_o^2 k_B T_o}{V_o B_T}$	0	$\frac{\rho_o k_B T_o}{B_T}\ \times$ $(\frac{\partial \xi}{\partial Z})_{T,\rho}$
δZ	0	$\frac{-k_B T_o^2}{c_V^\infty}\ \times$ $(\frac{\partial S}{\partial \xi})_{T,\rho}$	$\frac{-k_B T_o B_S^\infty}{\rho_o}\times$ $(\frac{\partial \rho}{\partial \xi})_{S,P}$	0	$k_B T_o\ \times$ $(\frac{\partial Z}{\partial \xi})_{S,\rho}$	$k_B\ T_o$
$\delta\xi$	$-k_B c_P\ \times$ $(\frac{\partial T}{\partial Z})_{S,P}$	0	0	$\frac{\rho_o k_B T_o}{B_T}\times$ $(\frac{\partial \xi}{\partial Z})_{T,\rho}$	$k_B T_o$	$k_B T_o\ \times$ $(\frac{\partial \xi}{\partial Z})_{T,P}$

$$R_{min} \simeq \tfrac{1}{2} \rho_o \int_{V_o} (\delta S\delta T + \frac{1}{\rho_o^2} \delta P\delta \rho + \delta Z\delta \xi)\, dV \; . \tag{39}$$

If we take ρ, T and Z as independent variables, (39) becomes

$$R_{min} \simeq \tfrac{1}{2} \rho_o \int_{V_o} \Big[\frac{c_V}{T_o} \delta T^2 + \frac{B_T}{\rho_o^3}\delta \rho^2 + (\frac{\partial \xi}{\partial Z})_{T,\rho}\delta Z^2 + 2(\frac{\partial S}{\partial Z})_{T,\rho} \times \delta T\delta Z\Big]\, dV \; . \tag{40}$$

We now define

$$\rho(\vec{k}) = \frac{1}{V_o} \int_{V_o} \delta\rho(\vec{r},o)\, e^{-i\vec{k}.\vec{r}}\, d^3 \vec{r} \quad \text{etc.} \tag{41}$$

Therefore

$$\delta\rho = \sum_k \rho(\vec{k})\, e^{i\vec{k}.\vec{r}} \qquad \text{etc.} \tag{42}$$

Therefore

$$\int \delta\rho^2 dV = \sum_{k,k'} \int \rho(\vec{k})\rho(\vec{k}')\, e^{i\vec{k}.\vec{r}}\, e^{i\vec{k}'.\vec{r}}\, dV$$

$$= V_o \sum_k \rho(\vec{k})\rho(-\vec{k}) \; . \tag{43}$$

Similarly,

$$\int \delta T^2 dV = V_o \sum_k T(\vec{k})T(-\vec{k}) \tag{44}$$

$$\int \delta T\delta Z dV = V_o \sum_k T(\vec{k})Z(-\vec{k}) = V_o \sum_k T(-\vec{k})Z(\vec{k}) \; . \tag{45}$$

Therefore

$$R_{min} \simeq V_o \sum_{k>0} \{\frac{\rho_o c_V}{T_o} T(\vec{k})T(-\vec{k}) + \frac{B_T}{\rho_o^2} \rho(\vec{k})\rho(-\vec{k}) + \rho_o(\frac{\partial \xi}{\partial Z})_{T,\rho} \times Z(\vec{k})Z(-\vec{k}) + 2\, \rho_o(\frac{\partial S}{\partial Z})_{T,\rho} T(\vec{k})Z(-\vec{k})\} \; . \tag{46}$$

Now from (42), we have

$$\rho^*(\vec{k}) = \rho(-\vec{k}) \text{ etc.} \tag{47}$$

Let us define

$$\rho(\vec{k}) = \rho_1(\vec{k}) + i\rho_2(\vec{k}) \text{ etc.} \tag{48}$$

Therefore

$$\rho(-\vec{k}) = \rho_1(\vec{k}) - i\rho_2(\vec{k}) \tag{49}$$

$$\sum_k \rho(\vec{k})\rho(-\vec{k}) = \sum_k (\rho_1^2 + \rho_2^2) \ . \tag{50}$$

From (45), we have

$$\sum_k (T_1Z_1 + T_2Z_2) + i \sum_k (T_2Z_1 - T_1Z_2)$$

$$= \sum_k (T_1Z_1 + T_2Z_2) - i \sum_k (T_2Z_1 - T_1Z_2) \ .$$

Hence $\sum_k (T_2Z_1 - T_1Z_2) = 0$. $\quad$ (51)

Therefore $\sum_k T(\vec{k})Z(-\vec{k}) = \sum_k (T_1Z_1 + T_2Z_2)$. $\quad$ (52)

Hence (46) becomes

$$R_{min} \simeq V_o \sum_{k>0} \sum_{i,=1,2} \{\frac{\rho_o c_V}{T_o} T_i^2 + \frac{B_T}{\rho_o^2}\rho_i^2 + \rho_o(\frac{\partial \xi}{\partial Z})_{T,\rho} Z_i^2$$

$$+ 2\rho_o(\frac{\partial S}{\partial Z})_{T,\rho} T_iZ_i\} \ . \tag{53}$$

From (53), we can conclude that quantities with the subscripts 1 and 2 are statistically independent. That is

$$< \rho_1\rho_2 > = <T_1T_2> = < T_1Z_2 > = 0 \text{ etc.} \tag{54}$$

Also, since the i=1 case involve the same coefficients as the i=2, we have

$$< \rho_1^2> = < \rho_2^2> \ , \ < T_1 Z_1> = < T_2 Z_2> \ \text{etc.} \tag{55}$$

Using (55) and (56), we have

$$\begin{aligned} &< \rho(\vec{k})\rho(-\vec{k})> = 2 < \rho_1^2 > \\ &< \rho(\vec{k})\rho(\vec{k})> = 0 \\ &< T(\vec{k})Z(-\vec{k})> = 2< T_1 Z_1> \\ &< T(\vec{k})Z(\vec{k})> = 0 \quad . \end{aligned} \tag{56}$$

Making use of (9)-15) and (56), we have

$$< \rho(\vec{k})\rho(-\vec{k})> = \frac{1}{\rho_o V_o} \{\frac{\rho_o^3 k_B T_o}{B_T}\} = \frac{\rho_o^2 k_B T_o}{V_o B_T} \tag{57}$$

$$\begin{aligned} &< T(\vec{k})\rho(-\vec{k})> =< Z(\vec{k})\rho(-\vec{k})> = 0 \\ &< T(\vec{k})T(-\vec{k})> = \frac{k_B T_o^2}{\rho_o V_o c_V^\infty} \\ &< Z(\vec{k})Z(-\vec{k})> = \frac{k_B T_o}{\rho_o V_o} (\frac{\partial Z}{\partial \xi})_{S,\rho} \\ &< Z(\vec{k})T(-\vec{k})> = - \frac{k_B T_o}{c_V^\infty} (\frac{\partial S}{\partial \xi})_{T,\rho} . \end{aligned} \tag{58}$$

One can obtain all the other fluctuations quantities from Table 2 by putting V_o to be ρ_o^{-1} there and then divide by $\rho_o V_o$. The results are summarized in Table 3.

Table 3. Mean square fluctuations of the Fourier transforms of the various thermodynamic quantities. (To read, see Table 2.)

Fluctuations of Fourier Components	$S(\vec{k})$	$T(\vec{k})$	$P(\vec{k})$	$\rho(\vec{k})$	$Z(\vec{k})$	$\xi(\vec{k})$
$S(-\vec{k})$	$\frac{k_B c_P}{\rho_o V_o}$	$\frac{k_B T_o}{\rho_o V_o}$	0	$-\frac{k_B T_o \beta}{V_o}$	0	$-k_B c_P \times (\frac{\partial T}{\partial Z})_{S,P}$
$T(-\vec{k})$	$\frac{k_B T_o}{\rho_o V_o}$	$\frac{k_B T_o}{\rho_o V_o c_V^\infty}$	$\frac{\beta^\infty B_T^\infty k_B T_o^2}{\rho_o V_o c_V^\infty}$	0	$-\frac{k_B T_o^2}{\rho_o V_o c_V^\infty} \times (\frac{\partial S}{\partial \xi})_{T,\rho}$	0
$P(\vec{k})$	0	$\frac{\beta^\infty B_T^\infty k_B T_o^2}{\rho_o V_o c_V^\infty}$	$\frac{k_B T_o B_S^\infty}{V_o}$	$\frac{\rho_o k_B T_o}{V_o}$	$-\frac{k_B T_o B_S^\infty}{\rho_o^2 V_o} \times (\frac{\partial \rho}{\partial \xi})_{S,P}$	0
$\rho(-\vec{k})$	$-\frac{k_B T_o \beta}{V_o}$	0	$\frac{\rho_o k_B T_o}{V_o}$	$\frac{\rho_o^2 k_B T_o}{V_o B_T}$	0	$\frac{k_B T_o}{B_T} \times (\frac{\partial \xi}{\partial Z})_{T,\rho}$
$Z(-\vec{k})$	0	$-\frac{k_B T_o^2}{\rho_o V_o c_V^\infty} \times (\frac{\partial S}{\partial \xi})_{T,\rho}$	$-\frac{k_B T_o B_S^\infty}{\rho_o^2 V_o} \times (\frac{\partial \rho}{\partial \xi})_{S,P}$	0	$\frac{k_B T_o}{\rho_o V_o} (\frac{\partial Z}{\partial \xi})_{S,\rho}$	$\frac{k_B T_o}{\rho_o V_o}$
$\xi(-\vec{k})$	$-\frac{k_B c_P}{\rho_o V_o^2} \times (\frac{\partial T}{\partial Z})_{S,P}$	0	0	$\frac{k_B T_o}{V_o B_T} \times (\frac{\partial \xi}{\partial Z})_{T,\rho}$	$\frac{k_B T_o}{\rho_o V_o}$	$\frac{k_B T_o}{\rho_o V_o} \times (\frac{\partial \xi}{\partial Z})_{T,P}$

When a system is close to the critical point, the quantities κ_T and c_P, and hence the fluctuations in ρ and S become anomalously large. Therefore the condition for statistical independence of neighbouring subvolumes is more difficult to satisfy. For small fluctuations, the homogeneity of the system is not too much destroyed so that one can neglect the spatial derivatives of the inhomogeneity distribution. In the language of Fourier transform, this is equivalent to saying that the predominant components [see Eq. (42)] have small k. If the inhomogeneity becomes pronounced one cannot neglect the spatial derivatives of the fluctuations, and must include them as corrections. For an isotropic medium, the first order correction to the calculation of mean square fluctuation of ρ must be of the form $(\nabla\delta\rho)^2$ [29]. The other possible form of $\nabla^2\delta\rho$ when integrated represents an irrelevant surface effect, while a form like $\delta\rho\nabla^2\delta\rho$ can be transformed into a term involving $(\nabla\delta\rho)^2$ plus another irrelevant surface term. Because of the presence of the terms $(\nabla\delta\rho)^2$, the evaluation of $\langle\delta\rho^2\rangle$ is difficult and depends on the shape of the region also. The calculation of the fluctuations of the Fourier components is easily done and is of importance for the light scattering problem. Since the fluctuations of ρ and those of T and Z are statistically independent, we shall choose these as independent variables and can in the following omit the T and Z description, or assume that they are constant. In this case, we have from (40),

$$R_{min} \simeq \tfrac{1}{2} \int \left[\frac{B_T}{\rho_o^2}\, \delta\rho^2 + \frac{b}{\rho_o^2}\, (\nabla\delta\rho)^2\right] dV \ , \tag{59}$$

where b is a positive constant in order that the free energy F is a minimum at $\rho=\rho_o$, where $\Delta F = R_{min}$. Using (42) and the procedures in obtaining (57), we have

$$< \rho(k)\rho(-k)> = \frac{\rho_o^2 k_B T_o}{V(B_T+bk^2)} \ , \tag{60}$$

where V is the scattering volume.

In Brillouin scattering, k^2 can be obtained from (1-32).

A-4 Fluctuations of Fourier components for Multiple Ordering Processes

If there are present in the liquid n ordering processes described by ordering parameter $\xi_1, \ldots \xi_n$ corresponding to ordering forces $Z_1 \ldots Z_n$, then Eq. (38) is generalized to

$$R_{min} = \tfrac{1}{2} \int \rho_o(\delta U - T_o\delta S + P_o\delta V - \sum_{i=1}^{n} Z_i\ \delta\xi_i)\ dV \ . \tag{61}$$

If we take ρ, T, $Z_1 \ldots Z_n$ as independent variables, (61) becomes

$$R_{min} \simeq \tfrac{1}{2}\,\rho_o \int \Big[\frac{c_V}{T_o}\,\delta T^2 + \frac{B_T}{\rho_o^3}\delta\rho^2 + \sum_i \Big(\frac{\partial\,\xi_i}{\partial\,Z_i}\Big)_{T,\rho}\delta Z_i^2$$

$$+\ 2\sum_i \Big(\frac{\partial\,S}{\partial\,Z_i}\Big)_{T,\rho}\ \delta T\delta Z_i\Big]\ dV\quad . \tag{62}$$

If we define $\rho(\vec{k})$, $T(\vec{k})$ and $Z_i(\vec{k})$ etc. as in (41), and follow the same procedure as before, we get

$$< \rho(\vec{k})\rho(-\vec{k})> \ = \frac{\rho_o^2 k_B T_o}{V\ B_T}$$

$$< T(\vec{k})T(-\vec{k})> \ = \frac{k_B T_o^2}{\rho_o V c_V^{\infty}}$$

$$< Z_i(\vec{k})Z_i(-\vec{k})> \ = \frac{k_B T_o}{\rho_o V}\Big(\frac{\partial\,Z_i}{\partial\,\xi_i}\Big)_{S,\rho}$$

$$< Z_i(\vec{k})Z_j(-\vec{k})> \ = 0 \text{ for } \ i \neq j$$

$$< Z_i(\vec{k})\rho(-\vec{k})> \ = 0$$

$$< T(\vec{k})\rho(-\vec{k})\ > \ = 0 \text{ etc.} \tag{63}$$

The other fluctuation quantities can be obtained easily.

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List of Important Symbols

b = bulk viscosity
B_S = adiabatic bulk modulus
B_T = isothermal bulk modulus
c = velocity of light in vacuum
c_P = isobaric specific heat
c_V = isochoric specific heat
G^∞ = shear modulus at infinite frequency
$2I_B$ = integrated intensity of the Brillouin components
I_c = integrated intensity of the Rayleigh component
k = wave number of hypersonic sound wave
k_B = Boltzmann constant
$n(\vec{r},t)$ = number density of the scattering medium
T = temperature
v = velocity of temporally absorbed sound wave
v' = velocity of spatially absorbed sound wave
v_o = sound velocity at zero frequency
v^∞ = sound velocity at infinite frequency
v_B = sound velocity measured from the Doppler shifted Brillouin components
v_d = $v_o\ k\ \tau_{SV}$
x_1 = $v_o\ k\ \tau_{TV}$
x_2 = $v_o\ k\ \tau_\eta$
x_η = $v_o\ k\ \tau_\eta$

z = v^2/v_o^2

z' = v'^2/v_o^2

z_B = v_B^2/v_o^2

z_∞ = B_S^∞/B_S

Z = order force

α = This symbol has been used to denote different quantities, namely the polarizability [Chap. 1], the sound absorption per wavelength [Chap.2] and a dimensionless quantity involving the thermal conductivity [Chaps. 5, 7]

α_e = average polarizability of the molecules in the scattering medium

β = coefficient of volume expansion

Γ = sound absorption per second

ε = dielectric constant

η = shear viscosity

γ = specific heat ratio

κ_o = wave number of the incident light

κ' = wave number of the scattered light

κ_S = adiabatic compressibility

κ_T = isothermal compressibility

χ = thermal conductivity

λ = wavelength of the incident light

ω = angular frequency of the hypersonic sound waves

Ω_o = angular frequency of the incident light

Ω = angular frequency of the scattered light

$\rho(\vec{r},t)$ = density of the scattering medium

τ_η = shear relaxation time

θ $\equiv$ $\Gamma/v_o k$. It also denotes the scattering angle.