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RAYLEIGH-BRILLOUIN SCATTERING AND STRUCTURAL RELAXATION OF A VI--ETC(U)

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Rayleigh - Brillouin Scattering and Structural
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Abstract

The linear response theory using a complete set of dynamic variables involving density, velocity and energy fluctuations is used to analyze the Rayleigh-Brillouin spectrum of a viscoelastic liquid. An exact equation including the effect of structural relaxation has been obtained. The result is discussed in the fast and slow relaxation limits. In the former case, the Rayleigh-Brillouin spectrum is identical to that predicted by the classical hydrodynamic equations, whereas in the latter case a new structural central peak is found, in addition to the anomalous dispersion and relaxation effects present in the frequency and linewidth data associated with the Brillouin peak. The evolution of structural relaxation and its effect on the entire Rayleigh-Brillouin spectrum is described. The structural central peak is most pronounced with the frequency dispersion and the linewidth maximum are present. The theoretical result has been used to calculate the Rayleigh-Brillouin spectra of polypropylene glycol at various temperatures. The results of the frequency shift, the spectral linewidth and the Landau-Placzek ratio are in good agreement with the experiment.

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I. Introduction

The study of molecular dynamics of a viscoelastic liquid using the Rayleigh-Brillouin scattering technique is of current research interest. Rayleigh-Brillouin scattering arises from density fluctuations and the scattering spectrum contains information about the translational motion of an ensemble of molecules. In a viscous molecular liquid consisting of polymeric molecules, interactions between molecules as well as between segments of the same molecule play a very important role in the Rayleigh-Brillouin spectrum. In such a system, a considerable frequency dispersion as well as a maximum in the linewidth of the Brillouin doublet are known to occur.¹ Accompanied with the frequency dispersion and linewidth anomaly, one also finds significantly more intensity distributed in the region between the unshifted Rayleigh and Brillouin peaks than that found in a simple molecular liquid. These experimental results cannot be accounted for in terms of the classical hydrodynamic theory of simple fluids.²

To explain the anomalous sound dispersion and attenuation maximum of a highly viscous liquid, Isakovich and Chaban³ have provided a phenomenological theory in which the viscous liquid is modeled as a "micro-inhomogeneous medium" consisting of several regions. The occurrence of diffusion and energy exchange mechanisms between different regions of the medium is shown to be responsible for the attenuation of the hypersonic wave. Although this theory can qualitatively account for the dispersion and attenuation phenomena of the hypersonic wave in polymeric liquids,⁴ it does not have a satisfactory statistical mechanics foundation.

We have recently used the linear response theory to analyze the Brillouin scattering results of bulk liquid polypropylene glycols (PPG)

and polyethylene glycols (PEG). The analysis was carried out using a two coupled variables (density and velocity) theory, and the theoretical result was found capable of giving a satisfactory interpretation of the frequency dispersion and linewidth data in both PPG⁵ and PEG.⁶ It was shown that the second moment of the intersegmental interaction potential and its associated relaxation dynamics are responsible for the anomaly found in the linewidth and frequency shift of the Brillouin peak. The theoretical results cannot, however, account for the entire Rayleigh-Brillouin spectral distribution, due to the fact that energy fluctuation is not included in the theoretical analysis.

In this paper, we report the result of a complete theoretical analysis of the Rayleigh-Brillouin scattering spectrum using the linear response theory. This theoretical result includes the energy fluctuation and is applicable not only to the frequency shift and linewidth data of a polymeric liquid but also to the intensity ratio between the Rayleigh and Brillouin components. We also show how the structural relaxation mechanism can give rise to a new central peak. This new central peak is due to coupling between the translation and the structural rearrangement motion in a viscoelastic liquid. We draw an analogy between this dynamic structural central peak and the central peak associated with the structural phase transition in ferroelectrics and the translation rotation coupling in orientationally disordered solids. We show how the central peak disappears in the limit of fast modulation.

II. Theory

For a viscoelastic liquid made up of a collection of identical scattering elements, the isotropic part of the Rayleigh-Brillouin spectrum observed at scattering angle θ is determined by the q th mode of

the Fourier transform of the time correlation function of density fluctuations given by

$$C_{\rho\rho}(q,t) = \langle \delta\rho(q,t) \delta\rho^*(q,0) \rangle \quad (1)$$

where $\delta\rho(q,t)$ is the q th mode of the fluctuation of density, q being the scattering vector whose amplitude is given by $|q| = \frac{4n\pi}{\lambda_1} \sin \frac{\theta}{2}$. Here λ_1 is the wavelength of the incident light and n being the index of refraction of the liquid. In this section, we shall study the density fluctuation in viscoelastic liquids by calculating the q th mode of the density fluctuation spectrum.

For an isotropic fluid system, it is easy to see by symmetry considerations that density ($\delta\rho$), velocity (V) and energy ($\delta\epsilon$) fluctuations form a set of three dynamic variables, which do not couple to any other variables. These are given respectively by

$$\delta\rho = \sum_j e^{iqz_j} \quad (2)$$

$$V = \sum_j \dot{z}_j e^{iqz_j} \quad (3)$$

$$\delta\epsilon = \sum_j \frac{1}{2} m_j (\dot{x}_j^2 + \dot{y}_j^2 + \dot{z}_j^2) + \frac{1}{2} \sum_{i \neq j} U_{ij} e^{iqz_j} \quad (4)$$

where in Eqs. (2)-(4) the direction of the scattering vector q is chosen to be along the z -direction. x_j , y_j and z_j are the coordinates of the j th scatterer. In a polymeric fluid these can be regarded as the coordinates of the j th segment of a polymer chain. V is the component of velocity in the direction of q , as the transverse components will not be coupled to the density fluctuation and thus have no effect at all on the polarized Rayleigh-Brillouin spectrum of an isotropic fluid system.⁷ U_{ij} is the interaction potential between scatterers i and j . In Eqs. (2)-(4), the q dependence in $\delta\rho$, V and $\delta\epsilon$ is not written out explicitly.

The set of variables defined in Eqs. (2)-(4) ($\delta\rho$, V , $\delta\epsilon$) gives rise to the collective motion of a sound wave. The dynamic behavior of the collective variables are mostly conveniently described by relaxation functions determined by variables not included in $\delta\rho$, V , and $\delta\epsilon$. To analyze the effect of relaxation on $\delta\rho$, V and $\delta\epsilon$, we use the Zwanzig-Mori formalism.⁸ We shall show that the final equations obtained are capable of describing the sound dispersion and attenuation behavior in a polymeric liquid. We shall also show that in the limit of fast relaxation the equations reduce to the usual hydrodynamic results.

A) Dynamic equations

We start from the assumption that for the time scale of interest, the dynamics of the system is governed by the evolution of the set of secular variables $\{\delta\rho, V, \delta\epsilon\}$. We use the Zwanzig-Mori projection operator technique to calculate the motion of secular variables. Before proceeding, we note that the quantity $\langle\delta\epsilon\delta\rho^*\rangle$ is non-zero. Therefore, we use, instead of $\delta\rho$, V and $\delta\epsilon$, a set of orthonormal variables \underline{A} given by

$$\underline{A} = \begin{pmatrix} \xi_1 \\ \xi_2 \\ \xi_3 \end{pmatrix} \quad (5)$$

where

$$\xi_1 = \delta\rho / \langle|\delta\rho|^2\rangle^{1/2} \quad (6)$$

$$\xi_2 = V / \langle|V|^2\rangle^{1/2} \quad (7)$$

$$\xi_3 = \left[\frac{\delta\epsilon}{\langle|\delta\epsilon|^2\rangle^{1/2}} - n\xi_1 \right] \frac{1}{\sqrt{1-n^2}} \quad (8)$$

and

$$n = \frac{\langle \delta \epsilon \delta \rho^* \rangle}{\langle |\delta \epsilon|^2 \rangle^{1/2} \langle |\delta \rho|^2 \rangle^{1/2}} \quad (9)$$

From the definition given above, one has $\langle \underline{A} \underline{A}^+ \rangle = \underline{I}$, where \underline{I} is a 3×3 unit matrix. The angular brackets indicate an ensemble average. We show in Appendix I that if local equilibrium is assumed ξ_3 is proportional to the temperature fluctuation.

For the column vector \underline{A} of dynamic variables, the equation of motion is given formally by the Liouville equation

$$\frac{\partial}{\partial t} \underline{A}(t) = i \underline{L} \underline{A}(t) \quad (10)$$

where \underline{L} is the classical Liouville operator governing the time evolution of $\underline{A}(t)$. While it is straightforward to write down a formal expression for \underline{L} in terms of the kinetic and potential energy operators of the system, in practice this is seldom done for a complex molecular system such as a polymer, due to its large number of internal degrees of freedom and the intermolecular and intramolecular potential functions. For the present work it is only necessary to utilize the formalistic symmetry properties of the Liouville operator such as time reversal, reflection and translation symmetry. In its formal definition the Liouville operator is self-adjoint.

Following the well known procedure the equation of motion for $\underline{A}(t)$ can be shown to follow a generalized Langevin equation,⁸

$$\frac{\partial}{\partial t} \underline{A}(t) = i \underline{\Omega} \underline{A}(t) - \int_0^t d\tau \underline{K}(\tau) \cdot \underline{A}(t-\tau) + \underline{F}(t) \quad (11)$$

where the frequency matrix is given by

$$\underline{\Omega} = \langle (\underline{L}\underline{A})\underline{A}^+ \rangle, \quad (12)$$

other quantities are given by

$$\underline{K}(\tau) = \langle \underline{F}(\tau)\underline{F}^+ \rangle \quad (13)$$

$$\underline{F}(\tau) = e^{iQL\tau}\underline{F} \quad (14)$$

$$\underline{F} = iQL\underline{A} \quad (15)$$

where $Q = (1-P)$, P being the projection operator defined as

$$PG = \langle \underline{G}\underline{A}^+ \rangle \langle \underline{A}\underline{A}^+ \rangle^{-1} \underline{A} \quad (16)$$

In the small q limit, Eq. (14) can be approximated by⁷

$$\underline{F}(\tau) = e^{iL\tau}\underline{F} \quad (17)$$

Substituting Eq. (5) into Eq. (12), and with the help of Eqs. (6)-(8), we obtain the frequency matrix

$$\underline{\Omega} = \begin{pmatrix} 0 & \omega_T & 0 \\ \omega_T & 0 & S \\ 0 & S^* & 0 \end{pmatrix} \quad (18)$$

where

$$\omega_T = q \left(\frac{NkT}{m} \right)^{1/2} \langle |\delta\rho|^2 \rangle^{-1/2} \quad (19)$$

Equation (19) reduces to the well known result $q(\rho m \chi_T)^{-1/2}$ in the small q limit. Here χ_T is isothermal compressibility.

The parameter S is given by

$$S = \langle (L\xi_2)\xi_3^* \rangle = \frac{1}{\sqrt{1-n^2}} \left[\frac{\langle (LV)\delta\epsilon^* \rangle}{\langle |V|^2 \rangle^{\frac{1}{2}} \langle |\delta\epsilon|^2 \rangle^{\frac{1}{2}}} - n\omega_T \right] \quad (20)$$

and is real only in small q limit. We shall show shortly that S is related to the difference between the isothermal and adiabatic sound frequencies.

The dissipation part can be calculated by the following. According to Eq. (15), one can readily find that

$$\underline{F} = Q i L \underline{A} = i L \underline{A} - i \Omega \underline{A} = \begin{pmatrix} 0 \\ f_2 \\ f_3 \end{pmatrix} \quad (21)$$

where

$$f_2 = i L \xi_2 - i \omega_T \xi_1 - i S \xi_3 \quad (22)$$

and

$$f_3 = i L \xi_3 - i S^* \xi_2 \quad (23)$$

Thus the memory function matrix $\underline{K}(\tau)$ has the general form,

$$\underline{K}(\tau) = \begin{pmatrix} 0 & 0 & 0 \\ 0 & K_{22}(\tau) & 0 \\ 0 & 0 & K_{33}(\tau) \end{pmatrix} \quad (24)$$

where $K_{22}(\tau) = \langle f_2(\tau) f_2^* \rangle$ and $K_{33}(\tau) = \langle f_3(\tau) f_3^* \rangle$. $K_{23}(\tau)$ and $K_{32}(\tau)$ vanish at $\tau=0$ and are assumed to be negligible at finite τ .

Equation (11) together with the frequency matrix given in Eq. (18) and the memory function matrix given in Eq. (24) can be solved by the Laplace transform technique. Taking the Laplace transform on both sides of Eq. (11), we obtain,

$$\underline{X}(z) \underline{A}(z) = [z \underline{I} - i \underline{\Omega} + \underline{K}(z)] \underline{A}(z) = \underline{A}(0) + \underline{F}(z) \quad (25)$$

where $\underline{A}(z)$ and $\underline{K}(z)$ are the Laplace transforms of $\underline{A}(t)$ and $\underline{K}(t)$, respectively. The expression for $\underline{X}(z)$ is given by

$$\underline{X}(z) = \begin{pmatrix} z & -i\omega_T & 0 \\ -i\omega_T & z+K_{22}(z) & -iS \\ 0 & -iS^* & z+K_{33}(z) \end{pmatrix} \quad (26)$$

The Rayleigh-Brillouin spectral density is equal to the real part of $\langle \xi_1(z) \xi_1^* \rangle_{z=i\omega}$. Thus we only need calculate this quantity from Eq. (25). From Eq. (25) and also using the fact that $\langle F(z) \xi_1^* \rangle = 0$, we obtain after some calculation,

$$\langle \xi_1(z) \xi_1^* \rangle = \frac{1}{|X|} \{ (z+K_{22}(z))(z+K_{33}(z)) + S^2 \} \quad (27)$$

where $|X|$ is the determinant of $\underline{X}(z)$, and is given by

$$|X| = [z(z+K_{22}(z)) + \omega_T^2][z+K_{33}(z)] + zS^2 \quad (28)$$

The Rayleigh-Brillouin spectral density is thus equal to

$$\begin{aligned} I(q, \omega) &= \text{Re} \langle \xi_1(z) \xi_1^* \rangle_{z=i\omega} \\ &= \text{Re} \left\{ \frac{[z+K_{22}(z)][z+K_{33}(z)] + S^2}{[z(z+K_{22}(z)) + \omega_T^2][z+K_{33}(z)] + zS^2} \right\}_{z=i\omega} \end{aligned} \quad (29)$$

Equation (29) is the dynamic equation describing the density-density fluctuation. This equation will be used to interpret the Rayleigh-Brillouin spectra of a viscoelastic liquid in Section IV.

B) Adiabatic frequency

Before proceeding to study the property of the dynamic equation, we want to associate the quantity S with the well known physical quantity. One can relate the quantity S to adiabatic sound frequency

by diagonalizing Eq. (18). This gives rise to three eigenvalues

$$\lambda_+ = \sqrt{\omega_T^2 + S^2} = \omega_s \quad (30)$$

$$\lambda_- = -\sqrt{\omega_T^2 + S^2} = -\omega_s \quad (31)$$

$$\lambda_0 = 0 \quad (32)$$

The corresponding normalized eigenvectors are found to be

$$\phi_{\pm} = \frac{1}{\sqrt{2}} \begin{pmatrix} \frac{\omega_T}{\omega_s} \\ \pm 1 \\ \frac{S}{\omega_s} \end{pmatrix} \quad (33)$$

and

$$\phi_0 = \begin{pmatrix} \frac{S}{\omega_s} \\ 0 \\ \frac{\omega_T}{\omega_s} \end{pmatrix} \quad (34)$$

In the absence of relaxation effects, ξ_1 can be expressed in terms of ϕ_{\pm} and ϕ_0 as

$$\xi_1 = \frac{\delta\rho}{\langle |\delta\rho|^2 \rangle^{1/2}} = \frac{1}{\sqrt{2}} \left(\frac{\omega_T}{\omega_s} \phi_+ + \frac{\omega_T}{\omega_s} \phi_- + \frac{\sqrt{2}S}{\omega_s} \phi_0 \right) \quad (35)$$

The eigenvectors ϕ_+ and ϕ_- are associated with undamped acoustic waves propagated with frequency ω_s and $-\omega_s$ respectively. The third eigenvector ϕ_0 is associated with the unshifted Rayleigh central peak. The intensity of each peak is proportional to the square of the co-

efficient of the corresponding eigenvector. Thus, with the help of Eq. (35), we obtain the Landau-Placzek ratio as

$$LP = \frac{I_c}{2 I_B} = \frac{S^2}{\omega_T^2} = \frac{\omega_s^2}{\omega_T^2} - 1 \quad (36)$$

Since the Landau-Placzek ratio in the absence of relaxation is equal to $\gamma-1$, where γ is C_p/C_v , it follows immediately the result $\omega_s = \sqrt{\gamma}\omega_T$, which is the adiabatic sound frequency.

III. Effect of Relaxation

To consider the effect of relaxation we need return to Eq. (29). The resonance property of $I(q, \omega)$ depends significantly on the quantities $K_{22}(i\omega)$ and $K_{33}(i\omega)$ as well as the values of ω_T and ω_s . This can be seen by equating to zero the denominator on the right hand side of Eq. (29) after setting $z = i\omega$,

$$(i\omega)^3 + (i\omega)^2 [\lambda_2(\omega) + \lambda_3(\omega)] + i\omega[\lambda_2(\omega)\lambda_3(\omega) + \omega_s^2] + \omega_T^2\lambda_3(\omega) = 0 \quad (37)$$

where

$$\lambda_i(\omega) = K_{ii}(i\omega) = \int_0^\infty e^{-i\omega t} K_{ii}(t) dt \quad (38)$$

Because of Eq. (38), Eq. (37) is in general a complex equation of frequency and does not yield a simple solution. Nevertheless, it can be shown that in the limit of small q , the memory function is a decaying function of time and for simplicity can be approximated as

$$K_{ii}(t) = \alpha_i e^{-t/\tau_i} \quad (39)$$

where $\alpha_i = K_{ii}(0)$, and τ_i are the correlation times given by

$$\tau_i = \frac{1}{K_{ii}(0)} \int_0^{\infty} K_{ii}(t) dt \quad (40)$$

In this approximation, we obtain from Eq. (38)

$$\lambda_i = \alpha_i \frac{\tau_i}{1 + i\omega\tau_i} \quad (41)$$

Using Eq. (41), one sees that Eq. (37) is at least fourth order in ω , and it leads to a four peak structure in the Rayleigh-Brillouin spectrum. We now consider two limiting cases.

A) Fast relaxation, $1/\tau_i > \omega \approx \omega_s$

In this case λ_i becomes $\alpha_i \tau_i$ and Eq. (37) reduces to

$$(i\omega)^3 + (i\omega)^2 [\alpha_2 \tau_2 + \alpha_3 \tau_3] + (i\omega) [\alpha_2 \tau_2 \alpha_3 \tau_3 + \omega_s^2] + \omega_T^2 \alpha_3 \tau_3 = 0 \quad (42)$$

which is exactly the results obtained from the linearized equations of hydrodynamics.² Rayleigh-Brillouin scattering spectra predicted by this equation have been discussed extensively in the literature.⁷

Equation (42) has three roots: two correspond to the Brillouin side bands and one to the unshifted Rayleigh peak. For most liquids the condition $\omega_s \gg \alpha_i \tau_i$ ($i = 2, 3$) applies, and one can obtain the three roots of Eq. (42) by a perturbation technique. The results are given by

$$\omega_{\pm} = \pm \omega_s + i \frac{1}{2} \left[\left(1 - \frac{1}{\gamma}\right) \alpha_3 \tau_3 + \alpha_2 \tau_2 \right] \quad (43)$$

$$\omega_0 = + i \frac{1}{\gamma} \alpha_3 \tau_3 \quad (44)$$

Thus we note that in the fast relaxation limit, due to the large value of $1/\tau_i$ ($i = 2$ or 3) the peak frequency of the sound wave is de-

terminated by ω_s and its width by $\alpha_1 \tau_1$. The width of the unshifted Rayleigh peak is determined only by $\alpha_3 \tau_3 / \gamma$.

To give a comparison with the hydrodynamic result,⁷ one makes the following identifications:

$$\alpha_2 \tau_2 \rightarrow D_v q^2 \quad (45)$$

$$\alpha_3 \tau_3 \rightarrow \gamma D_T q^2 \quad (46)$$

where D_v and D_T are the longitudinal kinematic viscosity and the thermal diffusivity, respectively. These are related to shear viscosity (η_s), bulk viscosity (η_v) and thermal conductivity (λ) by

$$D_v = (\eta_v + \frac{4}{3} \eta_s) / m \rho_0 \quad (47)$$

$$D_T = \lambda / m \rho_0 C_p \quad (48)$$

Here the various symbols have their usual meanings.

Using the expressions for $K_{ii}(t)$ (Eqs. (22) and (23)) one can also obtain microscopic expressions for the transport coefficients. The microscopic expressions for the transport coefficients have been given in the literature. The dynamics of the density fluctuation in the fast relaxation limit was first discussed by Mori.⁹

B) Slow relaxation, $1/\tau_2 \leq \omega \approx \omega_s$

This is the relevant case for most viscous liquids, and understanding of this case is necessary for analysis of the Rayleigh-Brillouin data in polymeric liquids.

Since the dynamics of thermal conductivity processes has only a negligible effect on the relaxation behavior of the sound wave, the

frequency dependence of λ_3 can be ignored. Thus one can set

$$\lambda_3 = \alpha_3 \tau_3 \quad (49)$$

and

$$\lambda_2 = \frac{\alpha_2 \tau_2}{1 + i \omega \tau_2} \quad (50)$$

where τ_2 will be referred to as the structural relaxation time.

One further substitutes Eqs. (49) and (50) into Eq. (37) to find its solution for ω . The computer calculation of the spectrum using the exact expression, Eq. (29), has shown that α_i ($i=2,3$) is only a fraction of ω_s^2 for a polymeric liquid (see Section IV). Therefore, Eq. (37) can be solved as a perturbation of α_i/ω_s^2 . The perturbation solution of Eq. (37) to first order in α_i/ω_s^2 ($i=2,3$) gives four roots

$$\omega_1 = \frac{1}{\gamma} \alpha_3 \tau_3 = i D_T q^2 \quad (51)$$

$$\omega_{\pm} = \pm \omega_s \pm \frac{\alpha_2 \omega_s \tau_2^2}{2[1 + (\omega_s \tau_2)^2]} + \frac{i}{2[1 + (\omega_s \tau_2)^2]} \{ \alpha_2 \tau_2 + (1 - \frac{1}{\gamma})(\alpha_3 \tau_3 + \omega_s^2 \tau_2^2 \alpha_3 \tau_3) \} \quad (52)$$

$$\omega_2 = i \left[\frac{1}{\tau_2} - \frac{\alpha_2 \tau_2}{1 + \omega_s^2 \tau_2^2} \right] \quad (53)$$

One sees that the root ω_1 is identical to the unshifted Rayleigh peak given in Eq. (44), indicating that it is free from the effect of structural relaxation provided that the frequency dependence of λ_3 is ignored. The roots ω_{\pm} correspond to a high frequency doublet with resonance centered around the real part of ω_{\pm} and the width given by the imaginary part. The peak frequency as well as the linewidth of the Brillouin doublet are modified significantly by the effect of

structural relaxation. One notes that Eq. (52) reduces to Eq. (43) in the limit of $\omega_s \tau_2 \rightarrow 0$.

A new feature in this case is the presence of an additional central peak with its width given by Eq. (53). The width of this central peak is determined by the structural relaxation τ_2 and shows a frequency dependence due to its coupling to the sound wave.

The perturbation solution given in Eqs. (51)-(53) are new results. These are important for the interpretation of the Brillouin scattering spectra of viscoelastic liquids. We should remark that these roots differ from Mountain's results on thermal relaxation arising from the coupling of internal degrees of freedom of molecules to translation.¹⁰⁻¹² Mountain has shown that such a coupling gives rise to a relaxation central peak whose linewidth is given by $(v_s/v)^2 1/\tau$, where v_s and v are the low frequency adiabatic sound velocity and the sound velocity at finite frequency, respectively; τ is the thermal relaxation time. Our expression is somewhat simpler than Mountain's expression for thermal relaxation.

The Brillouin frequency and linewidth given in Eq. (52) also differ from Mountain's result. Despite the fact that Mountain deals with thermal relaxation due to coupling of the internal degrees of freedom to translation and we are concerned with structural relaxation due to coupling of internal as well as external degrees of freedom to translation, the difference between the two results is due to different methods used. In the present work a general statistical mechanical theory is employed to analyze the structural relaxation phenomena, whereas in Mountain's calculation a modified Navier-Stokes equation allowing for a frequency dependent bulk viscosity is used.

The validity of the modified hydrodynamic equation in a form given in ref. 10 is yet to be established.

It is interesting to note that structural relaxation has a significant effect on the Rayleigh-Brillouin spectrum of a polymer liquid consisting of flexible polymer chains. At high temperature the structural relaxation rate is fast compared with the frequency of the hypersonic wave and in this case the structural relaxation contributes mainly to the Brillouin doublet (Eq. (52)) through the $\alpha_2\tau_2$ term. In this case the intensity of the structural central peak is smeared out over a wide range of frequency and is not detectable (see Fig. 3A). At intermediate temperature when the structural relaxation rate $1/\tau_2$ is the order of ω_s the linewidth of the Brillouin component doublet displays a maximum. This can be demonstrated by taking the derivative of the imaginary part of Eq. (52) with respect to τ_2 and then setting the result to zero. This gives τ_2 in terms of ω_s . In this case, the hypersonic velocity displays considerable dispersion [c.f. Eq. (52)], and the linewidth of the structural central peak is approximately equal to ω_s . Thus the structural central mode contributes significantly to the intensity of the Brillouin doublet (Fig. 3B) as well as the intensity in the region between the unshifted Rayleigh and the Brillouin peaks. At low temperature, on the other hand, the structural relaxation rate is slow compared to the hypersonic frequency, but fast compared to the thermal diffusion rate; in this case the structural relaxation manifests itself as a broad line centered at the laser frequency (see Fig. 3D). Lastly at temperatures close to the glass transition temperature, the structural relaxation is very slow or nearly frozen-in, and the structural central peak

becomes very narrow and hidden under the ordinary Rayleigh diffusion peak (see Fig. 3F).

We remark finally that the central peak due to structural relaxation has a close analogy to the dynamic central peak associated with the structural phase transition in ferroelectric crystals¹² as well as with the central peak in orientationally disordered crystals which arise as a result of the dynamic coupling of translation and rotation. In fact the treatment given in the present work is closely parallel to that given in ref. 13 for dynamics of translations and rotation in molecular crystals.

C) Rayleigh-Brillouin spectral density

Using Eq. (29), we can also obtain an expression for the Rayleigh-Brillouin spectrum as a function of frequency. For this we separate $\lambda_2(\omega)$ and $\lambda_3(\omega)$ into real and imaginary parts,

$$\lambda_2(\omega) = \alpha_2'(\omega) + i\alpha_2''(\omega) \quad (54)$$

$$\lambda_3(\omega) = \alpha_3'(\omega) + i\alpha_3''(\omega) \quad (55)$$

Substituting Eqs. (54) and (55) into Eq. (29) and after carrying out some algebraic manipulations, we obtain

$$I(q, \omega) = \frac{N_1 D_1 + N_2 D_2}{D_1^2 + D_2^2} \quad (56)$$

where

$$N_1 = - \left(1 + \frac{\alpha_2''(\omega)}{\omega} \right) \left(1 + \frac{\alpha_3''(\omega)}{\omega} \right) \omega^2 + \alpha_2'(\omega) \alpha_3'(\omega) + \left(1 - \frac{1}{\gamma} \right) \omega_s^2 \quad (57)$$

$$N_2 = \omega \left[\alpha_2'(\omega) + \alpha_3'(\omega) + \frac{\alpha_2''(\omega)}{\omega} \alpha_3'(\omega) + \alpha_2'(\omega) \frac{\alpha_3''(\omega)}{\omega} \right] \quad (58)$$

$$D_1 = -\omega^2 \left[\alpha_2'(\omega) + \alpha_3'(\omega) + \frac{\alpha_2''(\omega)}{\omega} \alpha_3'(\omega) + \alpha_2'(\omega) \frac{\alpha_3''(\omega)}{\omega} \right] + \frac{\alpha_3'(\omega)}{\gamma} \omega_s^2 \quad (59)$$

$$D_2 = \omega \left[-\omega^2 \left(1 + \frac{\alpha_2''(\omega)}{\omega} \right) \left(1 + \frac{\alpha_3''(\omega)}{\omega} \right) + \omega_s^2 \left(1 + \frac{\alpha_3''(\omega)}{\omega\gamma} \right) + \alpha_2'(\omega) \alpha_3'(\omega) \right] \quad (60)$$

The detailed forms of $\alpha_2'(\omega)$, $\alpha_2''(\omega)$, $\alpha_3'(\omega)$ and $\alpha_3''(\omega)$ depend on the specific time dependence of the memory functions $K_{22}(t)$ and $K_{33}(t)$. There are techniques available to obtain the asymptotic frequency dependence of $\lambda_2(\omega)$ and $\lambda_3(\omega)$. For example if short-time dynamic processes are important in determining the memory functions, one may expand $\lambda_i(\omega)$ in a power series in ω^{-1} and calculate the moments of memory functions.¹⁴ On the other hand, if the long-time dynamic processes are important, we may expand $\lambda_i(\omega)$ in a power series in ω . However, for the purpose of illustrating the effect of structural relaxation it suffices to use here the functional forms given by Eq. (41) for the calculation of the Rayleigh-Brillouin spectrum in the entire frequency region.

In the next section, we shall apply the present theoretical results to interpret the Rayleigh-Brillouin spectrum of a highly viscous polymeric liquid such as polypropylene glycol. We shall show that the structural relaxation plays a very important role in determining $I(q, \omega)$ and in order to account for the experimental results it is very important to retain the frequency dependence in $\lambda_2(\omega)$, although the frequency dependence of $\lambda_3(\omega)$ is unimportant. In the subsequent section we suppress the frequency dependence of λ_3 and equate it to

$$\gamma D_T q^2.$$

IV. Comparison With Experimental Results

We now use Eq. (56) together with Eqs. (57)-(60) and Eq. (41) and a least squares fitting procedure to calculate the Rayleigh-Brillouin spectrum, using the parameters suitable for polypropylene glycol (PPG). The data considered are the frequency shift, linewidth and the Landau-Placzek ratio as a function of temperature.

For the comparison we first use a trial and error procedure to compute the spectrum at high temperature such that the theoretical spectrum fits the measured one. This gives a set of reference data points needed for subsequent calculations of the theoretical spectra at other temperatures.

The reference data set consists of ω_s , τ_2 , α_2 and D_T appropriate for the high temperature (400 K) spectrum of PPG M.W. 425. To obtain results for the spectra at other temperatures, we assume that τ_2 has an Arrhenius temperature dependence

$$\tau_2 = \tau_2^\circ \exp(E_a/kT) \quad (61)$$

This assumption is justified from the experimental results for PPG.⁴ Thus instead of τ_2 we replace it by τ_2° and E_a for calculating the results at other temperatures.

Since accurate experimental data for the frequency shift (ω_B), linewidth (Γ) and intensity are available for PPG-425,¹ we have found that the following least squares fitting procedure is most economical in computer time. We used Eq. (56) to obtain theoretical values for ω_B and Γ and then compared with the observed ω_B and Γ until the

standard deviation (in the least squares sense) between the experimental and theoretical values are simultaneously minimized. This procedure gives a tentative set of parameters ω_s , τ_2° , E_a , α_2 and D_T , which are consistent with the observed frequency and linewidth values. To improve the theoretical fit, we calculate the intensity and compare the results with the experimental data. This is accomplished by a fitting cycle to check the self-consistency of all experimental data available. In cycle 1, we use the best values parameters ω_s , τ_2° , E_a , α_2 and D_T . This set gives a good fit to all values of ω_B and Γ , but it may not fit the intensity properly. The set of parameters is then varied to generate the best integrated intensity results for Rayleigh and Brillouin peaks. In this process, a new set of parameters are generated to fit the frequency and linewidth. The cycle is repeated until the set of parameters fits simultaneously all of the ω_B , Γ and intensity results.

In the process of curve fitting, we have found that the intensity of the central Rayleigh component is affected significantly by the value of D_T . Furthermore, we have also found that the values obtained for D_T can be correlated with an Arrhenius equation given by

$$D_T = D_T^\circ e^{-E_t^\circ/kT} \quad (62)$$

with $D_T^\circ = 0.98(\text{GHz})/q^2$ and $E_t^\circ = 3.16 \text{ kcal/mole}$. This gives the value of $\gamma D_T q^2$ equal to 4.9 MHz at 300 K. The theoretical fits to the experimental data of ω_B and Γ are also improved if the temperature dependence of ω_s is allowed. This is expected as the adiabatic sound frequency is expected to decrease with increasing temperature. Thus for convenience we assume

$$\omega_s = \omega_s^\circ (1 - mT) \quad (63)$$

The best values of the parameters are $\omega_s^0 = 11$ GHz and $m = 0.0017$ K⁻¹. Using these we obtain $E_a = 4.4$ kcal/mole, $\tau_2^0 = 2.36 \times 10^{-14}$ sec and $\alpha_2 = 0.438 \omega_s^2$ for the best fit. α_2 is fairly insensitive to the temperature change. We have tried other temperature dependences for ω_s and have also obtained good fits to both ω_B and Γ , but the results obtained for E_a differ within 15% at the most. This is about the experimental error involved in determining E_a . With all of the parameters available, we have calculated the ω_B and Γ values as a function of temperature. The results are shown in Fig. 1, together with the experimental values for comparison. The agreement is quite good. The slight deviation for the range between 300 and 350 K is due to the assumed simple form of Eq. (63). The calculated Landau-Placzek values for PPG-425 for the temperature range between 185 and 400 K are shown in Fig. 2, together with the experimental results.

Due to the presence of the structural relaxation, a few words about the determination of the Landau-Placzek ratio are in order. In Fig. 2, the calculated intensity ratio excludes the intensity contribution from the structural central peak. While this is easily done theoretically, it is difficult to accomplish experimentally, especially in the temperature region where the structural relaxation is most pronounced. Efforts were made to minimize the contribution from the structural relaxation in determining the accurate Landau-Placzek ratio. This was done by first integrating the Brillouin intensity beyond the peak frequency. The total Brillouin intensity of each peak is assumed to be twice this value. This thus neglects a small correction due to lineshape asymmetry, and due to the intensity at the wing from the structural central peak. The error arising from this procedure

is insignificant at both high and low temperatures. However, in the temperature range where the structural relaxation is most significant the error is somewhat larger. The Rayleigh intensity was determined by first extrapolating the wing of the Rayleigh peak to the baseline and then integrating the intensity. This tends to over-estimate the intensity by including a small contribution due to the structural central peak, but the error is believed to be small in this case. The Landau-Placzek ratio data determined this way are thus more reliable than those reported in ref. 1. One notes in Fig. 2 that the agreement between theoretical and experimental results is rather good. The larger discrepancy in the temperature range between 220 and 300 K is presumably due to the experimental difficulty in separating accurately the Rayleigh and the Brillouin intensities from the complete experimental spectra.

Using the obtained best set of parameters appropriate for PPG-425, we have then computed the Brillouin-Rayleigh spectra using Eq. (56), together with Eqs. (57)-(60) and Eqs. (49) and (50). Six representative theoretical spectra at 400, 350, 310, 280, 240 and 200 K are shown in Fig. 3A-F. These spectra clearly demonstrate the evolution of the effect of structural relaxation on the Rayleigh-Brillouin spectrum. These spectra when convoluted with the instrumental function are in good agreement with the observed spectra, thus indicating that the present theory is adequate in interpreting the Rayleigh-Brillouin scattering of polymeric liquids in which the structural relaxation plays a very important role. In Fig. 3, one notes that while the width of the Brillouin doublet increases with decreasing temperature between 400 and 310 K, there is an increase

in the intensity in the region between the Rayleigh and the Brillouin peaks. This is associated with the central peak due to structural relaxation, similar to the Mountain peak observed in simple molecular liquids.^{15,16} However, as the temperature is decreased further, the Brillouin peaks narrow and the structural central peak becomes gradually localized to the wing area of the thermal diffusion Rayleigh peak. The behavior of the structural central peak is remarkably sensitive to the temperature variation.

V. Summary and Conclusion

We have used the linear response theory to analyze the Rayleigh-Brillouin scattering spectrum of a viscoelastic liquid. The theory includes a complete set of dynamic variables involving density, velocity and energy fluctuations. An exact equation including the effect of structural relaxation has been obtained. In the fast relaxation limit it is shown that the Rayleigh-Brillouin scattering is identical to that predicted by the classical hydrodynamic equation. New results are obtained for the slow relaxation case. In this case it is shown that in addition to the unshifted Rayleigh peak a new central peak is also present. This new peak is due to dynamic coupling of the translational motions of the scattering particles with collective structural relaxation, in analogy to the Mountain peak which arises from the coupling of translation to intramolecular vibration of simple molecules. Our theoretical results for the Brillouin peak and the central peak linewidth differ from those obtained by Mountain in the case of thermal relaxation. Mountain's calculation is based upon modified hydrodynamic equations and ours is

in terms of the generalized Langevin equation derived by using Zwanzig-Mori's projection operator technique. The structural central peak considered here is analogous to the dynamic central peak associated with the phase transition in solids.

We have described the evolution of structural relaxation and its effect on the Rayleigh-Brillouin spectrum. The structural central peak is most pronounced when the frequency dispersion and the linewidth maximum are present. We have also used the theoretical result to calculate the Brillouin frequency shift, spectral linewidth and the Landau-Placzek ratio as well as the entire Rayleigh Brillouin spectrum as a function of temperature. We show that the theory including structural relaxation gives a good fit to the experimental results of polypropylene glycol.

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Appendix

We show here that the dynamic variable ξ_3 defined in Eq. (8) in the text is proportional to the temperature fluctuation.

Since $\delta\rho(\underline{q})$ and $\delta\epsilon(\underline{q})$ are related to $\delta\rho(\underline{r})$ and $\delta\epsilon(\underline{r})$ by⁷

$$\delta\rho(\underline{q}) = \int_V \delta\rho(\underline{r}) e^{i\underline{q}\cdot\underline{r}} d^3r \quad (\text{A-1})$$

and

$$\delta\epsilon(\underline{q}) = \int_V \delta\epsilon(\underline{r}) e^{i\underline{q}\cdot\underline{r}} d^3r \quad (\text{A-2})$$

where $\delta\rho(\underline{r})$ and $\delta\epsilon(\underline{r})$ are respectively the fluctuations in number density and energy density.

If the system under consideration is in local equilibrium, then from the first law of thermodynamics, we have

$$\delta\epsilon = T_0 \delta s + \left(\frac{\epsilon_0 + p_0}{\rho_0} \right) \delta\rho \quad (\text{A-3})$$

where T_0 , ρ_0 , ϵ_0 and p_0 are respectively the temperature, number density, energy density and pressure at equilibrium. $\delta s = \delta S/V$, V being the volume and δs the entropy fluctuation per unit volume.

Using thermodynamics, one also has

$$\delta s = - \frac{\alpha}{\rho_0 \chi_T} \delta\rho + \frac{m\rho_0 C_V}{T_0} \delta T \quad (\text{A-4})$$

$\delta\rho$ and δT are independent thermodynamic variables so that $\langle \delta\rho \delta T \rangle = 0$.¹⁷

Substituting Eq. (A-4) into Eq. (A-3), we obtain

$$\delta\epsilon = \left[\left(\frac{\epsilon_0 + p_0}{\rho_0} \right) - \frac{\alpha T_0}{\rho_0 \chi_T} \right] \delta\rho + m\rho_0 C_V \delta T \quad (\text{A-5})$$

and

$$\langle \delta \epsilon \delta \rho \rangle = \left[\left(\frac{\epsilon_0 + p_0}{\rho_0} \right) - \frac{\alpha T_0}{\rho_0 \chi_T} \right] \langle (\delta \rho)^2 \rangle \quad (\text{A-6})$$

After establishing Eq. (A-6), we consider ξ_3 (Eq. (8))

$$\xi_3 = \left(\frac{1}{\sqrt{1-n^2}} \right) \frac{1}{\langle |\delta \epsilon(\underline{q})|^2 \rangle^{\frac{1}{2}}} \left\{ \delta \epsilon(\underline{q}) - \frac{1}{\langle |\delta \rho|^2 \rangle} \langle \delta \epsilon(\underline{q}) \delta \rho^*(\underline{q}) \rangle \delta \rho(\underline{q}) \right\} \quad (\text{A-7})$$

Using Eqs. (A-1) and (A-2), we can write

$$\begin{aligned} & \langle \delta \epsilon(\underline{q}) \delta \rho^*(\underline{q}) \rangle \\ &= \int \int d^3 r d^3 r' e^{i \underline{q} \cdot (\underline{r} - \underline{r}')} \langle \delta \epsilon(\underline{r}) \delta \rho(\underline{r}') \rangle \\ &= \left[\frac{\epsilon_0 + p_0}{\rho_0} - \frac{\alpha T_0}{\rho_0 \chi} \right] \int \int d^3 r d^3 r' e^{i \underline{q} \cdot (\underline{r} - \underline{r}')} \langle \delta \rho(\underline{r}) \delta \rho(\underline{r}') \rangle \\ &= \left[\frac{\epsilon_0 + p_0}{\rho_0} - \frac{\alpha T_0}{\rho_0 \chi} \right] \langle |\delta \rho(\underline{q})|^2 \rangle \end{aligned} \quad (\text{A-8})$$

Substitution of Eq. (A-8) into Eq. (A-7) gives

$$\xi_3 = \frac{1}{\langle |\delta \epsilon(\underline{q})|^2 \rangle^{\frac{1}{2}} \sqrt{1-n^2}} \left\{ \delta \epsilon(\underline{q}) - \left(\frac{\epsilon_0 + p_0}{\rho_0} - \frac{\alpha T_0}{\rho_0 \chi_T} \right) \delta \rho(\underline{q}) \right\} \quad (\text{A-9})$$

Using Eq. (A-5), one can reduce this equation immediately to

$$\xi_3 = \frac{m \rho_0 C_v}{\langle |\delta \epsilon|^2 \rangle^{\frac{1}{2}} \sqrt{1-n^2}} \delta T(\underline{q}) \quad (\text{A-10})$$

Thus ξ_3 is proportional to $\delta T(\underline{q})$.

Figure Captions

- Figure 1. Comparison of the measured and calculated Brillouin peak frequency and linewidth data of PPG 425 as a function of temperature.
- Figure 2. Comparison of the measured and calculated Landau-Placzek ratio data of PPG 425 as a function of temperature.
- Figure 3. Simulated Rayleigh-Brillouin spectra for PPG 425.
(A) at 400 K, $\tau_2\omega_s = 0.12$; (B) at 350 K, $\tau_2\omega_s = 0.34$;
(C) at 310 K, $\tau_2\omega_s = 0.91$; (D) at 280 K, $\tau_2\omega_s = 2.2$;
(E) at 240 K, $\tau_2\omega_s = 9.1$; and (F) at 200 K, $\tau_2\omega_s = 64$.

Figure 1.

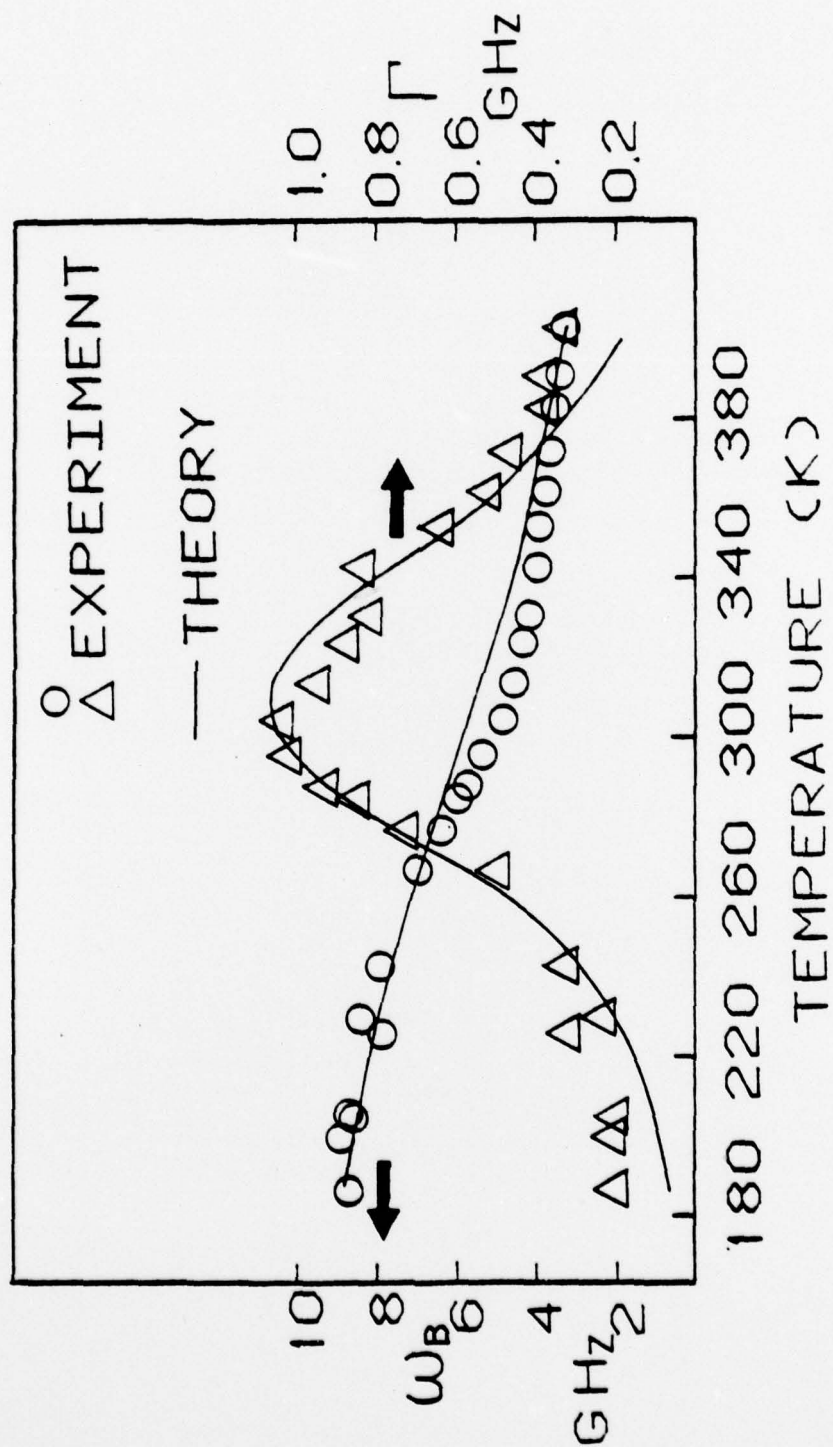


Figure 2.

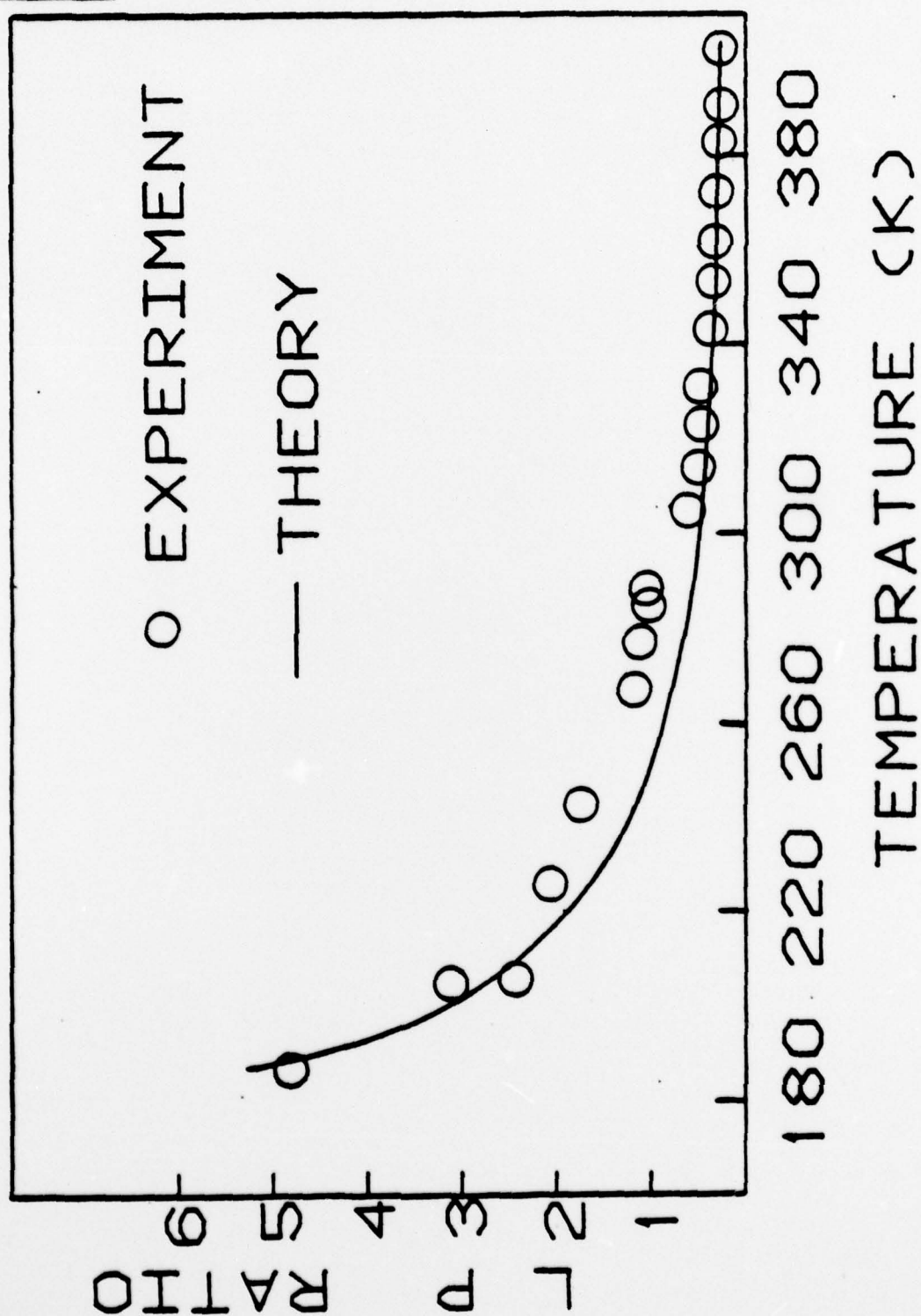
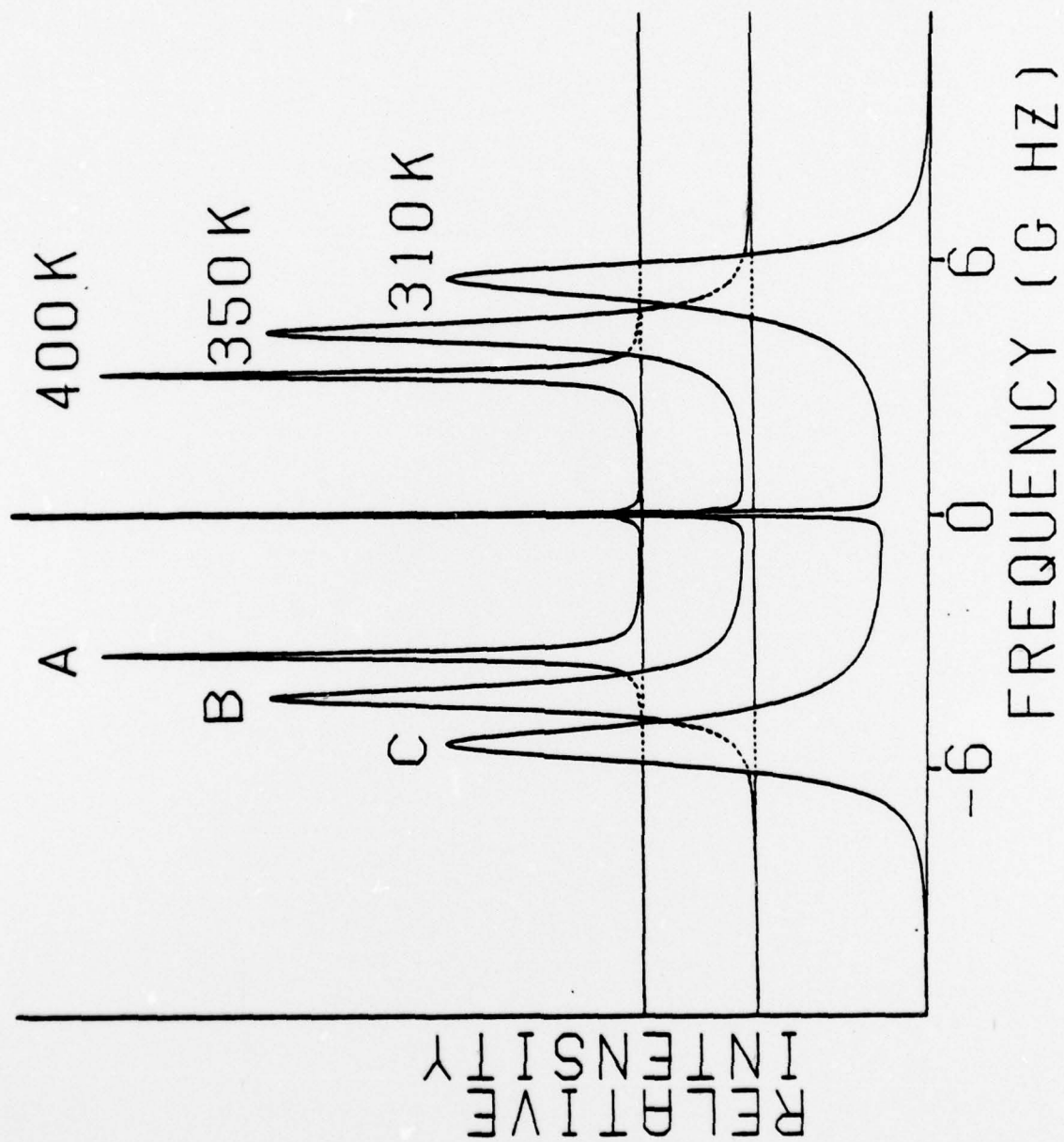
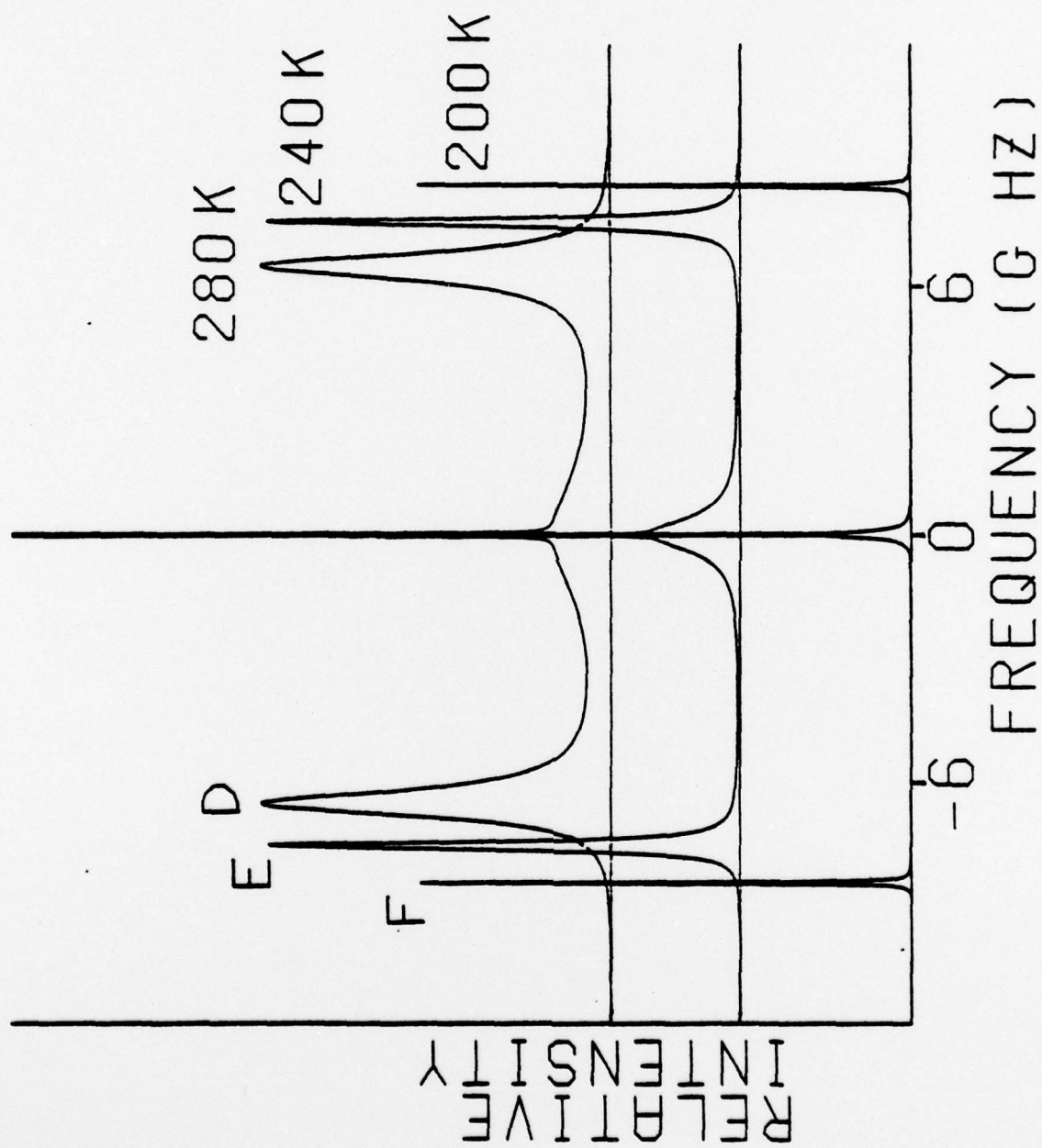


Figure 3.



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