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BRILLOUIN SCATTERING AND SEGMENTAL MOTION OF A POLYMERIC LIQUID--ETC(U)

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N00014-75-C-0908

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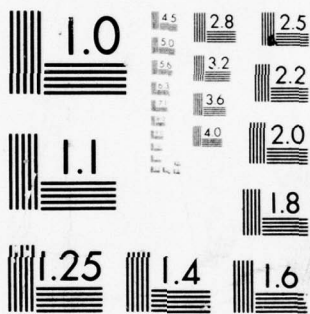
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REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER (14) TR-15	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) Brillouin Scattering and Segmental Motion of a Polymeric Liquid, I.		5. TYPE OF REPORT & PERIOD COVERED (9) Technical / rept.
6. AUTHOR(s) (10) Y.-H. Lin and C. H. Wang		7. PERFORMING ORG. REPORT NUMBER
9. PERFORMING ORGANIZATION NAME AND ADDRESS Department of Chemistry University of Utah Salt Lake City, UT 84112		8. CONTRACT OR GRANT NUMBER(s) (15) N00014-75-C-0908
11. CONTROLLING OFFICE NAME AND ADDRESS		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS NR 051-562
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office) (12) 32p.		13. REPORT DATE (11) 1 March 1978
16. DISTRIBUTION STATEMENT (of this Report) a. According to the attached distribution list b. Others may obtain copies of this report from the Office of Technical Services, Department of Commerce.		12. NUMBER OF PAGES 27
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		15. SECURITY CLASS. (of this report) Unclassified
18. SUPPLEMENTARY NOTES To be published in The Journal of Chemical Physics		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Brillouin scattering viscous polymer fluid, polypropylene glycol, segmental motion in polymers, structural relaxation.		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The effect of segmental motion on the density-density correlation function of a viscous polymer liquid has been analyzed using a generalized relaxation equation developed by Zwanzig and Mori. It is shown that for polymer liquids of high viscosity Brillouin scattering is closely associated with the structural relaxation associated with the motion of chain segments. A single relaxation time theory is shown to yield good agreement with the experimental results on polypropylene glycol. The torsional motion involving a small number of monomer units is shown to be responsible for the dispersion and attenuation of the		

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Task No. NR 051-562

TECHNICAL REPORT NO. 15

BRILLOUIN SCATTERING AND SEGMENTAL MOTION
OF A POLYMERIC LIQUID, I

By

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Prepared for Publication
in the
The Journal of Chemical Physics

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March 1, 1978

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ABSTRACT

The effect of segmental motion on the density-density correlation function of a viscous polymer liquid has been analyzed using a generalized relaxation equation developed by Zwanzig and Mori. It is shown that for polymer liquids of high viscosity Brillouin scattering is closely associated with the structural relaxation associated with the motion of chain segments. A single relaxation time theory is shown to yield good agreement with the experimental results on polypropylene glycol. The torsional motion involving a small number of monomer units is shown to be responsible for the dispersion and attenuation of the hypersonic wave. The fact that the Brillouin scattering spectrum of a polymer liquid is insensitive to the change of molecular weight is discussed. We have shown that temporal modulation of the spatial second moment of the intermolecular or inter-segmental interaction energy is responsible for the relaxation process involved in Brillouin scattering.

INTRODUCTION

Measurements of viscoelastic properties of undiluted polymers and polymer solutions can provide information about the nature and rates of the configurational rearrangements. A knowledge of the translational and rotational motion of polymer molecules and their segments has been important in elucidating the structure of macromolecules in the liquid state.¹

Modern developments in optical technology have made polarized Rayleigh-Brillouin scattering spectroscopy one of the most useful methods for the investigation of viscoelasticity of macromolecules in the high frequency (10^9 Hz) range.

Recent experimental studies have shown that the Rayleigh-Brillouin spectra of polymer fluids are sensitive to the molecular configurational rearrangements and segmental motion of flexible polymer chains.² There is at present, however, no procedure or guideline with which quantitative information about the polymer dynamics can be extracted from the experimental data using this technique. The field of inelastic laser light scattering of polymers and polymer solutions is presently in a stage of development.

In the low frequency range, the bead-spring (Rouse-Zim) model provides an adequate description of the dynamic properties of macromolecules in solution. At high frequencies the polymer chain dynamics are governed by localized motion involving only a few segments. The length of the polymer chain is not expected to greatly affect the chain dynamics. In other words, one does not expect the Brillouin spectrum of polymers to be sensitive to the change of molecular weight. This was indeed observed experimentally.^{3,4}

However, we still do not know at present how the small scale motion involving very few segments affects the Rayleigh-Brillouin spectrum of a polymer solution. In other words, we do not know how to relate the hypersonic data of a polymer system to the dynamics of segmental motion.

To analyze the type of information that one may learn by studying the Brillouin-Rayleigh spectrum of a polymer fluid, we have investigated theoretically the effect of polymer segmental motion on the density-density time correlation function. The density-density time correlation function is proportional to the Fourier transform of the observed Brillouin-Rayleigh spectrum. In the present paper, we have analyzed the relaxation process involved in affecting the peak frequency and the linewidth of the Brillouin spectrum of a polymer liquid. Finally, we have used the linear response theory introduced by Zwanzig to analyze the motion of the normal mode of a bulk polymer liquid. We have interpreted the Brillouin spectra of pure polypropylene glycol liquids in terms of this new theoretical result.

THE DENSITY-DENSITY CORRELATION FUNCTION OF A POLYMER FLUID

Consider a pure polymer fluid which is made up of a collection of identical polymer segments. Each macromolecule contains n -segments and the illuminated volume contains N molecules. The polarized Brillouin-Rayleigh spectrum is determined mainly by the Fourier transform of the time correlation function $C(t)$, given by⁵,

$$C(t) = \sum_p \sum_{p'} \sum_j \sum_k \langle e^{iq \cdot [R_j^p(t) - R_k^{p'}]} \rangle \quad (1)$$

where $C(t)$ is the q th spatial component of the density-density correlation function; p and p' are indices denoting the macromolecules, and j, k denote the segments in a macromolecule. $\underline{R}_j^p(t)$ is the position (the bead position) vector of segment j and polymer p with respect to the laboratory coordinate frame at time t . The summation over p, p', j and k are over all polymer segments inside the scattering volume. $\underline{q}$ is the wave vector of the excitation mode selected through the Bragg condition in light scattering. The amplitude of $\underline{q}$ is equal to

$$q = \frac{4\pi n}{\lambda_0} \sin\theta/2 \quad (2)$$

where λ_0 is the wavelength of incident light in vacuum, n is the index of refraction and θ is the scattering angle.

For fluids consisting of small size molecules, one can analyze $C(t)$ in terms of entropy and pressure fluctuations. These fluctuations can then be calculated using the linearized hydrodynamic equations with frequency dependent transport coefficients in a manner similar to that of ordinary low viscosity fluids consisting of small molecules. As the polymer molecule increases in size, the center of mass motion becomes very slow and the diffusive entropy fluctuations then dominate the time evolution of $C(t)$. Moreover, in ordinary low viscosity fluids, the width of the Brillouin doublet is predicted to increase with increasing viscosity.⁶ For polymer fluids of high viscosity this prediction would lead to such wide Brillouin peaks that they would not be observable. In Fig. 1 the peak frequency and linewidth of the Brillouin peak of polypropylene glycols are shown as a function of viscosity. For the experimental data at two temperatures the frequency as well as the line-

width appear to be independent of viscosity. This is in complete disagreement with theoretical results. In fact the Brillouin peaks of highly viscous polymer fluids are quite sharp near T_g .² The discrepancy between the results of an ordinary fluid and a polymer fluid is believed to be due to the segmental motion that is present in the polymer fluid. The segmental motion leads to the breakdown of the Navier-Stokes equation. As a result the usual hydrodynamic equations cannot be used to calculate the Brillouin spectrum of a polymer fluid. The structural relaxation which has a dominant effect on the propagation and absorption of the hypersonic wave in a liquid consisting of macromolecules, but this is not adequately accounted for in the hydrodynamics equation.

For a polymer fluid consisting of flexible polymer segments, the correlation function $C(t)$ is expected to depend strongly on temperature, due to the fact that the structural relaxation time of a polymer fluid depends strongly on temperature. At high temperature, the rate of segmental relaxation is comparable with the frequency of the hypersonic sound wave; in this case the segmental motion will contribute significantly to the linewidths of the Brillouin side bands. At low temperature, the rate of segmental fluctuations is slow compared with the hypersonic frequency, but fast compared to the thermal diffusion rate. In this case the segmental motion will manifest itself as a broad line superimposed upon the central Rayleigh component arising from the translational diffusion. Therefore, the time evolution of $C(t)$ is associated with the whole region of the Brillouin-Rayleigh spectrum.

The question of great interest is what are the effects of the structural relaxation on the Brillouin-Rayleigh spectrum? To answer this question a microscopic theory on structural relaxation is in order.

In order to develop a microscopic theory for the Brillouin scattering spectrum of a bulk polymer, one needs to investigate the correlation function $C(t)$ as defined in Eq. (1) which can also be written as

$$C(t) = \langle \delta\rho(\underline{q}, t) \delta\rho^*(\underline{q}) \rangle \quad (3)$$

where $\delta\rho(\underline{q}, t)$ is the $\underline{q}$ th spatial Fourier component of the density fluctuation and is given by

$$\delta\rho(\underline{q}, t) = \sum_p \sum_j e^{i\underline{q} \cdot \underline{R}_j^p(t)} = \sum_p \sum_j e^{i\underline{q} \cdot \underline{Z}_j^p(t)} \quad (4)$$

where the direction of $\underline{q}$ is taken to be parallel to the Z-axis, and each polymer segment j of polymer p contributes to the density fluctuation by a term $e^{i\underline{q} \cdot \underline{Z}_j^p}$. To calculate $C(t)$ using a microscopic equation, we first realize that the density fluctuation does not occur independently. The momentum and energy density fluctuations couple also to the density fluctuation. In this paper we suppress the coupling of the density and energy. This is justified because our primary interest lies in the study of the Brillouin doublet in which the effect of thermal conductivity can be neglected for an isothermal system.

Among the three components of momentum density, only the longitudinal component in the direction of $\underline{q}$ is coupled to $\delta\rho$, as the coupling to the transverse components perpendicular to $\underline{q}$ is prevented by symmetry.⁵ The expression for the longitudinal momentum density is given by

$$g_z(\underline{q}, t) = \sum_p \sum_j m_{pj} \dot{Z}_j^p(t) e^{i\underline{q} \cdot \underline{Z}_j^p(t)} \quad (5)$$

where m_{pj} is the mass of j segment of polymer p .

The q th mode of the density fluctuation gives rise to two Brillouin peaks: the Stokes and anti-Stokes peaks. The two peaks correspond to acoustic waves propagating in two opposite directions. We show in Appendix I that the two acoustic modes with opposite frequency, ω_q , are represented by the dynamic variables ξ_+ and ξ_- which are given by

$$\xi_{\pm} = \frac{1}{\sqrt{2}} \left(\frac{\delta\rho^{(q)}}{\langle |\delta\rho|^2 \rangle^{1/2}} \pm \frac{g_z^{(q)}}{\langle |g_z|^2 \rangle^{1/2}} \right) \quad (6)$$

Thus the density fluctuation $\delta\rho$ can be expressed in terms of ξ_+ and ξ_- ,

$$\delta\rho = \frac{1}{\sqrt{2}} (\xi_+ + \xi_-) \quad (7)$$

The density-density correlation function $C(t)$ is then given by

$$C(t) = \frac{1}{2} \langle |\delta\rho|^2 \rangle \{ \langle \xi_+(t) \xi_+^* \rangle + \langle \xi_-(t) \xi_-^* \rangle + \langle \xi_+(t) \xi_-^* \rangle + \langle \xi_-(t) \xi_+^* \rangle \} \quad (8)$$

where the first two terms on the right hand side of Eq. (8) corresponds to the two acoustic waves propagating in opposite directions. The last two terms vanish at $t = 0$, but are finite at $t \neq 0$ due to the dynamic coupling of the two acoustic modes with opposite ω_q . These can contribute to the intensity to the central Rayleigh component. These can be neglected in calculating the spectrum of the Brillouin doublet. Therefore, calculation of the Brillouin spectrum reduces to the calculation of the correlation functions given by

$$C_{\pm}(t) = \langle \xi_{\pm}(t) \xi_{\pm}^* \rangle \quad (9)$$

Since both ξ_+ and ξ_- depend on the same q and give similar physical results, in the following we shall use ξ_q for either ξ_+ or ξ_- , and $C_q(t)$ for $C_{\pm}(t)$.

In principle, if one has a proper expression for the equation of motion of $\xi_q(t)$, the correlation function $C_q(t)$ can then be calculated according to the method of irreversible statistical mechanics. Formally, the equation of motion for $\xi(t)$ is given by

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

where L is the Liouville operator which governs the time evolution of the dynamic variable $\xi_q(t)$. While it is straight-forward to write down a formal expression for L in terms of the kinetic and potential energy operators in a many body system, in practice this is never done in a polymer system due to the large number of internal degree of freedom and unknown intra- and inter-molecular potential functions. For a dilute polymer solution, Kirkwood's generalized diffusion equation or the stochastic Fokker-Planck equation has been employed to evaluate the time correlation functions associated with the intrinsic viscosity⁷ and internal viscosity⁸, however, an appropriate Liouville operator for a bulk polymer has not yet been developed.

Nevertheless, even in the absence of an appropriate Liouville operator, useful insight on the behavior of the linewidth and frequency shift of a Brillouin spectrum of a polymer fluid can be obtained from Eq. (10) using the linear response theory developed by Zwanzig⁹.

We start by defining a projection operator P such that when it operates on a general function G , it yields

$$PG = \sum_q \xi_q \langle \xi_q \xi_q^* \rangle^{-1} \langle G \xi_q^* \rangle \quad (11)$$

where G is a function of ξ_q and may be time dependent.

The correlation function $C_q(t)$ can be constructed by using P according to

$$\begin{aligned} P \xi_q(t) &= \sum_k \xi_k \langle \xi_k \xi_k^* \rangle^{-1} \langle \xi_q(t) \xi_k^* \rangle \\ &= \xi_q \langle \xi_q \xi_q^* \rangle^{-1} C_q(t) \end{aligned} \quad (12)$$

where we have assumed that there is no correlation between normal modes of different wave vectors.

According to the well-known procedure⁹, the equation of motion for $C_q(t)$ can be shown (using Eqs. (11) and (12) to follow a generalized Langevin equation,

$$\frac{\partial C_q(t)}{\partial t} = i \omega_q C_q(t) - \int_0^t d\tau K(\tau) C_q(t-\tau) \quad (13)$$

where the frequency ω_q is given by

$$\omega_q = \langle [L \xi_q] \xi_q^* \rangle \langle \xi_q \xi_q^* \rangle^{-1} \quad (14)$$

and $K(\tau)$ is the memory function given by

$$K(\tau) = \langle \Gamma(\tau) F^*(0) \rangle \langle \xi_q \xi_q^* \rangle^{-1} \quad (15)$$

where

$$F(\tau) = e^{i(1-P)L\tau} F(0) \quad (16)$$

and

$$F(0) = F = (1-P) i L \xi_q \quad (17)$$

The generalized Langevin equation as given in Eq. (13) is very useful because of its mathematical simplicity and ease of application. This equation can be used to calculate the Brillouin spectrum when the macroscopic hydrodynamic equations fail. Using this equation, we can translate physical ideas about the nature of Brillouin scattering from a polymer fluid into mathematical terms with a minimum set of assump-

tions about the complex nature of the fluid state of macromolecules.

In the absence of an explicit Liouville operator to calculate ω_q and $K(\tau)$, we can argue that for a polymer fluid, there are strong interactions between translational and orientational motions of each segment and between segments so that the normal modes ξ_q should equilibrate rapidly. Thus, we may expect a set of fully quantized vibrational states with an energy separation approximately equal to the hypersonic frequency. In flexible chain molecules at ordinary temperatures, the vibrational relaxation rates for the quantized vibrational modes are fast. Moreover, there will also be a distribution of relaxation times for chain segments to change from one state to another. Therefore, for the normal mode given in Eq. (6), the frequency ω_q may take a real finite value. We assume that ω_q is equal to the undamped hypersonic frequency. We show in Appendix I that ω_q is related to the isothermal compressibility of the polymer liquid.

The memory function $K(\tau)$ decays exponentially with a distribution of relaxation times,

$$K(\tau) = \int f(\tau_r) e^{-\tau/\tau_r} d\tau_r \quad (18)$$

where $f(\tau_r)$ is the distribution function of relaxation times. For a single relaxation time τ_R , $f(\tau_r)$ is proportional to a delta function $\delta(\tau_r - \tau_R)$.

Knowing ω_q and $K(\tau)$, we can now solve Eq.(13) by the Laplace transform technique.

$$\text{Define} \quad \hat{C}_q(z) = \int_0^\infty C_q(t) d^{-z}t \quad dt \quad (19)$$

$$\hat{K}(z) = \int_0^\infty K(t) e^{-zt} dt \quad (20)$$

we obtain by taking the Laplace transform of Eq. (13),

$$\hat{C}_q(z) = \frac{\langle \epsilon_q \epsilon_q^* \rangle}{z - i\omega_q + K(z)} \quad (21)$$

where

$$\hat{K}(z) = \int_0^\infty \frac{f(\tau_r) d\tau_r}{z + \tau_r^{-1}} \quad (22)$$

The Brillouin spectrum corresponds to the real part of $\hat{C}_q(i\omega)$. We shall call this function $I_q(\omega)$, which can be calculated from Eqs. (20) and (21). The result for $I_q(\omega)$ is

$$I_q(\omega) = \text{Re } \hat{C}_q(i\omega) = \frac{\langle \epsilon_q \epsilon_q^* \rangle \int_0^\infty \frac{\tau_r f(\tau_r)}{1 + \omega^2 \tau_r^2} d\tau_r}{\left[\int_0^\infty \frac{\tau_r f(\tau_r)}{1 + \omega^2 \tau_r^2} d\tau_r \right]^2 + \left[\omega - \omega_q - \int_0^\infty \frac{\tau_r^2 f(\tau_r) d\tau_r}{1 + \omega^2 \tau_r^2} \right]^2} \quad (23)$$

APPLICATION TO BULK POLYMER LIQUIDS

Although it is believed in general a distribution of relaxation times is involved in a polymer system, we shall show that the single relaxation time model provides a satisfactory interpretation of the Brillouin scattering spectrum of a viscoelastic polymer liquid. To illustrate this we assume

$$K(\tau) = A e^{-\tau/\tau_R} \quad (24)$$

where τ_R is the relaxation time and A is the amplitude of $K(\tau)$ at $\tau = 0$, and is given by

$$A = \left\{ \langle |\epsilon_q|^2 \rangle - \frac{|\langle \epsilon_q \epsilon_q^* \rangle|^2}{\langle |\epsilon_q|^2 \rangle} \right\}^{-1} \quad (25)$$

In this model, Eq. (23) reduces to

$$I_S(\omega) = \frac{A^2 \tau_R^2}{1 + \omega^2 \tau_R^2} \left\{ (A \tau_R / 1 + \omega^2 \tau_R^2)^2 + (\omega - \omega_q - \omega A \tau_R^2 / 1 + \omega^2 \tau_R^2)^2 \right\} \quad (26)$$

Equation (26) can now be used to analyze the experimentally determined Brillouin spectra of bulk polypropylene glycol. The Brillouin spectra of this polymer liquid at various molecular weights have been accurately measured in our laboratory. To fit the experimental spectra, one notes that Eq. (26) contains three adjustable parameters: ω_q (the unperturbed acoustic frequency), A (the amplitude of the memory function $K(\tau)$ at $\tau = 0$) and τ_R (the relaxation time of the memory function). However, the nature of these parameters is well understood and no ambiguity to the curve fit will exist.

It is easy to show that A corresponds to the square of the modulation amplitude associated with the torsional motion of polymer segments in the direction perpendicular to the propagation direction of the hypersonic wave.

The unperturbed acoustic frequency ω_q also depends weakly on temperature. According to Eq. (26), the $I_S(\omega)$ function has a maximum at $\omega = \omega_p$, which is related to ω_q according to

$$\begin{aligned} \omega_p &= \omega_q \left\{ \frac{1}{1 - A \tau_R^2 / 1 + \omega_p^2 \tau_R^2} \right\} \\ &\approx \omega_q (1 + A \tau_R^2 / 1 + \omega_p^2 \tau_R^2) \end{aligned} \quad (27)$$

The second equality holds because $A \tau_R^2 / (1 + \omega_p^2 \tau_R^2) \ll 1$.

Equation (27) gives the dispersion relation for ω_p . For $\omega_p \tau_R < 1$, the dispersion curve has a reverse S-shape when ω_p is plotted as a function of temperature, provided that we assume

$$\tau_R = \tau_0 \exp (E_a/kT) \quad (28)$$

At high temperature one has $A\tau_R^2 \ll 1$, and ω_p approaches ω_q . Thus ω_q is equal approximately to the Brillouin peak frequency at high temperature when the amplitude of modulation is small compared with the relaxation rate.

We have used the least squares fitting procedure to fit the theoretical peak frequency and linewidth as computed by using Eq. (26) to the experimental values at various temperatures. The fit was carried out by first generating a spectrum at one temperature using reasonable values of A , τ_0 , and E_a . The theoretical spectrum was then compared with the experimental one. The procedure was repeated with different values of A , τ_0 and E_a until the theoretical spectrum quite resembles the experimental one. Next the spectra were generated at all temperatures, from which the peak frequencies and linewidths were read and compared with the experimental values. The difference between theoretical and experimental values is then minimized with a least squares fitting program by further adjusting the values of A , τ_0 , and E_a .

In Fig. 2, we show the Brillouin peak frequencies and the spectral linewidths (the half width at half height) determined by the curve fitting procedure, also including the experimental results between 280 and 400 K for comparison. The agreement between the theoretical and experimental results is quite good in this temperature region, considering the fact that only three parameters (A , E_a and T_0) were used to fit

two separate sets of data: frequency shifts and linewidths. It should also be pointed out the agreement between the experiment and theory, given in Figure 2 could be improved if we allow ω_q to depend on temperature. As shown in Appendix I, ω_q is proportional to $(\rho\chi_T)^{-1/2}$, where ρ and χ_T are density and isothermal compressibility of the fluid, respectively. Both quantities depend on temperature slightly. Increasing temperature has a tendency of decreasing ω_q because $\rho\chi_T$ increases slightly with increasing temperature. As a result, the peak frequency and linewidth shown in Figure 2 will be depressed downward at high temperature and pushed upward at low temperature, thus bringing a better agreement with the experimental result than the fit using a temperature independent ω_q which is used in the present work. However, since we don't have complete ρ and χ_T data for PPG, the present procedure is sufficient to demonstrate the validity of the theory.

Below 280 K, the calculated Brillouin peak frequencies are smaller than the experimental values, due to the fact that the relaxation rate τ_R^{-1} becomes comparable to ω_q at this temperature. In this situation, one would expect strong coupling between the normal mode ξ_q and the velocity F , and we can no longer consider F to be a fast dynamic variable to modulate ξ_q ; both must be considered with equal weight. Moreover, since ω_q is about equal to the modulation amplitude $\sqrt{\Lambda}$, in this situation the precise functional form of the memory function becomes important, and we do not expect that Eq. (24) is valid at low temperature.

We now consider in more detail the quantity Λ , which is a measure of the square of modulation amplitude associated with the motion of polymer segments in the direction perpendicular to ξ_q . In Appendix II,

we show that A can be written as

$$A = \frac{1}{2} \left\{ \frac{1}{Nm} \sum_p \sum_{p'} \sum_i \sum_j \left\langle \frac{\partial^2 u}{\partial z_i^p \partial z_j^{p'}} \right\rangle e^{iq(z_i^p - z_j^{p'})} + \frac{3kT}{m} q^2 - \omega_q^2 \right\} \quad (29)$$

where u is the total potential energy of the system and m is the mass of monomer. The $3kTq^2/m$ term can be calculated and is found to be only about one quarter of the value of ω_q^2 for PPG in the temperature range considered. The important term for A thus comes from the potential energy part.

We then assume that the range of intermolecular interaction potential is short compared with the wavelength of light (or q^{-1}), and in this case we can expand the phase factor $e^{iq(z_i^p - z_j^{p'})}$ in powers of q . The first non-vanishing q dependent term is found to be equal to¹⁰

$$\begin{aligned} A_p &= \frac{q^2}{2} \frac{1}{Nm} \sum_p \sum_{p'} \sum_i \sum_j \left\langle \frac{\partial^2 u}{\partial z_i^p \partial z_j^{p'}} (z_i^p - z_j^{p'})^2 \right\rangle \\ &= \frac{q^2}{2} \frac{1}{Nm} \sum_p \sum_{p'} \sum_i \sum_j \left\langle \frac{\partial^2 u}{\partial (z_i^p - z_j^{p'})^2} (z_i^p - z_j^{p'})^2 \right\rangle \end{aligned} \quad (30)$$

According to Eq. (25), A is positive, and thus A_p must be greater than the ω_q^2 term, this is consistent with the stability condition condition for a physical system for which we always have $\frac{\partial^2 u}{\partial (z_i^p - z_j^{p'})^2} > 0$.

One notes that A_p vanishes when $z_i^p = z_j^{p'}$. Thus the existence of A_p depends on the presence of intermolecular (or inter-segmental) interactions. This result is important in the case of dilute polymer solution, in which the polymer dynamics depends only on the polymer-solvent and intrachain interactions.

Since the intermolecular interaction u is short-range, it may be expanded in terms of power series of the intermolecular (or inter-seg-

mental) distance along the direction q ,

$$u = u_0 + \sum_{p,p',i,j} \frac{\partial u}{\partial (z_i^p - z_j^{p'})} (z_i^p - z_j^{p'}) + \frac{1}{2} \sum_{p,p',i,j} \frac{\partial^2 u}{\partial (z_i^p - z_j^{p'})^2} (z_i^p - z_j^{p'})^2 + \dots \quad (31)$$

Comparing with Eq. (31), we may consider A_p in Eq. (30) as the spatial second moment of the intermolecular potential energy. For $t \neq 0$ this spatial second moment changes because of molecular motion which modulates the intermolecular distance and relative orientations. For macromolecules, the center of mass motion is slow; the torsional motion involving only relatively small numbers of segments is thus most effective in the modulation of the second moment.

Our computer curve-fitting result in PPG indicates that the modulation amplitude $\sqrt{A}$ is insensitive to temperature variation. The value of $\sqrt{A}$ is also found equal to ω_q throughout the 280 - 400 K temperature range. On the other hand the relaxation time τ_R is found strongly temperature dependent. Using Eq. (28), we have found $\tau_0 = 0.94 \times 10^{-13}$ sec and the activation energy $E_a = 3.1 \pm (0.02)$ kcal/mole. Within the entire temperature range we have further found that $\sqrt{A} \tau_R$ is less than unity. This validates the second step of Eq. (27), thus indicating that the Brillouin scattering spectra of PPG between 280 and 400 K may be described in terms of a stochastic process of fast modulation.

As pointed out above, the relaxation time cannot be associated with the center of mass motion, but rather with the motion involving a small number of segments. The rapid motion of a chain segment from one position to another will involve a local reorganization of the structure of the polymer liquid. The microscopic picture is apparently implied in

the phenomenological theory of structural relaxation in a viscous liquid developed by Isakovich and Chaban.¹¹ In reference 11, the diffusion of holes taking place in the viscoelastic liquid is considered to be the mechanism for the structural relaxation process. In our present microscopic theory τ_R is the measurement of relaxation times associated with the modulation of the spatial second moment of the potential energy. Relaxation occurs because of fluctuations of segmental positions. Thus, the present microscopic theory serves to provide the Isakovich and Chaban phenomenological theory with a more satisfactory statistical foundation.

Finally, it should be pointed out that despite the fact that we expect in general a distribution of relaxation times for a polymer system, the single relaxation time model seems to fit satisfactorily the experimental results. This may be understood from Eq. (30) because only the modulation of the short-range intersegmental interaction potential can make a contribution to the memory function $K(\tau)$. The dispersion and relaxation in the Brillouin scattering spectrum of a bulk polymer liquid involves only short-range localized segmental motions. The distribution of relaxation times due to the motion of an entire polymer chain will not enter into the picture. This suggests that the Brillouin scattering spectrum of a bulk polymer liquid should be independent of molecular weight. This is clearly in agreement with the experimental result on polypropylene glycol.^{2,3,4}

SUMMARY AND CONCLUSION

We have analyzed the effect of segmental motion on the density-density correlation function of a polymer fluid. The density-density

correlation function is proportional to the Fourier transform of the Brillouin-Rayleigh spectrum which one can measure experimentally.

We have utilized the linear response theory to analyze the Brillouin spectra in terms of the dynamics of polymer chain segments in bulk polymer systems. We have shown that for polymer fluids of high viscosity Brillouin scattering is due to normal modes associated with the motion of chain segments. When the modulation amplitude is small compared with the relaxation rate, we have shown that a single relaxation time theory will provide a satisfactory description of the hypersonic frequency and Brillouin spectral linewidth data as a function of temperature. By comparing the theoretical expression with the experimental result we have also obtained the activation energy associated with the relaxation time and the modulation amplitude. The latter quantity is then used to delineate the mechanism involved in causing the dispersion and attenuation of the hypersonic wave. It is found that the localized motion which causes modulation of the second moment of the intermolecular interaction potential is responsible for the dispersion and attenuation of the hypersonic wave. We have thus established the fact that Brillouin scattering probes only short-ranged localized motion. We have also explained why the Brillouin scattering spectrum of a viscoelastic polymer liquid does not depend on the molecular weight.

Another significant result in the present work is that the Brillouin spectral linewidth is related to the relaxation of a correlation function of the velocity of normal modes associated with the chain segments of different macromolecules. It is thus clear from the mathematical point of view that the maximum position in the Brillouin line-

width versus temperature curve will not necessarily correspond to maximum point in the NMR T_1 or $(T_{1\rho})$ versus temperature data because the three techniques are sensitive to different types of relaxation processes. We expect in general that Brillouin scattering will provide supplementary information which cannot be obtained or extrapolated from other relaxation techniques.

Acknowledgment:

We thank the National Science Foundation and the Office of Naval Research for support of this research.

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APPENDIX I

The frequency ω_q and the isothermal compressibility.

The frequency ω_q given by Eq. (14) can be either positive or negative depending on whether ξ_q substitutes for ξ_+ or ξ_- . In either case, the derivation is similar. We give only the derivation associated with ξ_+ . Substituting Eq. (6) into Eq. (14) we obtain

$$\begin{aligned} \omega_q = \frac{1}{2} \{ & \langle L \frac{\delta\rho}{\langle |\delta\rho|^2 \rangle^{\frac{1}{2}}} \rangle \frac{g_z^*}{\langle |g_z|^2 \rangle^{\frac{1}{2}}} \rangle \\ & + \langle L \frac{g_z}{\langle |g_z|^2 \rangle^{\frac{1}{2}}} \rangle \frac{\delta\rho^*}{\langle |\delta\rho|^2 \rangle^{\frac{1}{2}}} \rangle \end{aligned} \quad (I,1)$$

Since the Liouville operator, L , is Hermitian, Eq. (I,1) can be rewritten as

$$\omega_q = \frac{1}{2} \{ (-i) \frac{\langle (iL\delta\rho)g_z^* \rangle}{\langle |\delta\rho|^2 \rangle^{\frac{1}{2}} \langle |g_z|^2 \rangle^{\frac{1}{2}}} + (i) \frac{\langle g_z(iL\delta\rho)^* \rangle}{\langle |\delta\rho|^2 \rangle^{\frac{1}{2}} \langle |g_z|^2 \rangle^{\frac{1}{2}}} \} \quad (I,2)$$

Using the definitions for $\delta\rho$ and g_z (Eqs. (4) and (5)), we obtain

$$\omega_q = q \frac{(\frac{1}{m}) \langle |g_z|^2 \rangle^{\frac{1}{2}}}{\langle |\delta\rho|^2 \rangle^{\frac{1}{2}}} \quad (I,3)$$

According to the principle of equipartition of energy, we have

$$\frac{1}{m} \langle |g_z|^2 \rangle^{\frac{1}{2}} = (N \frac{kT}{m})^{\frac{1}{2}} \quad (I,4)$$

where N is the total number of segments (light scatterers) within the scattering volume, V .

In the limit of small q , it is true that⁵

$$\langle |\delta\rho|^2 \rangle^{\frac{1}{2}} = (V\rho^2 kT\chi_T)^{\frac{1}{2}} = (N\rho kT\chi_T)^{\frac{1}{2}} \quad (I,5)$$

where ρ is the number of segments per unit volume. χ_T is the isothermal compressibility. Combining Eqs. (I,3), (I,4), and (I,5), we obtain the final expression for ω_q :

$$\omega_q = \frac{q}{(\rho m \chi_T)^{1/2}} = q C_T \quad (I,6)$$

where $C_T = (\rho m \chi_T)^{-1/2}$ is the expression for the isothermal sound velocity⁵. Equation (I,6) is exactly the definition of isothermal sound frequency. Similarly, for ξ_- , the result is:

$$\omega_q = -q C_T \quad (I,7)$$

where, as in (I,6), both q and C_T are the absolute values.

APPENDIX II

Reduction of the Expression of Modulation amplitude A.

Since ξ_q is normalized, using the result of Appendix I, we reduce Eq. (25) to

$$A = \{ \langle (iL\xi_q)(iL\xi_q)^* \rangle - \omega_q^2 \} \quad (II,1)$$

Substituting Eq. (6) into the above equation, we obtain a new expression for A:

$$A = \frac{1}{2} \left\{ \frac{\langle (iLg_z)(iLg_z)^* \rangle}{\langle |g_z|^2 \rangle} - \omega_q^2 \right\} \quad (II,2)$$

Using the definition of g_z and the principle of equipartition of kinetic energy for each segment, we now expand the first term of Eq. (II,2) into

$$\begin{aligned} \frac{\langle (iLg_z)(iLg_z)^* \rangle}{\langle |g_z|^2 \rangle} &= \frac{1}{Nm_kT} \left\{ \sum_i \langle (\dot{P}_{zi})^2 \rangle + q^2 \frac{\langle (P_{zi})^4 \rangle}{m^2} \right. \\ &\quad \left. + \sum_{i \neq j} \langle \dot{P}_{zi} \dot{P}_{zj} \rangle + iqkT(\dot{P}_{zj} - \dot{P}_{zi}) + q^2(kT)^2 \right\rangle e^{iq(Z_i - Z_j)} \end{aligned} \quad (II,3)$$

where the double summation $\sum_p \sum_j$ of Eq. (6) is replaced by the single summation $\sum_i$ (or $\sum_j$) of the segments over the whole scattering volume; the momentum of each segment in Z direction $m_{pj} \dot{Z}_j^p$ is replaced by P_{zj} . This can be done provided that each segment has the same mass m .

We understand that the ensemble average $\langle X \rangle$ of any physical quantity X is equivalent to multiplying X by the distribution function $\frac{e^{-\beta H}}{Z}$ and then integrating the product over the whole phase space. We shall assume that the Hamiltonian H has the form

$$H = \sum_i \frac{p_i^2}{2m_i} + u(r_1, r_2, \dots, r_N) \quad (II,4)$$

The ensemble averaging of each term in Eq. (II,3) can be carried out as follows,

$$\begin{aligned} \langle (\dot{p}_{zi})^2 \rangle &= \frac{1}{Z} \int e^{-\beta H} (\dot{p}_{zi})^2 d^N r d^N p \\ &= \frac{1}{Z} \int e^{-\beta H} \left(\frac{\partial u}{\partial z_i} \right)^2 d^N r d^N p \\ &= \frac{1}{\beta} \left\langle \frac{\partial^2 u}{\partial z_i^2} \right\rangle \end{aligned} \quad (II,5)$$

where to obtain the last step, we have carried out integration by parts.

It is easy to obtain,

$$\frac{q^2}{m^2} \langle p_i^4 \rangle = 3q^2 (kT)^2 \quad (II,6)$$

Likewise, we consider

$$\begin{aligned} \langle \dot{p}_i \dot{p}_j e^{iq(Z_i - Z_j)} \rangle &= \frac{1}{Z} \int e^{-\beta H} \left(\frac{\partial u}{\partial z_i} \right) \left(\frac{\partial u}{\partial z_j} \right) e^{iq(Z_i - Z_j)} d^N r d^N p \\ &= \frac{1}{Z \beta^2} \int \left(\frac{\partial^2 u}{\partial z_i \partial z_j} e^{-\beta H} \right) e^{iq(Z_i - Z_j)} d^N r d^N p \\ &\quad + \frac{1}{\beta} \left\langle \left(\frac{\partial^2 u}{\partial z_i \partial z_j} \right) e^{iq(Z_i - Z_j)} \right\rangle \\ &= \frac{1}{Z \beta^2} \int \left[iq \left(\frac{\partial}{\partial z_i} e^{-\beta H} \right) - iq \left(\frac{\partial}{\partial z_j} e^{-\beta H} \right) - q^2 e^{-\beta H} \right] \\ &\quad e^{iq(Z_i - Z_j)} d^N r d^N p \\ &\quad + M \\ &= \frac{q^2}{\beta^2} \langle e^{iq(Z_i - Z_j)} \rangle + M \end{aligned} \quad (II,7)$$

$$\text{where } M = \frac{1}{\beta} \left\langle \left(\frac{\partial^2 u}{\partial z_i \partial z_j} \right) e^{iq(Z_i - Z_j)} \right\rangle \quad (II,8)$$

In order to obtain Eq. (II,7) integrations by parts have been used repetitively.

Consider next the fourth term in Eq. (II,3)

$$\begin{aligned}
 & i q k T \langle (\dot{p}_j - \dot{p}_i) e^{i q (Z_i - Z_j)} \rangle \\
 &= \frac{i q}{\beta Z} \int \left(\frac{\partial H}{\partial Z_i} - \frac{\partial H}{\partial Z_j} \right) e^{-\beta H} e^{i q (Z_i - Z_j)} d^N r d^N p \\
 &\simeq \frac{i q}{\beta^2 Z} \int \left(\frac{\partial}{\partial Z_j} e^{-\beta H} - \frac{\partial}{\partial Z_i} e^{-\beta H} \right) e^{i q (Z_i - Z_j)} d^N r d^N p \\
 &= -\frac{2 q^2}{\beta^2} \langle e^{i q (Z_i - Z_j)} \rangle
 \end{aligned} \tag{II,9}$$

Combining Eqs. (II,3), (II,4), (II,5), (II,6), (II,7) and (II,9), and substituting the result into Eq. (II,2), we obtain the expression for A as

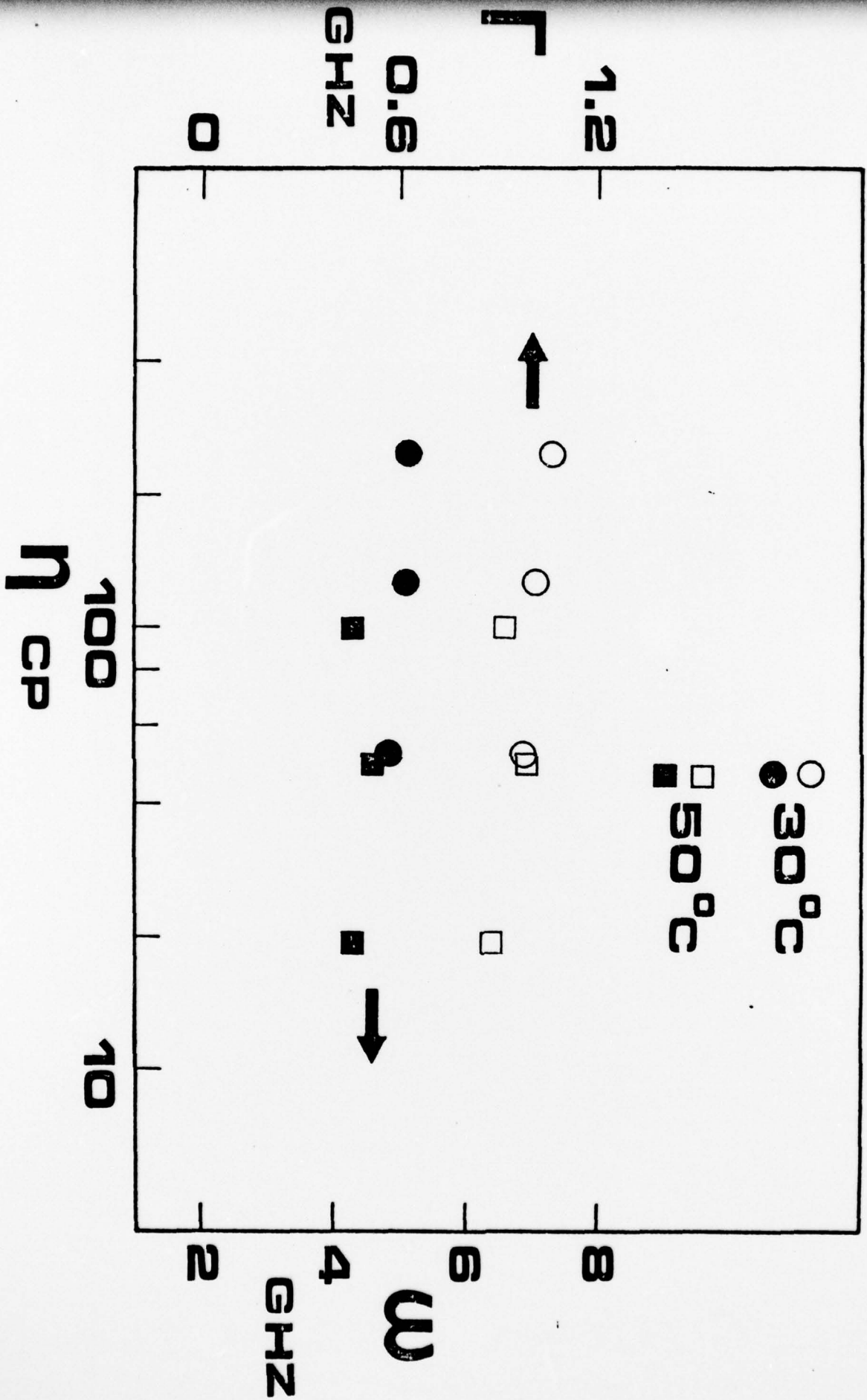
$$A = \frac{1}{2} \left\{ \sum_i \sum_j \frac{1}{N m} \left\langle \frac{\partial^2 u}{\partial Z_i \partial Z_j} \right\rangle e^{i q (Z_i - Z_j)} + \frac{3 k T q^2}{m} - \omega_q^2 \right\} \tag{II,10}$$

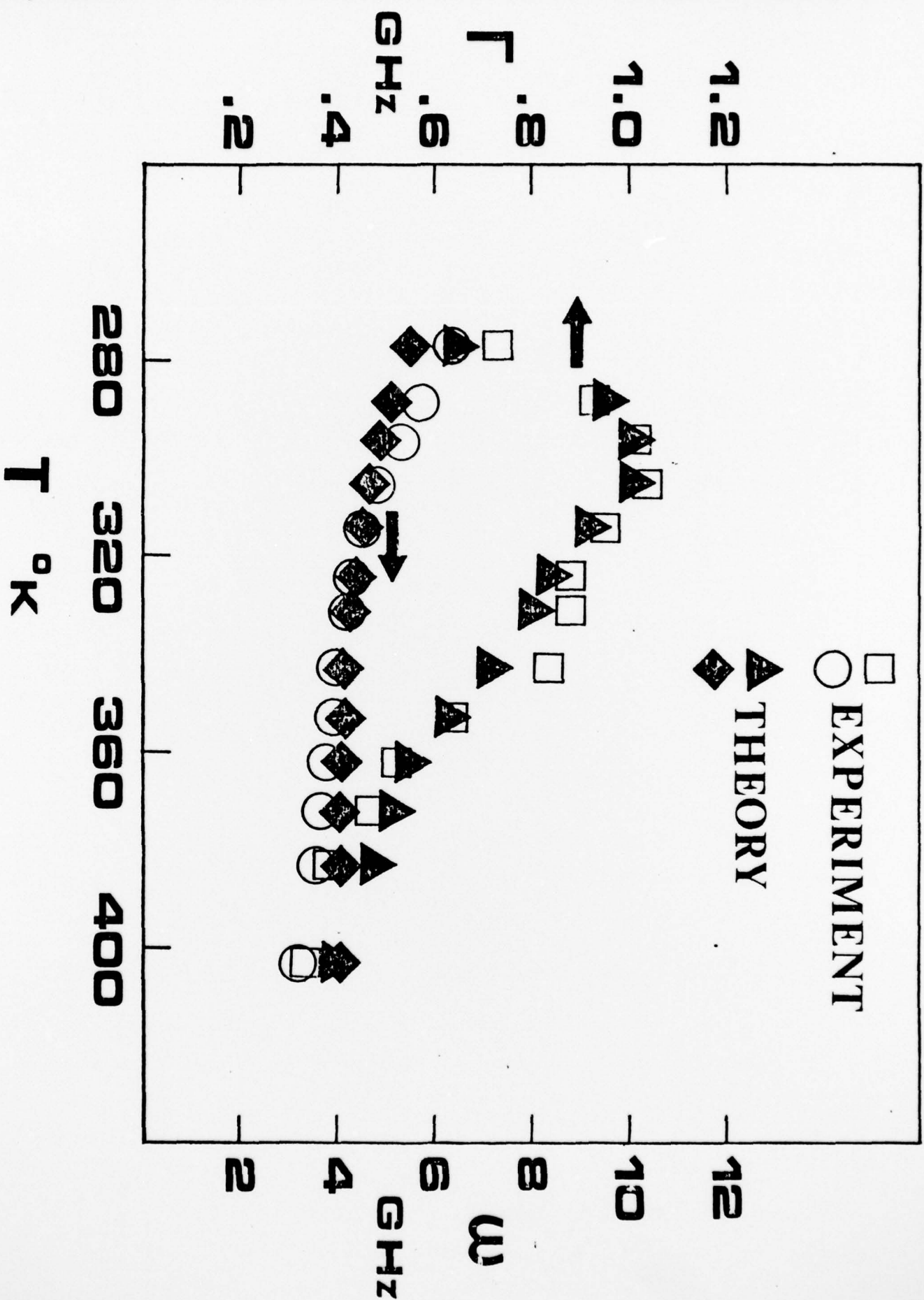
which is equivalent to Eq. (29) in the text.

Figure Captions

Figure 1. The Brillouin peak frequency and linewidth as a function of shear viscosity. The solid points are the frequency and empty ones are the linewidth.

Figure 2. Comparison of the theoretical and experimental Brillouin peak frequency and linewidth data as a function of temperature.





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