## LIGHT SCATTERING SPECTROSCOPIC STUDIES OF SILICONE FLUIDS

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#### ABSTRACT

# LIGHT SCATTERING SPECTROSCOPIC STUDIES

OF SILICONE FLUIDS

By

Katherine Emily Reed

A Brillouin light scattering spectroscopic study of both linear and cyclic polydimethylsiloxane liquids was undertaken to examine the effect of polymer chain length on various spectral parameters. Eight fluids were investigated at seven temperatures between 20°C and 85°C. The refractive index, Brillouin shift frequency and full Brillouin linewidth at half-height were obtained experimentally. These properties were found to be linearly decreasing functions of temperature for all fluids. The sonic velocity, adiabatic compressibility and sound absorption coeffcient were calculated and also found to vary linearly with temperature for each silicone.

At low molecular weights the molecular configuration, linear or cyclic, did not affect the acoustical properties. However, as the chain length or ring size increased the cyclic liquids exhibited larger shift frequencies and sonic velocities and lower compressibilities than the linear liquids.

At a single temperature the sonic velocity was found

Katherine Emily Reed

to increase rapidly to a molecular weight of approximately 1000 where it continued to rise very slowly with a further increase of molecular weight. Although experimental data supported Rao's Rule, a simpler empirical equation, relating the velocity linearly to reciprocal molecular weight, was found to adequately represent the data. In addition, the Brillouin shift frequency, full Brillouin linewidth and sound absorption coefficient varied with molecular weight in the same manner.

Landau-Placzek ratios were found to be relatively independent of temperature. Results were in good agreement with heat capacity data for silicones and other liquid polymers.

The acoustical parameters have been extended more than an order of magnitude in frequency in this study and are found to be in qualitative agreement with data obtained by ultrasonics.

### LIGHT SCATTERING SPECTROSCOPIC STUDIES OF SILICONE FLUIDS

Ву

Katherine Emily Reed

## A DISSERTATION

Submitted to Michigan State University in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

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TO MY HUSBAND

DR. PAUL G. GERTENBACH

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CHAPTER I

HISTORICAL

### LIGHT SCATTERING

The phenomenon of light scattering has been of interest to laymen and scientists for hundreds of years. Tyndall's success in simulating "blue sky" atmospheric scattering in the laboratory by passing white light through a gold sol and observing blue light perpendicular to the incident beam led to concentrated efforts to devise a workable theory of light scattering (1). He erroneously attempted to explain scattering using the laws of reflection, but it was Lord Rayleigh (2,3,4) who correctly identified it as a diffraction process and developed the foundation of elastic scattering of light for transparent, optically isotropic, non-interacting particles which were small compared to the wavelength of light. Later Smoluchowski (5) suggested that due to thermal motions of molecules in a liquid, the local density fluctuated through a region on the order of the wavelength of light. Using statistical thermodynamic fluctuation theory Einstein (6) derived a mathematical relationship between the total intensity of scattered light and density fluctuations. Mie (7) in 1908 developed a general electromagnetic theory of light scattering for non-interacting, spherical particles of arbitrary size which could be applied to systems in which the scatterers were large compared to  $\lambda_0$ , the wavelength of incident light.

The frequency distribution of the scattered light was first examined by Brillouin (8) in 1922. He treated the density fluctuations (also called sound waves, acoustical waves or phonons) which propagated throughout the medium with no directional bias. He maintained that the light scattered by these travelling fluctuations would undergo frequency shifts of equal magnitude analogous to the Doppler shift of classical physics and consequently derived the following equation:

$$\Delta \omega = \pm 2\omega_0 (V_c/c) n \sin \theta/2 \qquad [1]$$

where  $\omega_0$  is the incident frequency,  $\Delta \omega$  is the Brillouin frequency shift, c is the velocity of light,  $\theta$  is the angle of observation,  $V_{c}$  is the velocity of sound in the medium, and n is its refractive index. These Brillouin modes were observed first by Gross (9) in 1930. In Gross' work and all subsequent experiments an anomalous unshifted peak was also observed and was attributed for several years to a technical error such as dust. This central component was explained by Landau and Placzek (10) in 1934. By a fortuitous change of the two independent variables from density and temperature (used by Einstein) to entropy and pressure, they were able to effect a separation of the total intensity into two contributions: entropy fluctuations at constant pressure and pressure fluctuations at constant entropy. The entropy fluctuations were very slow, non-propagating thermal fluctuations, dissipated by thermal diffusion and, therefore,

had lifetimes dependent on the thermal diffusivity of the scattering medium. The unshifted intensity, commonly called the Rayleigh peak, was due to these isobaric entropy fluctuations. The pressure fluctuations, on the other hand, were propagating and gave rise to the Brillouin lines, one on either side of the Rayleigh component. The lifetime of the propagating acoustic wave was determined by the rate at which it was damped by losing energy to other modes of motion and to overcoming the intermolecular frictional forces and was in turn dependent upon the sound absorption coefficient.

Debye was responsible for extending the theory of light scattering to dilute solutions of macromolecules (11,12). After his initial suggestion many others made contributions to the thermodynamic theory of Rayleigh light scattering by small optically isotropic molecules (13,14,15). In the 1960's equivalent but more successful approaches were developed including an extrapolation of Van Hove's (16) theory of neutron scattering to light scattering (17) and the introduction of the phenomenological method of linearized hydrodynamics (18-24) in order to implicitly consider molecular interactions.

The development of intense, monochromatic radiation sources in the form of gas lasers in the early 1960's led to a surge in experimentation in light scattering spectroscopy. In addition, development of high resolution interferometers contributed to the increased accuracy of the experimental data and facilitated the observation of yet another intensity component called the "relaxation mode" or "Mountain line".

When it exists, it is evidenced by a low intensity background upon which the Rayleigh and Brillouin peaks are superimposed. The source of this added intensity is theorized to be coupling between the external translational modes of the scatterer and its internal vibrational modes. Energy in the form of acoustical waves in the medium is absorbed as vibrational energy and is later released thermally as the molecules relax back to their ground states.

### SILICONE FLUIDS

Since the silicones became industrially important in the 1940's, a wealth of information pertaining to their chemical and physical properties has been obtained and published. The silicones are organosilicon polymers in which the silicon atoms are bound through oxygen atoms to form chains or rings and have the following general form:

The usage of the term silicone became common when it was believed that there would be far reaching analogies between the chemical behaviors of carbon and silicon. The repeating unit  $R_2Si0$  appeared to correspond to a ketone  $R_2C0$ . Later it was found that the Si=0 bond was unstable compared to the C=0 bond and instead silicon formed single bonds to oxygen resulting in polymeric compounds. However the term "silicone" remained firmly implanted. There are many different silicones

but our attention in this work is restricted to the polydimethylsiloxane (PDMS) fluids and the following notation is used to designate specific molecules:



A number of both cyclic and linear molecules have been synthesized and fractionated to high purity from a polymer mixture of low molecular weights. In addition liquids containing a distribution of molecular weights are designated by their viscosities in centistokes. Several authors have compiled the information published in the literature concerning the silicones (25,26,27).

The structure of PDMS in absence of solvents or diluents is determined by the Si-O and Si-C bond distances and Si-O-Si and C-Si-C bond angles. It has long been known that the Si-O interatomic distance is considerably smaller than the sum of the atomic and ionic radii. The relatively large valence angle of the siloxane oxygen coupled with the large size of the Si atoms compared to those of C is thought to result in a long Si-CH<sub>3</sub> bond distance whose effect is to push the methyl groups so far from the Si-O-Si axis that virtually unrestricted rotation about the siloxane bond is possible. The small Si-O bond distance and large Si-O-Si bond angle have been explained using a resonance description of the bond including covalent, polar and double bond contributions (28). The presence of double bond character would explain the short Si-O bond and the large Si-O-Si angle. The partial donation of a lone pair of electrons from oxygen to the unfilled 3d levels of silicon  $(d\pi+p\pi)$ is thought to be responsible for the double bond character. The Si-C bond distance, on the other hand, has been found to be almost equal to the sum of the covalent radii and is probably basically a covalent single bond.

It is believed that the pure liquid molecular conformation is partially helical with siloxane bonds oriented toward the screw axis and methyl group pointed outward (29,30). This stable helix is believed to be due to the internal dipole compensation caused by the polar component of the siloxane bond giving rise to weak dipoles which align in the helix in such a way as to have opposing dipoles facing one another. Further evidence consists of entropy of dilution of the siloxanes in benzene and heat of mixing data (31). The high values of the entropy and lack of chain dependence on the heat of mixing both indicate that the liquid structure of a linear PDMS is destroyed upon solvation, so is considerably more ordered than many pure liquids.

PDMS rings with more than three -D- units are puckered.  $D_2$  is an unstable ring due to strain. Isolation of rings containing as many as thirty atoms has been accomplished. The physical behavior of the cyclic molecules is very different from that of their linear counterparts (25,26). Several

cyclic compounds are crystalline near room temperature. The temperature coefficient of viscosity is not as low for the cyclic as it is for the linear conformations (32). Also the viscosity of the cyclic molecules increases more rapidly with molecular weight than in the linear series (33).

The intermolecular forces in the polydimethylsiloxanes are unusually weak and lead to high compressibilities as well as other anomalous physical properties, including a low temperature coefficient of viscosity, low freezing and pour points, high vapor pressures and many others (34-38). The lack of change of viscosity with temperature has been interpreted in terms of the chemical structure of the linear molecules (29). Two opposing effects, the expansion of the helical coils and the increase in volume, which occur upon heating, are thought to somewhat compensate for one another resulting in very little net change in the mean intermolecular distances. However, this reasoning is speculative only and the physical factors responsible for the unusual behavior of the siloxanes remain unclear. Other investigators (39,40,41) have shown that the methyl groups also demonstrate virtually unhindered rotation and this is hypothesized to cause large space requirements for the methyl groups which in turn cause molecular volumes to be large (32) and intermolecular forces to be small.

Ultrasonic and viscoelastic techniques have been applied to the silicones to determine their acoustical properties. Weissler (42,43) was the first to investigate

the relationship between the velocity of sound and chain length and reported that at a molecular weight of 1000 the velocity reached an asymptotic value. Other workers have pursued this further (44,45,46,47) and have attempted to correlate their results with relaxation theories. Also Brillouin measurements were made recently on selected linear and cyclic polydimethylsiloxanes in order to elucidate the temperature and molecular weight dependence of their thermodynamic and acoustical properties (48).

The intent of this Brillouin scattering study was to examine spectroscopically several linear and cyclic polydimethylsiloxane liquids in order to determine the effects of chain length and molecular configuration on various acoustical properties including sonic velocity and sound absorption coefficient. It was hoped that this information would provide insights into the factors responsible for the weak intermolecular forces and unique liquid characteristics of this series. Further, it was hoped some information regarding the molecular motion responsible for phonon propagation and attentuation could be obtained.

CHAPTER II

THEORY

### THEORY

Light is scattered by a medium because it contains optical inhomogeneities. Inhomogeneities in pure materials are known to be caused by fluctuations in the optical dielectric constant. Static nonuniformities would not produce a frequency shift in the scattered light. However, time dependent thermal motions of molecules in a dense fluid create a frequency spectrum in the scattered light which is characteristic of the resulting time-dependent fluctuations. Light scattering theory has developed from hydrodynamic, quantum mechanical and statistical mechanical treatments.

When an electromagnetic wave strikes a scattering particle, it interacts with the polarizability and induces an oscillating dipole in the direction perpendicular to that of the incident electric vector. The magnitude of the induced dipole moment is directly proportional to the particle polarizability and the magnitude of the incident electric vector is given by

$$\mu_{\mathbf{x}} = \alpha_{\mathbf{x}\mathbf{y}} \stackrel{\rightarrow}{\mathbf{E}}_{\mathbf{y}}.$$
 [2]

The elctromagnetic wave, propagating in the z direction with its electric vector in the y direction, induces a dipole in the x direction proportional to the deformability

of the particle electron distribution. In general, the polarizability is a second order tensor but only the diagonal elements contribute when scattered light is polarized.

The intensity of the scattered light,  $I_{\theta}$ , for an isotropic sample is given by the Rayleigh equation (2,3)

$$I_{\theta} = I_{0} \frac{16\pi^{4} |\overline{\alpha}|^{2}}{r^{2} \lambda^{4}} (1 + \cos^{2} \theta)$$
 [3]

where I is the incident intensity, r is the distance from the scatterer to the point of observation,  $\lambda$  is the wavelength of light in the medium,  $\theta$  is the scattering angle measured from the direction of propagation of the incident radiation, and  $\overline{\alpha}$  is the average isotropic polarizability given by

$$\overline{\alpha} = \frac{1}{3}(\alpha_{xx} + \alpha_{yy} + \alpha_{zz}). \qquad [4]$$

A Clausius-Mossotti type equation was used by Bhagavantam (49) to express  $\overline{\alpha}$  in terms of the mean fluctuation of the dielectric constant about its average value

$$\overline{\alpha} = \frac{\mathbf{V} < |\Delta \varepsilon| >}{4\pi}$$
[5]

where V is the small spherical scattering volume. Substitution from Equation [5] into [3] gives

$$I_{\theta} = I_{0} \frac{\pi^{2} V^{2} < (\Delta \varepsilon )^{2} >}{r^{2} \lambda^{4}} (1 + \cos^{2} \theta), \qquad [6]$$

which is the initial equation used by Einstein and by Landau and Placzek in their statistical thermodynamic treatments of the intensity of scattered light. For simplicity Equation [6] is usually written for  $\theta = 90^{\circ}$ . Clearly the mean square fluctuation of the dielectric constant is the only unknown and cannot be directly evaluated. Instead it is evaluated in terms of two other linearly independent thermodynamic properties.

Einstein (6) expressed the fluctuation of the dielectric constant as fluctuations in the density and temperature:

$$\Delta \varepsilon = \left(\frac{\partial \varepsilon}{\partial \rho}\right)_{\mathbf{T}} \Delta \rho + \left(\frac{\partial \varepsilon}{\partial \mathbf{T}}\right)_{\rho} \Delta \mathbf{T} \qquad [7]$$

He then assumed that the contribution made by  $(\partial \varepsilon / \partial T)_{\rho}$ was negligibly small compared to  $(\partial \varepsilon / \partial \rho)_{T}$ . By eliminating the  $\Delta T$  term, Einstein developed the following equation for the intensity of light scattered at 90°.

$$I_{90} = I_{O} \frac{\pi^{2}V}{r^{2}\lambda^{4}} \left(\frac{\partial \varepsilon}{\partial \rho}\right)_{T}^{2} \rho^{2}kT\beta_{T} \qquad [8]$$

In this equation k is the Boltzmann constant and  $\beta_{\rm T}$  is the isothermal compressibility. The assumption that the change in dielectric constant with temperature at constant density is negligible has been experimentally determined to be valid for some substances but not for others (50).

The experimental verification of the existence of a frequency spectrum of scattered light led Landau and Placzek (10) to attempt a separation of the intensity into terms which corresponded to the lines of the Rayleigh-Brillouin triplet. By changing independent variables from density

and temperature to entropy and pressure,

$$\Delta \varepsilon = \left(\frac{\partial \varepsilon}{\partial S}\right)_{P} \Delta S + \left(\frac{\partial \varepsilon}{\partial P}\right)_{S} \Delta P, \qquad [9]$$

and proceding in the manner of Einstein, they succeeded in making the separation. The fluctuations in entropy and pressure have been shown to be statistically independent of one another (51), so the mean square dielectric constant fluctuation is given by

$$\langle (\Delta \varepsilon)^2 \rangle = \left(\frac{\partial \varepsilon}{\partial S}\right)^2 \langle (\Delta S)^2 \rangle + \left(\frac{\partial \varepsilon}{\partial P}\right)^2 \langle (\Delta P)^2 \rangle$$
[10]

where the angular brackets indicate an ensemble average over the initial states of the system.

Each term in [10] has been evaluated by statistical thermodynamics (51) and the results are

$$\left(\frac{\partial \varepsilon}{\partial S}\right)_{P} = \left(\frac{\partial \varepsilon}{\partial T}\right)_{P} \left(\frac{\partial T}{\partial S}\right)_{P} = \left(\frac{\partial \varepsilon}{\partial T}\right)_{P} \frac{T}{\rho V C_{P}},$$
 [11]

$$\langle (\Delta S)^2 \rangle = k \rho V C_p$$
, [12]

$$\left(\frac{\partial \varepsilon}{\partial \mathbf{p}}\right)\mathbf{s} = \left(\frac{\partial \varepsilon}{\partial \rho}\right)\mathbf{s}\left(\frac{\partial \rho}{\partial \mathbf{p}}\right)\mathbf{s} = \left(\frac{\partial \varepsilon}{\partial \rho}\right)\mathbf{s} \rho^{\beta}\mathbf{s}$$
 [13]

and  $\langle (\Delta P)^2 \rangle = kT/V\beta_S$  [14]

where  $C_p$  is the heat capacity at constant pressure and  $\beta_s$  is the adiabatic compressibility. By substituting for the appropriate terms into [10] we obtain

$$<(\Delta\varepsilon)^{2}> = (\frac{\partial\varepsilon}{\partial T})^{2} \frac{kT^{2}}{\rho VC_{p}} + (\frac{\partial\varepsilon}{\partial \rho})^{2} \frac{\rho^{2}\beta s^{kT}}{V}$$
 [15]

By using Equation [7] and the fact that  $(\partial T/\partial \rho)_{S} =$ 

 $(\partial P/\partial T) = T/C_V \rho^2$ , it is found that

$$\frac{\partial \varepsilon}{\partial \rho} = \left( \frac{\partial \varepsilon}{\partial \rho} \right)_{T} + \left( \frac{\partial \varepsilon}{\partial T} \right)_{\rho} \left( \frac{\partial P}{\partial T^{\rho}} \right)_{C_{V} \rho^{2}}^{T} .$$
 [16]

Then assuming that  $(\partial \varepsilon / \partial T)_{\rho}^{<<} (\partial \varepsilon / \partial \rho)_{T}^{}$  (53), the same assumption made by Einstein, results in elimination of the second term in [16], so that the final form of  $<(\Delta \varepsilon)^{2}>$ can be written

$$<(\Delta\varepsilon)^{2}> = \left(\frac{\partial\varepsilon}{\partial T}\right)_{P}^{2} \frac{kT^{2}}{\rho VC_{p}} + \left(\frac{\partial\varepsilon}{\partial\rho}\right)_{T}^{2} \frac{\rho^{2}\beta_{S}kT}{V}$$
 [17]

Now, substituting this expression into [6] we obtain an intensity equation containing two terms

$$I_{90} = I_{0} \frac{\pi^{2} V}{r^{2} \lambda^{4}} \left[ \left( \frac{\partial \varepsilon}{\partial T} \right)^{2} \frac{k T^{2}}{P_{\rho} C_{p}} + \left( \frac{\partial \varepsilon}{\partial \rho} \right)^{2} \frac{\rho^{2} k T \beta}{T} S \right] . \qquad [18]$$
  
Rayleigh Brillouin

The first term involves fluctuations with temperature at constant pressure and represents a nonpropagating mode. This component of the scattered light was thought to correspond to the unshifted Rayleigh line. The Rayleigh linewidth is proportional to the rate of decay of the fluctuations and broadened somewhat by the damping thermal dissipative processes. The second term involves fluctuations with density at constant temperature or entropy which are propagated through the medium. They can be viewed as successive compressions and rarefactions which propagate or travel in a wavelike manner. This component of the scattered intensity was thought to correspond to the mode which is shifted in frequency by an amount proportional to the velocity of the thermal waves. Since scattering can occur from waves travelling in opposite directions, this intensity component is actually divided between two lines which together are called the Brillouin doublet and are equally shifted in frequency from the Rayleigh line. The lifetimes of these propagating thermal sound waves are determined by the rate at which they are damped by losing energy to other modes of motion and intermolecular frictional forces.

The remarkable similarity between the Einstein total intensity equation and the Brillouin intensity term in their equation led Landau and Placzek to propose the intensity ratio which bears their names:

$$\frac{I_{\text{TOTAL}}^{\text{Einstein}}}{I_{\text{BRILLOUIN}}^{\text{Landau, Placzek}}} = \frac{I_{\text{R}}^{+2I_{\text{B}}}}{2I_{\text{B}}} = \frac{I_{\text{O}}^{(\pi^{2}V/r^{2}\lambda^{4})} [(\partial \varepsilon/\partial \rho)_{\text{T}}^{2}] \rho^{2}kT\beta_{\text{T}}}{I_{\text{O}}^{(\pi^{2}V/r^{2}\lambda^{4})} [(\partial \varepsilon/\partial \rho)_{\text{T}}^{2}] \rho^{2}kT\beta_{\text{S}}}$$
[19]

This intensity ratio is usually rearranged to the following form and is called the Landau-Placzek ratio.

$$\frac{I_{R}}{2I_{B}} = \frac{\beta_{T}}{\beta_{S}} - 1 = \frac{C_{P}}{C_{V}} - 1 = \gamma - 1$$
[20]

Thus absolute scattering intensities are not necessary to obtain heat capacity ratios of the medium.

The statistical thermodynamic method as delineated above provides only a qualitative treatment of light scattering. It is based on equilibrium thermodynamics and as such its conclusions are not completely accurate. For example, this approach does not predict or take into account any frequency dependence or dispersion of any of the parameters in the equations. Cummins and Gammon (53) have added correction terms for dispersion to [18] and [20] but we must turn to the linearized hydrodynamic theory of irreversible thermodynamics for a detailed development of the time and frequency dependences of the thermodynamic and hydrodynamic variables.

The hydrodynamic theory of fluctuations differs from the thermodynamic approach because it examines the behavior in time of density fluctuations and takes into account the effect of density fluctuations in adjacent volume elements. The function which contains information about the fluctuations is the generalized structure factor,  $S(\vec{k},\omega)$ , and is the space and time Fourier transform of the density-density correlation function. Here  $\vec{k}$  is the change in the wave vector and  $\omega$  is the shift in the angular frequency of the scattered light. The intensity of the scattered light is directly proportional to  $S(\vec{k},\omega)$  as given by

 $I(\vec{R},\omega) = I_{O}(\alpha^{2}\Omega^{4}N/2\pi c^{4}R^{2}) \sin^{2}\phi S(\vec{k},\omega) \qquad [21]$ 

where N spherically symmetric molecules of polarizability  $\alpha$  scatter light at an angle  $\phi$  measured from the electric

vector of the incident wave to  $\vec{R}$ , the point of observation. The angular frequency of the scattered light is  $\Omega$ , the shift in the angular frequency is  $\omega$ , and the change in the wave vector is  $\vec{k}$  which is defined by

$$\vec{k} = \vec{k}_1 2 \sin(\theta/2)$$
 [22]

where  $\theta$  is the scattering angle measured from the direction of propagation of the incident light and  $\mathbf{k}_1$  is the wave vector of the incident light. In order to obtain the correlation function from which the generalized structure factor is deduced, it is necessary to solve the linearized hydrodynamic equations for the time-dependent,  $\mathbf{k}^{\text{th}}$  Fourier component of the density. The following development is essentially that of Mountain (18-23) and details of the calculations are omitted in order to more clearly demonstrate the method.

The linearized hydrodynamic equations are the continuity equation, the longitudinal part of the Stokes-Navier equation, and the energy transport equation. The continuity equation assumes that matter appearing in a volume element does so by flowing through a boundary of that element and is given by

$$\frac{\partial \rho_1}{\partial t} + \rho_0 \operatorname{div} V = 0 \qquad [23]$$

where  $\rho_0$  is the equilibrium value of the density,  $\rho_1$  is the time-dependent density increment, and V is the flow velocity. The Navier-Stokes equation is

$$\rho_0 \left(\frac{\partial V}{\partial t}\right) + \left(\frac{C_0^2}{\gamma}\right) \operatorname{grad} \rho_1 + \frac{C_0^2 \beta \rho_0}{\gamma} \operatorname{grad} T_1 - \left(\frac{4}{3} \operatorname{s}^{+} \eta_B\right) \operatorname{grad} \operatorname{div} V = 0$$

[24]

and the energy transport equation is

$$\rho_0 C_V \left( \frac{\partial T_1}{\partial t} \right) - \frac{C_V (\gamma - 1)}{\beta} \left( \frac{\partial \rho_1}{\partial t} \right) - \lambda V^2 T_1 = 0$$
 [25]

where T and T are the equilibrium and time-dependent o l values of the temperature,  $\beta$  is the thermal expansion coefficient,  $\lambda$  is the thermal conductivity,  $\eta_{s}$  and  $\eta_{b}$  are the shear and bulk viscosities,  $\gamma$  is the heat capacity ratio, and C<sub>o</sub> is the low frequency limit of the sound velocity.

The first step in Mountain's adaption of Van Hove's neutron scattering method is to obtain the Fourier and Laplace transforms of the linearized hydrodynamic equations of motion and next to solve the resulting equations for the Fourier-Laplace transform of the density, designated as n(k,s) and given by

$$n(k,s) = n(k) \frac{s^{2} + (a+b)k^{2}s + abk^{4} + C_{0}^{2}(1-1/\gamma)k^{2}}{s^{3} + (a+b)k^{2}s^{2} + (C_{0}^{2}k^{2}+abk^{4})s + aC_{0}^{2}k^{4}/\gamma}$$

[26]

where  $a = \lambda/\rho_0 C_V$ ,  $b = (4\eta_S/3 + \eta_B)/\rho_0$  and s is a dummy variable used to evaluate the Fourier and Laplace transforms of the density fluctuations. The inverse Laplace transform of n(k,s) is n(k,t), the time-dependent k<sup>th</sup> Fourier component of the density. In order to obtain the inverse Laplace transform of [26], it is necessary to find the roots to the cubic equation in the denominator, called the dispersion equation:

$$s^{3} + (a+b)k^{2}s^{2} + (C_{0}^{2}k^{2}+abk^{4})s + aC_{0}^{2}k^{4}/\gamma = 0$$
 [27]

An approximate solution to [27] consisting of a power series of coefficients is preferred to the exact algebraic one because it is more easily evaluated and interpreted in terms of the physical parameters characterizing the system. The lowest order solutions to the dispersion equation are

$$s = \pm iC_{0}k - \frac{1}{2} \left[ \frac{4\eta_{s}/3 + \eta_{B}}{\rho_{0}} + \frac{1}{\rho_{0}} (\frac{\lambda}{C_{V}} - \frac{\lambda}{C_{P}}) \right] k^{2} \quad [28]$$

$$s = -\frac{\lambda k^{2}}{\rho_{0}C_{P}} \quad . \quad [29]$$

The real component of the first solution is the halfwidth at half-height of a Brillouin line

$$\Gamma k^{2} = \frac{1}{2} \left[ \frac{4\eta_{S}/3 + \eta_{B}}{\rho_{0}} + \frac{1}{\rho_{0}} \left( \frac{\lambda}{C_{V}} - \frac{\lambda}{C_{P}} \right) \right] k^{2}$$
 [30]

and  $\Gamma$  is the temporal absorption coefficient or lifetime of the fluctuation.

It is now possible to determine n(k,t), the inverse Laplace transform of n(k,s) and the lowest order terms are

$$n(k,t) = n(k) \left[ \frac{C_{p} - C_{v}}{C_{p}} \exp(-\lambda k^{2} t / \rho_{0} C_{p}) + \frac{C_{v}}{C_{p}} \exp(-\Gamma k^{2} t) \cos C_{0} k t \right].$$
[31]

The k<sup>th</sup> component of the density-density correlation function can now be constructed from n(k,t) as indicated by

$$F(k,t) = n(-k)n(k,t)$$
 [32]

$$= \langle n(-k)n(k) \rangle \left[ \frac{C_{p} - C_{V}}{C_{p}} \exp(-\lambda k^{2} t / \rho_{0}C_{p}) + \frac{C_{V}}{C_{p}} \exp(-\Gamma k^{2} t) \cos C_{0} k t \right]$$
[33]

It is now possible to write the generalized structure factor, which is directly proportional to the scattered light intensity and related to F(k,t) as follows

$$S(k,\omega) = 2Re \int_{0}^{\infty} dt \exp(i\omega t) F(k,t)$$
 [34]

Since

$$S(k,\omega) = S(k)\sigma(k,\omega)$$
[35]

where

$$S(k) = \langle n(-k)n(k) \rangle$$
, [36]

the function  $\sigma(\mathbf{k}, \omega)$ , the ordinary structure factor, contains the frequency distribution of the scattered light and is

$$\sigma(\mathbf{k},\omega) = \frac{C_{\rm p} - C_{\rm V}}{C_{\rm p}} \frac{2\lambda k^2 / \rho_0 C_{\rm p}}{(\lambda k^2 / \rho_0 C_{\rm p})^2 + \omega^2} + \frac{C_{\rm v}}{C_{\rm p}} \left[ \frac{\Gamma k^2}{(\Gamma k^2)^2 + (\omega + C_0 k)^2} + \frac{\Gamma k^2}{(\Gamma k^2)^2 + (\omega - C_0 k)^2} \right] [37]$$

All terms are easily recognized as Lorentzian in shape since -1  $I_{term} \propto (A+B\omega^2)$ . The first term corresponds to a density fluctuation relieved by a thermal diffusion process where  $\lambda/\rho_0 C_v$  is the thermal diffusivity. This is a nonpropagating mode; therefore, there is no shift from the incident frequency, and information about the Rayleigh line is contained in this term. The second term represents a propagating decay in the fluctuation and results in two Brillouin components which are equally shifted from the incident frequency.

The frequency spectrum of light scattered by most pure substances cannot be accurately predicted by this analysis. With the exception of liquid metals, most materials have been found to exhibit experimental sound absorptions which are always larger than classically predicted. Two general processes are thought to be responsible for the excess absorption and are dispersive relaxation phenomena. The first is a thermal relaxation in which there is a weak coupling between the internal vibrational and external translational degrees of freedom of the molecule. The equilibrium distribution of energy is disturbed by the periodic compressing and decompressing of volume elements by the travelling sound wave. The exchange of energy between the internal and external modes which occurs while the system is returning to equilibrium may be expressed by a simple rate equation

$$dE(T_{i})dt = -\left[E(T_{i}) - E(t)\right]/\tau'$$
 [38]

where  $\tau'$  is the relaxation time and T<sub>i</sub> and T are the temperatures of the internal and external degrees of freedom. In light scattering theory the relaxation is described by
introducing a frequency dependent bulk viscosity

$$\eta_{\rm B} = \eta_{\rm B}^0 + \eta_{\rm B}^{\prime} / (1 + i\omega\tau')$$
 [39]

or by adding an additional hydrodynamic equation for a new state variable, the internal degree of freedom. The second type of relaxation process assumes that the passage of a sound wave actually induces a structural change in the molecule and the relaxation time is determined by the rate at which the molecule returns to its initial structure.

Mountain (19) has extended his hydrodynamic treatment of the spectral distribution of scattered light to include a thermal relaxation process which can be described by a single relaxation time. He introduced a bulk viscosity consisting of two terms, one dependent and the other independent of frequency. The modification, therefore, was incorporated into the Navier-Stokes equation which became

$$\rho_{0} \left(\frac{\partial V}{\partial t}\right) + \left(\frac{C^{2}}{\gamma}\right) \text{ grad } \rho_{1} + \left(\frac{C^{2}_{0}\beta\rho_{0}}{\gamma}\right) \text{ grad } T_{1} - \left(4\eta_{S}/3+\eta_{B}\right) \text{ grad div } V$$
$$- \int_{0}^{t} \eta'(t-t') \text{ grad div } V(t')dt = 0$$

[40]

where  $\eta_B$  is the frequency independent part and  $\eta'$  is the Fourier transform of the frequency dependent part. The procedure to obtain the generalized structure factor was identical to that previously outlined so only the significant results are presented here. The most striking difference appears in the ordinary structure factor as an additional

intensity mode.

$$\sigma(\mathbf{k},\omega) \simeq (1-1/\gamma) \left[ \frac{2\lambda k^2 / \rho_0 C_p}{(\lambda k^2 / \rho_0 C_p)^2 + \omega^2} \right] +$$

$$\left[\frac{(C_{\infty}^{2}-C_{0}^{2})k^{2}-(V^{2}/C_{0}^{2}-1)(C^{3}/V^{2}\tau^{2}+C_{0}^{2}k^{2}(1-1/\gamma)}{C^{4}_{0}/V^{4}\tau^{2}+V^{2}k^{2}}\right]$$

$$X \quad \left[ \frac{2C_0^2/V^2\tau}{C_0^4/V^4\tau^2 + \omega^2} \right]$$

+ 
$$\left[\frac{\left[1-C_{0}^{2}/V^{2}\left(1-1/\gamma\right)\right]\left[V^{2}k^{2}+C_{0}^{2}/V^{2}\tau^{\frac{3}{2}}-(C_{\infty}^{2}-C_{0}^{2})k^{2}\right]}{C_{0}^{4}/V^{4}\tau^{2}+V^{2}k^{2}}\right]$$
x 
$$\left[\frac{\Gamma_{B}}{\Gamma_{B}}+\frac{\Gamma_{B}}{\Gamma_{B}}\right]$$
[41]

$$X \qquad \left[ \frac{\Gamma_{B}}{\Gamma_{B}^{2} + (\omega - Vk)^{2}} + \frac{\Gamma_{B}}{\Gamma_{B}^{2} + (\omega + Vk)^{2}} \right] \qquad [41]$$

As in [37] all terms are Lorenzian in character. The first term is identical to the Rayleigh mode obtained in the absence of relaxation. The second term is also a nonpropagating mode of decay and is related to the coupling between the internal and external degrees of freedom of the molecules. The last term corresponds to the phonon modes or Brillouin lines and contains terms in  $\tau$ , the relaxation time of the new thermal process. Not only the intensity but also the linewidth of a Brillouin line is altered by the presence of relaxation. The linewidth is not a simple additive property as can be seen by comparing the following expression

$$2\Gamma_{B} = ak^{2} + b_{0}k^{2} - (\frac{C_{0}^{2}}{V^{2}})(\frac{ak^{2}}{\gamma}) + (\frac{b_{1}k^{2}}{1+V^{2}k^{2}\tau^{2}})(1-ak^{2}\tau)$$
 [42]

with equation [30]. In light scattering experiments the unshifted relaxational line is a very broad low intensity line upon which the Rayleigh-Brillouin triplet is superimposed and is recognized by a low intensity between the Rayleigh line and its associated Brillouin lines.

The intensity ratio in the case of relaxation is a much more complicated expression than the classical Landau-Placzek result because the unshifted intensity of the new thermal mode is included when evaluating I<sub>C</sub>, and the Brillouin intensity is also affected:

$$\frac{I_{C}}{2I_{B}} = \frac{(1-1/\gamma) (C_{0}^{2}-C_{0}^{2})k^{2} - (V^{2}/C_{0}^{2}-1) [(C_{0}^{4}/V^{2}\tau^{2}) + C_{0}^{2}k^{2} (1-1/\gamma)]}{[1-C_{0}^{2}/V^{2} (1-1/\gamma)] [V^{2}k^{2} + C_{0}^{2}/V^{2}\tau^{2}] - (C_{\infty}^{2}-C_{0}^{2})k^{2}}$$

Equation [43] reduces to the classical Landau-Placzek value when phonon frequencies are small, that is,  $Vk\tau <<1$ . And when the phonon frequencies are large,  $Vk\tau >>1$ , the result is

$$\frac{I_{C}}{2I_{B}} = (\gamma-1) \left[ 1 + \left(\frac{\gamma}{\gamma-1}\right) \left(\frac{C^{2}-C_{0}^{2}}{C_{0}^{2}}\right) \right] \qquad (44)$$

In actual practice it is difficult to compare the theoretical prediction with experiment because there is usually large error involved in determining the intensity of the second nonpropagating mode because it is so broad. Mountain (20) has also deduced the ordinary structure factor for a thermal relaxation by introducing an equation of motion for the thermal property. A comparison of the two approaches gave identical results for a structural relaxation but slightly different ones in the higher order corrections for the case of coupling between the internal and external degrees of freedom.

Litovitz and Herzfeld (54) have developed a classification scheme for liquids based on the behavior of their sound absorption coefficients,  $\alpha$ , with temperature. All fluids except liquid metals have been shown to exhibit sound absorption coefficients significantly higher than predicted by the Stokes equation of classical absorption

$$\alpha_{class} = \frac{2}{3} \frac{\omega^2}{V^3 \rho_0} \eta + \frac{3}{4} (\gamma - 1) (\lambda / C_p)$$
 [45]

where the first term represents absorption due to viscosity and the second due to heat conduction. Liquid metals are alone in that they are the only fluids for which heat conduction is an important source of absorption. Liquids are divided into the following classifications:

Group I : Normal Liquids - Monatomic and Diatomic Liquids, Liquid Metals  $d\alpha/dT = 0$ Group II: Kneser Liquids - Most Organic and Some Inorganic Liquids  $d\alpha/dT > 0$ Group III: Associated Liquids - Water, Alcohols  $d\alpha/dT < 0$ 

The normal liquids have absorptions only slightly greater than the classical value. Kneser liquids have a positive temperature coefficient and have a ratio  $\alpha/\alpha_{class}$  which generally falls between 3 and 400. It is thought that the excess absorption is due to a thermal type of relaxation. Associated liquids, on the other hand, are characterized by a negative temperature coefficient, have a ratio  $\alpha/\alpha_{class}$ between 3 and unity, and probably owe their excess absorption to a structural relaxation process. CHAPTER III

EXPERIMENTAL INFORMATION

### APPARATUS

A. THE BRILLOUIN SPECTROPHOTOMETER The Brillouin spectrophotometer used for all light scattering measurements was designed and characterized by S. Gaumer (55). However, in order to elucidate the instrumentation necessary to obtain Brillouin spectra and because modifications have been incorporated recently, a block diagram, Figure 1, and brief description of the instrument follow. Further details as well as design considerations are available in the literature (55).

All optical components of the system were mounted on a vibrationally insulated aluminum slab which served as an optical bench. The light source was a frequency stabilized Spectra Physics argon ion laser. The most intense single mode of the 5145 Å line was chosen as the incident frequency. The mode was selected with the aid of a Spectra Physics Optical Spectrum Analyzer and an external etalon. The laser cavity itself contained a solid etalon which, when tuned, scanned the modes of the laser lines under examination. The analyzer output was displayed on a Tektronix Storage Oscilliscope which allowed the selection of a single mode. Typical laser output powers were in the 500 mw range. The exact polarization of a polarization rotator attached to the laser was calibrated by a piece of glass with known refractive index mounted at its Brewster angle. (55)





The laser light beam impinged on an adjustable mirror mounted on a triangular rail so that its position could be changed to accomodate different scattering angles. The mirror itself could be rotated and tilted on its mount in order to direct the light beam precisely along a carefully defined optical path. The purpose of this mirror was to deflect the incident light across a fully rotatable Bridgeport table to its center where the scattering sample was placed. Two pinholes were mounted exactly opposite one another on a platter which extended the full diameter of the table. Pinhole positions were adjustable in the vertical and horizontal directions with micrometer screws. At the center of the platter was a holder for the scattering cell holder.

Light scattered from the sample initially passed through two variable apertures located at the ends of a one inch diameter pipe. The aperture diameters were set at one millimeter and 0.5 centimeters repectively. The pipe was fitted through an opening in a light-tight aluminum box. The light next impinged on a 100 millimeter focal length acromatic antireflectively coated lens which collimated the light and directed it to the interferometer. A stray light collector located between the lens and the interferometer served to block all but the light emanating from the scattering volume of the sample. The aluminum housing was connected to the casing of a Tropel Model 350 Fabry-Perot type interferometer by a bellows.

The interferometer was mounted on a base plate designed to be adjustable both vertically and horizontally. The interferometer consisted of two optical flats which were one inch in diameter and polished to a flatness of  $\lambda/100$ , Each was coated on one side with a broad band dielectric to approximately 95% reflectivity and on the other side with an antireflective coating. The mirrors were glued into steel holders that were screwed to their mounts in the interferometer housing. In actual operation the rear mirror was stationary but its position could be adjusted slightly with three micrometer screws. The front mount was able to slide along invar rods so that the distance separating the mirrors, and therefore the free spectral range, could be adjusted. This mirror mount was attached to three matched piezoelectric crystals and linearly moved small distances while scanning. The crystals were subjected to a linear voltage ramp supplied by a Tropel Model 351 Ramp Generator. Maximum voltage attained was 700 volts which corresponded to a maximum displacement of the mirror on the order of one micron. The rear of the interferometer was attached by another bellows to a second light-tight aluminum box.

After analysis by the interferometer the light impinged on an antireflectively coated, 1000 millimeter focal length lens and was focused at a one millimeter diameter pinhole located at the rear of the box. Immediately behind the pinhole was a piece of polarizing film rotated to allow only

vertically polarized light to pass. A shutter separated the optical detection train from the EMI photomultiplier tube. The tube was cooled to -15°C by a Products For Research refrigeration unit. The signal from the photomultiplier was amplified by a Keithly high speed picoammeter whose signal was in turn fed to a Sargent Welch SRG strip chart recorder.

A new precise alignment procedure was developed in order to obtain Brillouin spectra of consistently high finesse. In this work values as high as 70 were obtained with 60 being a typical value. The few instances of lower finesse were directly attributable to the instability of the optics to mechanical disturbances transmitted from other laboratories. In the absence of such mechanical disturbances as well as significant changes in the temperature and humidity, the optics and especially the interferometer were stable over long periods of time. This represented a significant improvement over previous capabilities because it allowed an entire series of measurements to be made at a consistently high finesse, thereby reducing the instrumental linewidth and decreasing the intrinsic measurement error. The instrumental alignment was performed as delineated below.

- 1. Check mode structure and polarization of laser.
- 2. Define optical axis by placing in each aluminum box a pinhole which has been mounted and constructed for this purpose. Adjust position of He-Ne alignment laser so that its light beam

passes precisely through the center of each pinhole.

- 3. Rotate the Bridgeport table to 180° and adjust its pinholes in the light beam which now defines the optical axis.
- 4. Secure the collimating lens to the rail in the first aluminum box. Align lens so that the transmitted beam passes through the pinholes located in each box and so that the light reflected from the front and center surfaces is colinear and passes back through the center of the pinhole mounted on the Bridgeport table.
- 5. Insert and secure the aluminum light pipe and close apertures to their minima. Position aperture centers on the optical axis, then set diameters at 1.0 and 5.0 millimeters for the front and rear respectively.
- Position the pinhole which precedes the photomultiplier at the rear of the second aluminum box.
- 7. Screw in mounted interferometer mirrors. Locate approximate mirror separation desired and lock the front mirror. Measure true mirror separation with Vernier caliper.
- 8. Adjust interferometer base both vertically and horizontally until the reflection from the front mirror passes back through the pinholes

and lens along the optical axis.

- 9. Insert focusing lens and adjust so that the image is centered on the rear pinhole.
- 10. Roughly align interferometer mirrors by adjusting micrometer screws on rear mount until emerging light pattern is circularly symmetric.
- 11. Check alignment of focusing lens and rear pinhole and make small adjustments if necessary.
- 12. Remove the two alignment pinholes and close both aluminum boxes and the interferometer housing.
- 13. Rotate Bridgeport table to 90°.
- 14. Adjust angle of movable mirror and position so that argon ion laser beam is reflected and passes through the previously aligned pinholes on the Bridgeport table.
- 15. Fine tune the interferometer by examining the light scattered at 90° by a strong Rayleigh scatterer. Set ramp generator at its fastest scan rate and feed photomultiplier tube signal to oscilloscope. Nudge micrometer screws gently to ascertain their correct positions as indicated by maximum intensity of displayed Rayleigh lines. Finally, adjust each piezoelectric with its control on the ramp generator again tuning to maximum intensity of scattered light.

16. Positioning the sample cell completes the alignment procedure. Secure the scattering cell in the base of the temperature control block. With the three compressed spring adjustments allow the transmitted beam to pass through the far pinhole and the reflected beam to pass back into the laser beam.

All spectra were obtained by allowing the recorder to run at maximum speed as well as maximizing the time for one complete scan of the interferometer, in this case 1000 seconds. As shown in Figure 2 a typical spectrum consists of many spectral orders each of which is composed of a central or Rayleigh component and two equally displaced Brillouin lines. Since the voltage ramp to the interferometer piezoelectric crystals is not perfectly linear, especially at the beginning and end of the ramp, only the middle two spectral orders of each scan were used to extract the necessary data. Experimental parameters from four orders were averaged for each fluid at each temperature and were in good agreement with one another.

A preliminary spectrum was examined for each fluid in order to determine the proper mirror separation and to ascertain whether there was a depolarized component in the scattered light. For this work a proper mirror separation was judged to be that at which the distance between a Rayleigh line and its adjacent Brillouin line was equal to the distance separating Brillouin line of adjacent spectral orders.



Figure 2. Three Rayleigh-Brillouin Spectral Orders

In order to ensure that the Brillouin lines were associated with the Rayleigh lines nearest them, the initial mirror separation was taken to be very small so that spectral orders were separated by a large distance. Since a plot of  $v_{\rm B}$ /frs versus d is linear and passes through the origin, the slope was determined from the results of the preliminary spectrum. Then the mirror separation corresponding to one third of the free spectral range was calculated. All mirror separations used were approximately 1.40 centimeters. The depolarized component H<sub>V</sub> of the scattered light was found to be negligible in all fluids. The  $\rho_{\rm V}$  depolarization ratios of other fluids in the series have been reported (48) to be on the order of 10<sup>-2</sup> indicating very low H<sub>V</sub> intensities.

B. CONTROL AND MEASUREMENT OF TEMPERATURE A cross-sectional view of the thermostatted jacket used to thermally insulate and heat the scattering cell is shown in Figure 3. It was designed primarily by Gaumer (55) and modified as follows. An additional hole was drilled through the epoxy shell into the copper block to accomodate a thermometer. Asbestos tape served to insulate the copper block from a five foot strand of 28 gauge nichrome resistance wire wound around it. Another layer of asbestos tape was wrapped around the wire and secured by silicone tape. A voltage was supplied to the nichrome wire by a YSI Model 72 Temperature Controller. A thermistor inserted into the copper block and coated with Wakefield Thermal Compound provided temperature information



Figure 3. Cross-Sectional View of the Thermostatted Jacket

to the controller. It was found that the voltage supplied to the wire was excessively high and melted the wire so a Variac was used as a voltage divider. With the controller bandwidth set at 0.1°C and a Variac setting of 20, the temperature of the copper block was found to vary less than 0.1°C.

Due to the viewing slot in the thermostatted jacket, the sample was not completely insulated and it was therefore suspected that at higher temperatures the sample temperature would not equilibrate at the same temperature as the copper block. For this reason the thermostatted jacket was calibrated in terms of both the block and sample temperature. Two calibrated, accurate etched-stem mercury thermometers with divisions of 0.01°C were used as temperature probes. A Fisher NBS calibrated thermometer and an Owens-Illinois thermometer were inserted to the proper depth into the glycerine sample and the copper block respectively. The calibration data are given in Table 1. Plotting the copper block temperature versus the glycerine temperature yielded the calibration curve shown in Figure 4. The least-squares slope and intercept of the line were used to calculate the actual temperature from the observed block temperature in all Brillouin studies.

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Controller Setting	Block Temperature	Liquid Temperature
24.0°C	24.05°C	<b>24.</b> 10°C
26.0	25.90	25.90
28.0	27.70	27.75
30.0	29.50	<b>29.5</b> 5
32.0	31.55	31.60
34.0	33.65	33.55
36.0	35.65	35.45
38.0	37.55	37.25
40.0	39.50	39.05
50.0	49.50	48.50
60.0	59.50	58.20
70.0	69.60	68.00
80.0	79.55	77.80
90.0	89.55	87.25

Table 1. Measured Temperatures of the Copper Block and Sample Liquid at Various Controller Settings



Figure 4. Calibration Plot for the Thermostatted Jacket

#### SAMPLE PREPARATION

The following fluids were the generous gift of the Dow Corning Corporation:  $MD_5M$ ,  $MD_9M$ ,  $MD_{11}M$ ,  $MD_{13}M$ ,  $D_4$  and  $D_6$ . The remaining fluids, MDM and  $MD_2M$  were obtained from Ohio Valley Speciality Chemical Company. All samples had been analyzed by the respective companies to be greater than 99.5% pure and were used as obtained.

Since dust particles add intensity to the Rayleigh line thereby invalidating the Landau-Placzek ratio, it was necessary to clean the samples scrupulously. Each fluid was forced under pressure through a 0.25 micron pore size Millipore filter into the 1.0 inch O.D. scattering cell which had been attached to a 15 millimeter Fischer-Porter joint as shown in Figure 5. The filtering process was repeated until the liquid in the cell appeared totally free of dust. The fluid was then degassed by the standard freezepump-thaw method and then sealed under vacuum.

## **REFRACTIVE INDEX**

Refractive index measurements of all silicone fluids were made at five different temperatures with a Bausch and Lomb Abbe 3-L Refractometer. The temperature of the prisms was maintained by a Haake circulating bath temperature control unit. A Doric Thermocouple Indicator Type T DS-350 with digital temperature readout was used to determine the temperature of the liquid between the prisms. The digital voltmeter was calibrated by immersing the thermocouple in an



Figure 5. The Light Scattering Sample Cell

ice bath and five additional constant temperature baths whose temperatures were determined by the Fisher calibrated NBS thermometer. The calibration data are tabulated in Table 2 and plotted in Figure 6.

The refractive index data were obtained at 5890 Å, the sodium D line. The dispersion tables supplied by Bausch and Lomb allowed calculation of the refractive index at 5145 Å, the wavelength of the incident radiation.

Table 2. Measured and Corrected Temperatures Obtained During Refractive Index Measurements of Silicone Fluids

Measured	Corrected
-5.70°C	00.00°C
18.1	23.45
37.2	41.70
59.3	62.35
78.5	81.60
94.8	98.20



Figure 6. Calibration Plot for the Thermocouple

CHAPTER IV

RESULTS AND DISCUSSION

## **REFRACTIVE INDEX**

In order to calculate the velocity of the acoustic wave at various temperatures, it was necessary to determine the refractive index of the scattering fluid in the temperature range of interest for the Brillouin study. All measurements were made at 5890 Å, the sodium D line of an Abbe refractometer and since refractive index is a frequency dependent property, dispersion corrections were made to obtain the value at 5145 Å, the Brillouin excitation wavelength. Measured and calculated values of the refractive index at 5890 Å and 5145 Å respectively are presented as functions of temperature in Tables 3 - 11. Details of the correction procedure are given in the instrument manual.

All of the silicone fluids exhibited a linear decrease of refractive index with increasing temperature as shown in Figure 7. The least-squares slopes, intercepts and correlation coefficients are listed in Table 12 for the refractive index-temperature data at both wavelengths. The linearity indicates that there are no optical anomalies occuring in this temperature region. It is interesting to note that the molecules of cyclic conformation have refractive indicies significantly higher than their linear counterparts. Also, within the series of linear fluids, the refractive index at a single temperature increased with

Table 3. Refractive Index As a Function of Temperature for MDM Observed at 5890 Å and Calculated at 5145 Å

Temperature	<sup>n</sup> 5890	<sup>n</sup> 5145
34.1°C	1.3790 ± 0.0005	1.3824 ± 0.0010
44.9	1.3732	1.3762
52.6	1.3689	1.3720
63.2	1.3630	1.3659
72.5	1.3582	1.3614

Table 4. Refractive Index As a Function of Temperature for MD\_M Observed at 5890 Å and Calculated at 5145 Å<sup>2</sup>

Temperature	<sup>n</sup> 5890	<sup>n</sup> 51 <b>4</b> 5
34.1°C	1.3836 ± 0.0005	1.3870 ± 0.0010
44.9	1.3791	1.3823
52.6	1.3735	1.3769
63.2	1.3692	1.3723
72.5	1.3645	1.3677

Table 5. Refractive Index As a Function of Temperature for MD\_M Observed at 5890 Å and Calculated at 5145 Å<sup>5</sup>

Temperature	<sup>n</sup> 5890	<sup>n</sup> 5145
37.3°C	1.3885 ± 0.0005	1.3921 ± 0.0010
44.4	1.3841	1.3874
56.3	1.3795	1.3829
64.7	1.3762	1.3795
73.8	1.3712	1.3745
84.7	1.3636	1.3669

Table 6, Refractive Index As a Function of Temperature for MD<sub>9</sub>M Observed at 5890 Å and Calculated at 5145 Å<sup>9</sup>

Temperature	<sup>n</sup> 5890	<sup>n</sup> 51 <b>45</b>
34.0°C	1.3944 ± 0.0005	1.3979 ± 0.0010
43.3	1.3895	1.3925
51.1	1.3858	1.3892
63.2	1.3818	1.3848
72.5	1.3775	1.3808

Table 7. Refractive Index As a Function of Temperature for MD M Observed at 5890 Å and Calculated at 5145 Å<sup>11</sup>

Temperature	<sup>n</sup> 5890	<sup>n</sup> 5145
34.0°C	1.3950 ± 0.0005	1.3985 ± 0.0010
44.9	1.3904	1.3939
51.1	1.3866	1.3900
63.2	1.3829	1.3859
72.5	1.3791	1.3821

Table 8. Refractive Index As a Function of Temperature for MD<sub>13</sub>M Observed at 5890 Å and Calculated at 5145 Å

Temperature	<sup>n</sup> 5890	<sup>n</sup> 5145
34.1°C	1.3690 ± 0.0005	1.3995 ± 0.0010
44.9	1.3916	1.3952
52.0	1.3877	1.3913
63.2	1.3829	1.3862
72.5	1.3796	1.3827

Table 9.	Refractive Index As a Function of Temperature
	for D. C. 200 Fluid, Viscosity Grade 12,500 cts,
	Observed at 5890 Å and Calculated at 5145 Å

Temperature	<sup>n</sup> 5890	<sup>n</sup> 5145
34.0°C	1.4008 ± 0.0005	1.4042 ± 0.0010
45.7	1.3960	1.3996
52.5	1.3926	1.3962
62.5	1.3881	1.3917
72.5	1.3854	1.3885

Table 10. Refractive Index As a Function of Temperature for D<sub>4</sub> Observed at 5890 Å and Calculated at 5145 Å

Temperature	<sup>n</sup> 5890	<sup>n</sup> 51 <b>45</b>
34.0°C	1.3906 ± 0.0005	1.3938 ± 0.0010
44.6	1.3854	1.3889
52.0	1.3799	1.3834
63.7	1.3753	1.3784
72.5	1.3706	1.3739
78.1	1.3666	1.3695

Table 11. Refractive Index As a Function of Temperature for D Observed at 5890 Å and Calculated at 5145 <sup>6</sup>Å

Temperature	<sup>n</sup> 5890	<sup>n</sup> 5145
34.0°C	1.3965 ± 0.0005	1.3998 ± 0.0010
44.0	1.3920	1.3951
52.1	1.3876	1.3910
63.2	1.3830	1.3863
72.5	1.3790	1.3822
78.1	1.3750	1.3779



Figure 7. Refractive Index at 5145 Å as a Function of Temperature for All Silicone Fluids

	Table	12. Least-So Coeffici	quares Slopes, Int ents for Refracti	cercepts at ve Index vs	0°C, and Cor . Temperatur	relation e Plots
		5890 Å			5145 Å	
	Slope x10 <sup>4</sup> (°C)	-1 Intercept	<b>Correlation</b> <b>Coefficient</b>	Slope x10 <sup>4</sup> (°C) <sup>-</sup>	Intercept.	Correlation Coefficient
MDM	-5.4463	1.3976	0.99992	-5.5013	1.4010	0.99958
MD <sub>2</sub> M	-5.0399	1.4009	0.99669	-5.0952	1.4045	0.99761
MD <sub>5</sub> M	-4.5370	1.4072	0.99356	-5.0374	1.4109	0.99362
м <sup>6</sup> дм	-4.2633	1.4083	0.99655	-4.3077	1.4118	0.99595
MD <sub>11</sub> M	-4.0958	1.4086	0.99561	-4.2543	1.4127	0.99654
MD <sub>13</sub> M	-4.3540	1.4108	0.99822	-4.4709	1.4148	0.99861
12,500 cts	-4.1144	1.4146	0.99587	<b>-4</b> .1782	1.4184	0.99790
D4	-5.3218	1.4087	0.99728	-5.3970	1.4123	0.99721
D6	-4.7606	1.4128	0.99808	-4.8143	1.4163	0.99767

increasing molecular weight to a chain length of about thirteen silicon atoms where it then leveled off in an asymptotic manner as indicated by the small spread in refractive index over a large molecular weight range.

# VARIATION OF THE BRILLOUIN FREQUENCY SHIFT WITH TEMPERATURE AND MOLECULAR WEIGHT

When linearly polarized light is scattered by a substance, the scattered light exhibits a frequency distribution about the incident frequency which is characteristic of the time-dependent fluctuations in the medium. Entropy fluctuations and static inhomogeneties are responsible for the scattered component centered around the incident frequency. Light scattered by pressure fluctuations gives rise to three pairs of symmetrically displaced Brillouin lines corresponding to scattering from the longitudinal and shear waves (56). Only the longitudinal doublet is regularly observed in liquids. The magnitude of the Brillouin displacement,  $v_{\rm B}$ , is directly proportional to  $V_{\rm S}$ , the velocity with which the pressure or sound wave travels through the liquid, and is given by

$$v_{\rm B} = \pm 2v_0 (n/c) V_{\rm S} \sin \theta/2 \qquad [46]$$

where  $v_0$  is the incident frequency, n is the refractive index of the medium, c is the speed of light <u>in vacuo</u>, and  $\theta$  is the angle of observation. Values of the frequency shift are usually a few gigahertz (GHz).

The Brillouin shift is measured experimentally as shown in Figures 8 and 9. For a given liquid the frequency shift changes with liquid molecular weight. The values of the shifts as well as sound velocities and other parameters are listed for various temperatures for each liquid in Tables 14 through 21. Values of the Brillouin shifts at 30°C for the silicones and several other materials are tabulated below. The low frequency shifts of the silicone

Table 13. Brillouin Shift Frequencies of Some Substances at 30°C

Material	ν (GHz) B	Reference
Pyridine	6.3	57
Dimethylsulfoxide	6.0	57
Polypropylene Glycol	4.0	58
Polybutadiene	6.0	59
Polymethylmethacrylate (amorphous)	9.5	60
n-Alkanes	5.0	56
Silicones	3.3-3.7	This Work

fluids compared to common solvents and polymers are paralleled by low sound velocities as well and will be discussed in the next section.

The temperature dependences of the Brillouin shifts for the liquid silicones are illustrated in Figures 10 - 12. Over the temperature range examined each fluid exhibited a linear decrease in shift frequency with increasing temperature. This type of behavior is well established for pure liquids (61-64). The least-squares slopes, intercepts and correlation coefficients are listed for each silicone


Figure 8. Brillouin Spectra of  $MD_2M$  and  $MD_{13}M$  at 85°C



Figure 9. Brillouin Spectra of MDM at 25°C and 85°C

Table	14.	Observed Brillouin Frequency Shifts $(v_p)$ ,
		Velocities of Sound (V <sub>S</sub> ), Full Brilloun
		Linewidths at Half-Height ( $\Gamma_{\rm B}$ ), Sound Absorption
		Coefficients (a), and Refractive Indicies (n)
		of MDM as a Function of Temperature

ፕ( ℃)	<sup>n</sup> 5145	$v_{B}(GHz)$	V <sub>S</sub> (m/s)	$\Gamma_{\mathbf{B}}^{}(\mathbf{GHz})$	α(cm <sup>-1</sup> )
24.6	1.3875	3.61	946	0.254	1340
34.4	1.3821	3.48	916	0.238	1300
44.0	1.3768	3.27	864	0.212	1230
53.6	1.3715	3.11	825	0.199	1210
63.2	1.3662	2.99	796	0.191	1200
72.8	1.3610	2.84	759	0.180	1190
82.4	1.3557	2.86	719	0.170	1180

±0.1	±0.001	±0.03	±10	±0.005	±20

Table 15. Observed Brillouin Frequency Shifts  $(v_B)$ , Velocities of Sound  $(V_S)$ , Full Brillouin Linewidths at Half-Height  $(\Gamma_B)$ , Sound Absorption Coefficients  $(\alpha)$ , and Refractive Indicies (n)of MD<sub>2</sub>M as a Function of Temperature

т(°С)	<sup>n</sup> 51 <b>4</b> 5	ν <sub>B</sub> (GHz)	V <sub>S</sub> (m/s)	Γ <sub>B</sub> (GHz)	α(cm <sup>-1</sup> )
23.6	1.3924	3.48	909	0.297	1630
34.4	1.3870	3.33	873	0.286	1640
44.0	1.3821	3.19	840	0.270	1610
53.6	1.3772	3.07	811	0.244	1500
63.2	1.3723	2.96	785	0.233	1480
72.8	1.3674	2.84	756	0.228	1500
82.4	1.3625	2.78	742	0.201	1350

Uncertainties in Measured and Calculated Quantities

±0.1	±0.001	±0.03	±10	±0.005	±20

.

Table 16. Observed Brillouin Frequency Shifts  $(v_B)$ , Velocities of Sound  $(V_S)$ , Full Brillouin Linewidths at Half-Height  $(\Gamma_B)$ , Sound Absorption Coefficients (a), and Refractive Indicies (n) of MD<sub>5</sub>M as a Function of Temperature

Т(°С)	<sup>n</sup> 5145	ν <sub>B</sub> (GHz)	V <sub>S</sub> (m∕s)	Γ <sub>B</sub> (GHz)	α(cm <sup>-1</sup> )
24.4	1.3986	3.62	942	0.376	2000
34.4	1.3935	3.46	903	0.345	1910
44.0	1.3887	3.33	872	0.323	1850
53.6	1.3839	3.22	846	0.281	1660
63.2	1.3790	3.15	831	0.265	1590
72.8	1.3742	3.06	810	0.254	1570
82.4	1.3694	2.89	768	0.249	1620

±0.1	±0.001	±0.03	±10	±0.005	±20

Table 17. Observed Brillouin Frequency Shifts  $(v_B)$ , Velocities of Sound  $(V_S)$ , Full Brillouin Linewidths at Half-Height  $(\Gamma_B)$ , Sound Absorption Coefficients ( $\alpha$ ), and Refractive Indicies (n) of MD<sub>9</sub>M as a Function of Temperature

Т(°С)	<sup>n</sup> 5145	ν <sub>B</sub> (GHz)	V <sub>S</sub> (m/s)	Γ <sub>B</sub> (GHz)	α (cm <sup>-1</sup> )
23.4	1.4017	3.67	952	0.438	2300
34.4	1.3970	3.59	935	0.416	2220
44.0	1.3928	3.46	904	0.406	2240
53.6	1.3887	3.38	885	0.378	2130
63.2	1.3846	3.26	857	0.362	2110
72.8	1.3804	3.21	846	0.334	1970
82.4	1.3763	3.10	819	0.312	1900

±0.1	±0.001	±0.03	<b>±10</b>	±0.005	±20

Table 18. Observed Brillouin Frequency Shifts  $(v_B)$ , Velocities of Sound  $(V_S)$ , Full Brillouin Linewidths at Half-Height  $(\Gamma_B)$ , Sound Absorption Coefficients  $(\alpha)$ , and Refractive Indicies (n)of MD<sub>11</sub>M as a Function of Temperature

т(°С)	<sup>n</sup> 5145	$v_{B}^{}(GHz)$	V <sub>S</sub> (m/s)	$\Gamma_{B}^{(GHz)}$	a (cm <sup>-1</sup> )
23.6	1.4026	3.83	993	0.421	2260
34.4	1.3981	3.72	968	0.400	2070
44.0	1.3940	3.61	942	0.384	2040
53.6	1.3899	3.44	900	0.362	2010
63.2	1.3858	3.33	874	0.351	2000
72.8	1.3817	3.24	853	0.329	1930
82.4	1.3776	3.14	829	0.307	1850

±0.1	±0.001	±0.03	±10	±0.005	±20

Table 19. Observed Brillouin Frequency Shifts  $(v_B)$ , Velocities of Sound  $(V_S)$ , Full Brillouin Linewidths at Half-Height  $(\Gamma_B)$ , Sound Absorption Coefficients  $(\alpha)$ , and Refractive Indicies (n)of MD<sub>13</sub>M as a Function of Temperature

т(°С)	<sup>n</sup> 5145	ν <sub>B</sub> (GHz)	V <sub>S</sub> (m∕s)	Γ <sub>B</sub> (GHz)	α(cm <sup>-1</sup> )
24.0	1.4041	3.72	964	0.420	2180
34.4	1.3994	3.61	938	0.389	2070
44.0	1.3951	3.49	910	0.352	1930
53.6	1.3908	3.39	887	0.346	1950
63.2	1.3865	3.29	863	0.336	1940
72.8	1.3822	3.16	832	0.330	1980
82.4	1.3780	3.06	810	0.320	1980

±0.1	<b>±0.00</b> 1	±0.03	±10	±0.005	±20

Table 20. Observed Brillouin Frequency Shifts  $(v_B)$ , Velocities of Sound  $(V_S)$ , Full Brillouin Linewidths at Half-Height  $(\Gamma_B)$ , Sound Absorption Coefficients  $(\alpha)$ , and Refractive Indicies (n)of D<sub>4</sub> as a Function of Temperature

Т(°С)	<sup>n</sup> 5145	$v_{B}^{(GHz)}$	V <sub>S</sub> (m/s)	Γ <sub>B</sub> (GHz)	$\alpha$ (cm <sup>-1</sup> )
23.4	1.3997	3.31	860	0.462	2690
29.6	1.3963	3.30	860	0.460	2670
39.2	1.3911	3.24	847	0.444	2620
48.8	1.3860	3.16	829	0.378	2280
58.4	1.3808	3.10	817	0.360	2200
68.0	1.3756	2.97	786	0.318	2020
82.4	1.3678	2.74	729	0.274	1880

±0.1	±0.001	±0.03	±10	±0.005	±20

Table 21. Observed Brillouin Frequency Shifts  $(v_B)$ , Velocities of Sound  $(V_S)$ , Full Brillouin Linewidths at Half-Height  $(\Gamma_B)$ , Sound Absorption Coefficients  $(\alpha)$ , and Refractive Indicies (n) of D<sub>6</sub> as a Function of Temperature

т (°С)	<sup>n</sup> 5145	ν <sub>B</sub> (GHz)	V <sub>S</sub> (m∕s)	Γ <sub>B</sub> (GHz)	α (cm <sup>-1</sup> )
29.6	1.4020	3.74	971	0.531	2730
39.2	1.3974	3.56	927	0.515	2780
48.8	1.3928	3.35	880	0.463	2630
58.4	1.3882	3.32	870	0.417	2400
68.0	1.3836	3.14	826	0.375	2270
77.6	1.3789	3.01	794	0.359	2260

Uncertainties in Measured and Calculated Quantities

±0.1 ±0.001 ±0.03 ±10 ±0.005 ±20









in Table 22. Although both the slope and the intercept vary irregularly from liquid to liquid, the slope tends to decrease as the chain length increases.

The Brillouin shift frequency at a given temperature is also dependent on the molecular weight of the sample as well as its chain configuration, linear or cyclic. The Brillouin shift at 30°C is plotted versus molecular weight in Figure 13. The data of Kumar (48) at the molecular weight extremes are included to illustrate the behavior of the Brillouin shift over a broader molecular weight range. These data will also be included in subsequent molecular weight plots. Several interesting features are apparent in Figure 13. First, the curve is smooth and continuous indicating that no gross structural changes occur as the chain length increases. Also the slope is much greater at molecular weight values less than 1000. The cyclic molecules exhibit an analogous trend. The small rings,  $D_A$  and  $D_6$ , have shift frequencies approximately equal to those of their linear counterparts but the frequencies diverge as the number of silicon atoms in the ring or chain increases. It was found that the Brillouin shift at a single temperature was inversely proportional to the molecular weight of the liquid. Figure 14 shows the linear relationship between the shift and reciprocal molecular weight. Since MM and the 100 cts fluid (MW 6400) both fall on the least-squares line, this relationship apparently describes the behavior of the shift equally well at high and low molecular weights.

Table	22.	Linear	Lea	ast-Squ	ares	Slopes,	In	terce	epts	at	0° C	,
		and Con	rrel	lation	Coeff	icients	s of	the	Bril	<b>1</b> 00	in	
		Shift w	vs.	Temper	rature	Plots	for	<b>All</b>	Sili	lcon	es	

Fluid	Slope (GHz/°C)	Intercept (GHz)	Correlation Coefficient
MDM	-0.01615	4.005	0.9981
MD2 <sup>M</sup>	-0.01217	3.743	0.9956
MD <sub>5</sub> M	-0.01175	3.876	0.9935
MD <sub>9</sub> M	-0.00978	3.904	0.9967
MD <sub>11</sub> M	-0.01216	4.122	0.9966
MD <sub>13</sub> M	-0.01135	3.996	0.9999
<sup>D</sup> 4	-0.00940	3.587	0.9710
<sup>D</sup> 6	-0.01470	4.141	0.9886







## VARIATION OF THE VELOCITY OF SOUND WITH TEMPERATURE AND MOLECULAR WEIGHT

The velocity of sound obtained from the Brillouin shift frequency according to Equation [46] is related to the liquid structure through the adiabatic compressibility,  $\beta_S$ :

$$v_{\rm S} = (1/\rho\beta_{\rm S})^{\frac{1}{2}}$$
 [47]

where  $\rho$  is the density. In a light scattering experiment, the fixed wave vector is scattered by a travelling acoustic wave of the same wavelength as the incident light. The liquid is undisturbed because no gradient has been introduced and the measured frequencies and velocities are those of the thermally driven fluctuations inherent in the medium. Since the incident wave vector determines the frequencies which will scatter light, it is possible to examine other frequencies by changing the wave vector. This is done by changing the wavelength of the incident light or more commonly by varying the scattering angle. Dispersion in the sonic velocity is said to occur when the waves of different frequencies do not travel with the same velocity. Previous ultasonic and Brillouin studies have not reported velocity dispersion in the siloxanes (44,48,66). The results of Kumar and Friedlander (48,66) are reproduced in Table 23 to demonstrate that the velocities of the silicones are independent of frequency over the measured range.

Table 23. Velocity of Sound as a Function of Frequency For Several Silicones at 25°C

	ν <sub>B</sub> (GHz)	V <sub>S</sub> (m/sec)		ν <sub>B</sub> (GHz)	V <sub>S</sub> (m/sec)
	MM	U		MD <sub>7</sub>	м
50°	1.87 ± 0.05	827 ± 10	60°	2.73 ± 0.05	<b>1010</b> ± 10
60°	2.21	824	75°	3.30	1000
90°	3.40	897	90°	3.91	1030
120°	4.12	887	105°	4.32	1010
			135°	5.07	1010
	D	5		D	15
75°	$3.08 \pm 0.05$	932 ± 10	60°	$2.86 \pm 0.05$	1040 ± 10

D <sub>5</sub>			D <sub>15</sub>			
75°	3.08 ± 0.05	932 ± 10	60°	2.86 ± 0.05	1040 ± 10	
90°	3.58	932	75°	3.22	967	
105°	4.19	971	90°	3.75	969	
120°	4.58	973	120°	5.21	1090	
135°	4.88	973				

In an ultrasonic experiment a sonic wave of variable frequency is introduced into the sample and its velocity and spatial attenuation are measured. In this case the medium is disturbed by the sonic wave. In spite of this difference, velocities measured by the two techniques have been found to be in close agreement for many liquid systems (50,63,65).

For every liquid studied the velocity of sound was a linearly decreasing function of temperature as illustrated in Figures 15 - 17. The data are tabulated in Tables 14 - 21. The slopes, intercepts and correlation coefficients determined by the method of least-squares are listed in Table 24. With the use of thermodynamic relations, it can be shown that Equation [47] can be rewritten as

$$V_{S} = [C_{P}(\gamma-1)/a^{2}T]^{\frac{1}{2}}$$
 [48]

where  $C_p$  is the constant pressure heat capacity,  $\gamma$  is the heat capacity ratio , a is the coefficient of thermal expansion and T is the absolute temperature (75). Since  $C_p$ ,  $\gamma$  and a vary only slightly with temperature, Equation [48] correctly predicts that the velocity will decrease as the temperature increases. The ultrasonic data of Weissler (42) are presented in Table 25 in addition to the Brillouin velocities. As can be seen from the data, the Brillouin and ultrasonic velocity values agree within a few percent.







Table 24.	Linear Least-Squares Slopes, Intercepts at 0°C and Correlation Coefficients of the Velocity of Sound vs. Temperature Plots for All Silicones

Fluid	Slope (m/sec°C)	Intercept (m/sec)	Correlation Coefficient
MDM	-3.948	1044	0.9980
MD_M	-2.909	972	0.9952
MD_M	-2.776	1002	0.9922
MD M	-2.286	1008	0.9959
MD_M	-2.902	1064	0.9961
MD <sub>13</sub> M	-2.684	1030	0.9994
D <sub>4</sub>	-2.157	926	0.9606
<sup>D</sup> 6	-3.565	1069	0.9909

Liquid	MW	Ultrasonic V (m/sec) S	Brillouin V (m/sec) S
MM	162.2	<b>873 ±</b> 10	873 ± 10
MDM	236.3	901	925
MD <sub>2</sub> M	310.4	<b>91</b> 9	884
MDZM	384.5	931	929
MD <sup>S</sup> M	533.1	942	918
	720	953	983
MD M	829		939
MD <sup>9</sup> , M	978		976
	1126	966	949
100 <sup>3</sup> cts	6400	985	975

## Table 25. Ultrasonic and Brillouin Velocities of Sound for Linear Polydimethylsiloxanes at 30°C

In order to place in perspective the magnitudes of the velocities of sound for the silicones, the Brillouin velocity results for other polymers and a few organic liquids are listed in Table 26. The siloxane sound velocities, ranging from 875 to 975 meters per second, are significantly lower than those tabulated. High sound velocities have been empirically correlated with strong intermolecular forces and low compressibilities which are thought to facilitate passage of the sound wave. For this reason associated liquids such as dimethylsulfoxide have higher velocities than the nonpolar normal alkanes. In this respect the velocity of sound is a qualitative probe of the extent of intermolecular interaction. This interpretation leads to the supposition that the intermolecular forces in the siloxanes are weak in comparison to many liquids and are weaker than in the alkanes of corresponding chain length. Also, the increase of the sound velocity with molecular weight as shown in Figure 18 may be an effect of the increasing

Compound	V (m/sec) S	Reference
Polymethylmethacrylate	2870	60
Benzene	1500	53
Water	1480	53
Polybutadiene	1400	56
C <sub>14</sub> H <sub>30</sub>	1350	56
Toluene	1350	53
<sup>C</sup> 12 <sup>H</sup> 26	1310	56
Carbon disulfide	1250	53
Polypropylene glycol 425	1200	58
Acetone	1190	53
Acetic acid	1160	53
Ethyl alcohol	1160	53
n-Hexane	1110	53
Methyl alcohol	1110	53
Carbon tetrachloride	1000	53
Ethyl ether	1000	53
Silicones	900 - 1000	This Work

Table 26. Brillouin Velocity of Sound Data for Selected Polymers and Other Liquids at 20°C





interaction between siloxane functional groups. In long chain molecules there are a greater number of covalent bonds between the siloxane units than in short chain molecules. The decrease of the velocity of sound with increasing temperature can also be attributed to the increasing randomness of the liquid structure as the liquid is heated.

A Rayleigh-Brillouin light scattering study of polypropylene glycol 425, a polymer somewhat similar in structure to the siloxanes, has been reported by Wang and Huang over a broad range of temperatures (58). They examined the behavior of the velocity of sound with temperature as the polymer underwent transitions from the glass to rubber and finally to the liquid state. The behavior of the siloxanes very closely paralleled that of polypropylene glycol in the liquid region. From 40°C to 90°C the velocity of sound in polypropylene glycol varied from 1000 to 750 meters per second and the siloxane velocities fell in this same range. Also the temperature coefficients of velocity are virtually identical for the two types of polymer liquids.

The velocity of sound was found to depend not only on molecular weight but also on molecular structure. Figure 18 shows the smooth curve describing the relationship between the velocity and molecular weight for both linear and cyclic conformations. Since the velocity is calculated from the Brillouin shift frequency, the same

functional form is expected for both, as is indeed the case. The slope is higher at low molecular weights and the velocities of the cyclic fluids exhibit similar behavior but are somewhat higher than those of the corresponding linear fluids. A recent Brillouin study of normal alkanes,  $C_{12}$  to  $C_{36}$ , reported by Champion and Jackson (56) revealed that the sound velocity increased with increasing chain length, although no attempt was made to delineate the mathematical relationship. On the other hand, Wang and Huang (74) report no molecular weight dependence on the velocity for polypropylene glycol ranging from weight average molecular weight 425 to 1000.

Although Brillouin and ultrasonic theories do not contain any information pertaining to molecular weight, a semi-empirical approach was developed by Rao. He observed that for many unassociated organic liquids (67)

$$\frac{1}{v_{\rm S}} \frac{\partial v_{\rm S}}{\partial T} \frac{1}{p} \frac{\partial v}{\sqrt{\partial T}} \frac{1}{p} \approx -3 \qquad [49]$$

where V is the molar volume. In integral form this equation is

$$R = V \frac{1/3}{s} V$$
 [50]

where R is the Rao number. The validity of equation [49] was checked for several silicone fluids and ratios ranging from 2.7 to 2.9 were obtained. Rao predicted that R would be a linear function of molecular weight (67). Table 27 contains the molar volumes and Rao numbers for all the silicones studied.

Table 27. Rao Numbers, Molar Volumes and Related Quantities for All Silicones at 25°C

Fluid	V <sub>S</sub> (m/sec)	ρ(g/cc)	V(cc/mole)	R
MM	894	0.7619	212.9	2052
MDM	945	0.8200	288.4	2830
MD M	899	0.8536	364.0	3513
MD <sup>2</sup> M	945	0.8755	439.3	4312
MD <sup>3</sup> M	932	0.9110	585.2	5717
MD <sup>5</sup> M	995	0.9134	745.6	7445
MD/M	950	0.9223	898.7	8837
MD <sup>9</sup> , M	991	0.9305	1051	10,480
MD <sub>13</sub> <sup>11</sup> M	962	0.9335	1206	11,900

The linear relationship between the Rao number and molecular weight, MW, was verified for the silicones as shown in Figure 19. Therefore, according to Rao, the velocity of sound is given by the following third order equation

$$V_{S} = \rho^{3} [b(1/MW) + a]^{3}$$
[51]  
=  $\rho^{3} [b^{3} (1/MW)^{3} + 3ab^{2} (1/MW)^{2} + 3a^{2}b(1/MW) + a^{3}]$ 

where  $\rho$  is the density and a and b are the slope and intercept of the Rao number versus molecular weight plot. However, for the silicone fluids, a completely empirical first order equation

$$v_{\rm S} = (-3.10 \times 10^{-4})(1/MW) + 852 [52]$$

also fits the data as demonstrated in Figure 20. The contribution of the second and third order terms in Rao's equation give numbers on the order of 10 and 0.1 m/sec which are within the limits of experimental error for this



Figure 19. Rao Number as a Function of Molecular Weight for Linear Silicones





study. In order to determine which equation better describes the behavior of these liquids, a much larger data set would be necessary.

VARIATION OF THE ADIABATIC COMPRESSIBILITY WITH TEMPERATURE AND MOLECULAR WEIGHT

The compressibility is inversely related to the strength of the intermolecular forces or degree of association so it is a probe of liquid structure. It is possible to calculate the adiabatic compressibility of a liquid using the velocity of sound and density from

$$\beta_{\rm S} = 1/\rho V_{\rm S}^2 \qquad [53]$$

Table 28 lists the compressibilities of all siloxanes for which velocities of sound have been determined. The compressibilities of the silicones are unusually high. Values for some other liquids are given in Table 29 for comparison.

Adiabatic Compressibilities for Some Organic Table 29. Liquids at 25°C  $\beta_{\rm S} \times 10^{10} ~({\rm cm}^2/{\rm dyne})$ Liquid Reference Pyridine 0.438 57 Dimethylsulfoxide 0.406 57 Decane 0.935 56 Dodecane 0.847 56

The associated liquids, pyridine and dimethylsulfoxide, are much less compressible than the silicones and even

Table 28.	Velocities,	Densiti	ies	and	Adiaba	atic	3
	Compressibi	lities f	for	Silc	oxanes	at	25°C

Liquid	ρ(g/cm <sup>3</sup> )	V <sub>S</sub> (m/sec)	$3_{\rm S} \times 10^{10} ~({\rm cm}^2/{\rm dyne})$
ММ	0.7619	895 ± 10	1.64 ± 0.10
MDM	0.8200	945	1.37
MD <sub>2</sub> M	0.8536	899	1.45
MD <sub>3</sub> M	0.8755	946	1.28
MD <sub>5</sub> M	0.9110	933	1.26
MD <sub>7</sub> M	0.9134	996	1.10
MD9M	0.9233	951	1.20
MD <sub>11</sub> M	0.9305	992	1.09
MD <sub>13</sub> M	0.9335	963	1.16
100 cts	0.9579	990	1.06
D <sub>4</sub>	0.9500	872	1.38
D <sub>5</sub>	0.9528	933	1.20
D <sub>6</sub>	0.9621	980	1.08
D <sub>9</sub>	0.9756	1010	1.00
D <sub>15</sub>	0.9736	1050	0.94

the normal alkanes are for molecules of corresponding chain length. A possible explanation for these observations lies in the large space requirement of the methyl groups. Neutron scattering and nuclear magnetic resonance studies have demonstrated the high mobility of the methyl group hydrogen atoms which is attributed to rotation about the Si-C and Si-O bonds (39,71,72,73). In other words the molar volumes are large and the intermolecular forces are weak. Also, nearly free rotation about the silicon oxygen bond contributes to the overall mobility of the chain. This freedom of motion is considerably more restricted for cyclic molecules than linear ones as evidenced by the smaller molar volumes (32) and compressibilities of the cyclic liquids. The compressibilities of the cyclic molecules fall more rapidly with increasing molecular weight than do those of the linear molecules. The smallest ring containing three silicon atoms is planar so there is little rotation about the Si-O bond. As the ring increases in size, it puckers and there is increased floppiness or freedom of motion. Rings and corresponding chains containing at least nine siloxane units have equal compressibilities.

The compressibility of the linear series initially decreases with increasing molecular weight then reaches a limiting value. The statistical model for polymers considers the chain to be composed of molecular segments whose motions are virtually independent of one another (76). The asymptotic behavior of the compressibility may be related

to these segmental motions.

The compressibilities of four silicones were calculated for several temperatures and the results are tabulated in Tables 30 - 33. The listed densities have been calculated from the reported temperature coefficients of density for these liquids (26,68). Each fluid exhibited a linear increase in compressibility with increasing temperature as is shown in Figure 21. In general, the compressibility and its temperature coefficient decreased with increasing chain length.

## VARAIATION OF THE BRILLOUIN LINEWIDTH WITH TEMPERATURE AND MOLECULAR WEIGHT

The measured Brillouin linewidths were determined directly from the experimental Brillouin lines. An observed Brillouin line is actually a convolution of the true Brillouin line and the instrumental response function, the central of Rayleigh peak. Immediately prior to each series of Brillouin measurements, the linewidth at half-height of the instrumental response function was determined with the use of a strong Rayleigh scatterer. The central line of a Brillouin spectrum was considered the instrument response function because both had the same linewidth. Since the instrument function and the observed Brillouin line have been
Table 30.	Adiabatic Compressibility as a Function of	
	Temperature for MDM	

T(°C)	ρ(g/cm <sup>3</sup> )	$\beta_{s} \times 10^{10} (cm^2/dyne)$
24.6 ±0.1	0.8140 ±0.001	1.37 ±0.05
34.4	0.8039	1.48
44.0	0.7939	1.69
53.6	0.7839	1.87
63.2	0.7739	2.04
72.8	0.7639	2.27
82.4	0.7540	2.56

## Table 31. Adiabatic Compressibility as a Function of Temperature for MD<sub>2</sub>M

T(°C)	$\rho(g/cm^3)$	$\beta_{s} \times 10^{10} (cm^{2}/dyne)$
23.6 ±0.1	0.8521 ±0.001	1.42 ±0.05
34.4	0.8405	1.56
44.0	0.8301	1.71
53.6	0.8197	1.85
63.2	0.8093	2.01
72.8	0.7989	2.19
82.4	0.7885	2.30

Table 32	. Adiabat of Temp	ic Compressibilit erature for MD_M 5	y as a	Function
Т (	°C)	ρ <b>(g/cm<sup>3</sup>)</b>	β	x10 <sup>10</sup> (cm <sup>2</sup> /dyne)

		5	
24.4 ±0.1	0.8975 ±0.001	1.26 ±0.05	
34.4	0.8873	1.38	
44.0	0.8774	1.50	
53.6	0.8676	1.61	
63.2	0.8578	1.69	
72.8	0.8480	1.80	
82.4	0.8381	2.02	

## Table 33. Adiabatic Compressibility as a Function of Temperature for MD<sub>9</sub>M

т(°С)	$\rho(g/cm^3)$	$\beta_{\rm S} \times 10^{10} (\rm cm^2/\rm dyne)$
23.4 ±0.1	0.9233 ±0.001	1.19 ±0.05
34.4	0.9128	1.25
44.0	0.9037	1.35
53.6	0.8945	1.43
63.2	0.8854	1.54
72.8	0.8763	1.59
82.4	0.8671	1.72

;





successfully approximated by Lorentzian line shapes (48,57), the observed Brillouin linewidth is the sum of the linewidth of the true Brillouin line and the central line:

$$\Gamma_{B}^{exp} = \Gamma_{B}^{true} + \Gamma_{C}$$
 [54]

All linewidths reported in Tables 14 through 21 have been corrected for the contribution of the instrumental response function.

The behavior of the linewidth with temperature is shown for each silicone fluid in Figure 22 - 24. The linewidth was found to be a linearly decreasing function of temperature. The least-squares slopes, intercepts and correlation coefficients are given in Table 34. Although there is little information available in the literature for comparison, the same linear decrease of Brillouin linewidth with increasing temperature has been reported for pyridine and dimethylsulfoxide (57). Hydrodynamic theory predicts that the linewidth should be proportional to the viscosity of a simple non-relaxing fluid:

$$\Gamma_{\rm B} = \left[\frac{4\eta_{\rm S}/3 + \eta_{\rm B}}{\rho} + \frac{\lambda(\gamma - 1)}{\rho C_{\rm P}}\right] \vec{k}^2$$
 [55]

where  $\eta_{S}$  and  $\eta_{B}$  are the shear and bulk viscosities,  $\lambda$ is the thermal conductivity and  $\vec{k}^{2}$  is the square of the wave vector. For most liquids the second term in Equation [55] is very small compared to the first. For the silicones the maximum contribution of the thermal conductivity term







Table 34.	. Linear Least	-Squares Slopes, In	tercepts at 0°C,
	and Correlat	ion Coefficients of	the Full Brillouin
	Linewidth vs	. Temperature Plots	for All Silicones
Fluid	Slope	Intercept	Correlation

	(GHZ/°C)	(GHz)	Coefficient
MDM	-0.001444	0.2837	0.9919
MD <sub>2</sub> M	-0.001619	0.3378	0.9883
MD <sub>5</sub> M	-0.002302	0.4222	0.9711
мd <sub>9</sub> м	-0.002144	0.4925	0.9946
MD <sub>11</sub> M	-0.002214	0.4872	0.9840
MD <sub>13</sub> M	-0.001605	0.4420	0.9396
D4	-0.003432	0.5567	0.9864
D 6	-0.003946	0.6549	0.9889

was calculated to be 0.001 GHz, too small to be detected in this study. Since the viscosity is known to decrease slowly with temperature for the silicones (32), the experimental results are in qualitative agreement with theory.

The Brillouin linewidth was also found to vary with molecular weight as shown in Figure 25. Since the viscosity increases as the chain length is increased, this is not an unexpected result. Figure 26 demonstrates that the linewidth is a linear function of reciprocal molecular weight.

The reciprocal of linewidth has the dimension of time and may be described as a relaxation time or distribution of relaxation times. Although the molecular relaxation process occurring has not been interpreted for polarized Brillouin scattering, it is possible to estimate the activation energy for the process by assuming its temperature dependence is described by the Arrhenius equation

$$\frac{1}{\pi} \prod_{B} = A \exp(E/kT)$$
 [56]

where  $1/\pi\Gamma_{\rm B}$  is the relaxation time, A is a constant, E is the activation energy, k is the Boltzmann constant and T is absolute temperature. Table 35 contains the values of the relaxation times at various temperatures for all the silicones. The activation energy can be calculated from the slope of the line obtained by plotting  $\ln(1/\pi\Gamma_{\rm B})$  versus 1/T. The linearity of such a plot is established in Figure







Table	35.	Relaxation	Times	of the	Silicone	Fluids	s as a	Function	of Tem	peratu	re
	о Н°	$(1/_{B}^{\Gamma_{B}})$ x10 <sup>9</sup> sec		ы С	(1/g <sup>r</sup> B) x10 <sup>sec</sup>		ы. С	$(1/\pi\Gamma_B)$ x10 <sup>9</sup> sec		ы° С	$(1/\pi^{\Gamma}_{B})$ x10 <sup>9</sup> sec
MDM	24.6	1.25	MD <sub>2</sub> M	23.6	1.08	MD <sub>5</sub> M	24.4	0.847	м <sub>6</sub> дм	23.4	0.727
	34.4	1.34		34.4	1.11		34.4	0.925		34.4	0.765
	44.0	1.50		44.0	1.18		44.0	0.988		44.0	0.784
	53.6	1.59		53.6	1.30		53.6	1.13		53.6	0.842
	63.2	1.68		63.2	1.36		63.2	1.21		63.2	0.879
	72.8	1.77		72.8	1.40		72.8	1.25		72.8	0.953
	82.4	1.87		82.4	<b>1.</b> 58		82.4	1.28		82.4	1.02
MD11M	23.6	0.754	MD <sub>13</sub> M	23.9	0.758	D4	29.6	0.692	D6	29.6	0.601
	34.4	0.796		34.4	0.820		39.2	0.717		39.2	0.619
	44.0	0.829		44.0	0.904		48.8	0.842		48.8	0.689
	53.6	0.879		53.6	0.920		58.4	0.884		58.4	0.784
	63.2	0.909		63.2	0.947		68.0	1.00		68.0	0.851
	72.8	0.965		72.8	0.965		82.4	1.62		77.6	0.889
	82.4	1.04		82.4	0.995						

27 for two silicones. The activation energies are listed in Table 36.

Table 36. Activation Energies for Relaxational Processes in Silicone Fluids

Fluid	E(kcal/mole)	Fluid	E(kcal/mole)
MM	0.563	D	3.18
MDM	1.48	D4	1.91
MD_M	1.34	DG	0.774
MD <sup>2</sup> M	1.61	$D_{15}^{\mathbf{y}}$	0.886
MD <sup>5</sup> M	1.20	15	
MD <sup>9</sup> M	1.11		
$MD_{1,2}^{\perp \perp}M$	0.936		
100 <sup>°</sup> cts	0.742		

Energies for several different processes have been determined for the siloxanes and summarized in a paper by Flory (69). The barriers to rotation about the Si-C and Si-O bonds are approximately 1.5 to 2.0 and 0.4 kcal/mole respectively. In addition, Flory's rotational isomeric state model for the siloxanes defines three possible "states" for each Si-O bond and energy barriers between these states are about 1.0 to 2.0 kcal/mole. It is interesting to note that the energies calculated from the Brillouin linewidth data fall in this region. The small cyclic molecules, however, are characterized by higher energies which is not surprising in view of their more restricted molecular motions.



Figure 27. Temperature Dependence of Relaxation Times for MDM and  $MD_{13}M$ 

VARIATION OF THE ABSORPTION COEFFICIENT WITH TEMPERATURE AND MOLECULAR WEIGHT

The sonic absorption coefficient is calculated from

$$\alpha = \Gamma_{\rm B}/2V_{\rm S}$$
 [57]

where  $\Gamma_{\rm B}$  is the full Brillouin linewidth and  $V_{\rm S}$  is the velocity of sound. It is related to the efficiency of energy transfer from internal vibrational to external translational degrees of freedom. If this efficiency is low, then a large absorption will occur. As discussed in Chapter II, most liquids are classified into two groups on the basis of the sign of their temperature coefficient of the absorption of sound. Kneser liquids exhibit positive temperature coefficients while associated liquids are characterized by negative ones. Also, ultrasonic theory suggests that all liquids have absorption in excess of the classical Stokes value. The Stokes expression considers absorption due to viscosity alone and for light scattering experiments it is approximated by

$$\alpha_{\text{class}} = \frac{8\pi^2 v_B^2}{3v_S^3 \rho} \eta_S \qquad [58]$$

where  $\eta_{s}$  in the shear viscosity.

The absorption coefficients of the silicones are given at various temperatures in Tables 14 - 22. The least-squares slopes, intercepts and correlation coefficients are given in Table 37. The absorption coefficient was determined to be a linear function of temperature with a negative slope as shown in Figures 28 - 30. The negative slope places the silicones in the associated category. However, there is no evidence to support this implication. On the contrary, the high compressibilities and vapor pressures as well as other data indicate weak intermolecular forces. The unassociated normal alkanes (56) also have negative absorption temperature coefficients. According to Herzfeld and Litovitz (54) this apparent anomalous behavior is characteristic of viscous liquids.

In a series of papers, Hunter and coworkers investigated the behavior of the ultrasonic absorption coefficient of various silicone polymers (44,45,46). They found that the absorption increased with molecular weight, reached a maximum value, and then leveled off as the molecular weight further increased. The Brillouin absorption confirmed this trend as indicated in Figure 31. They also noted that the position of the maximum depended on the incident ultrasonic frequency and shifted to lower molecular weights as the frequency increased. The value reported by Hunter for the molecular weight of maximum absorption was 6400 at a frequency of 90 megacycles. The Brillouin frequency, however, is on the order of 2000 megacycles and the corresponding molecular weight is about 1000. As in the case of previous parameters, the absorption coefficient was found to be linear in reciprocal molecular weight as shown in Figure 32.







Table 37.	Linear Least-So and Correlation Coefficient vs.	quares Slopes, Int Coefficients of Temperature Plot	tercepts at 0°C, the Sound Absorption ts for All Silicones
Fluid	Slope (cm°C) <sup>-1</sup>	Intercept (cm <sup>-1</sup> )	Correlation Coefficient
MDM	-2.738	1380	0.9179
MD <sub>2</sub> M	-4.460	1770	0.9197
MD <sub>5</sub> M	-7.668	2150	0.9256
MD <sub>9</sub> M	-6.652	2480	0.9642
MD <sub>11</sub> M	-5.654	2320	0.9344
MD <sub>13</sub> M	-2.830	2160	0.6689
D_4	-15.16	3090	0.9789
D 6	-12.27	3170	0.9500







Hunter also pointed out that absorptions for the silicones were <u>less</u> than the classical Stokes values and that the deviation was more pronounced at higher frequencies. The Brillouin absorptions are also lower than the Stokes values as indicated by the ratio  $\alpha/\alpha$  listed in Table 38.

Table 38. Absorption Coefficient Ratios for Silicones at 25°C

Liquid	$\alpha$ (cm <sup>-1</sup> )	$^{\alpha/\alpha}$ class
MDM	1300	0.317
MD <sub>2</sub> M	1650	0.251
MD <sup>2</sup> M	1950	0.145
MDOM	2330	0.0954
MD, M	2250	0.0758
MD <sup>11</sup> <sub>n</sub> M	2200	0.0586
$D_1^{13}$	2700	0.263
D <sub>6</sub> <sup>4</sup>	2850	0.108
N. 6		

Hunter conjectures that the Stokes prediction is too large because the viscosity undergoes relaxation. Evidence for his position was provided by the  $\alpha/\alpha_{class}$  ratio varying from 2 at very low frequencies to 0.25 at high frequencies, thereby indicating a frequency dependent viscosity. The even smaller value of  $\alpha/\alpha_{class}$  at the hypersonic Brillouin frequencies provides further substantiation for his hypothesis.

## VARIATION OF THE LANDAU-PLACZEK RATIO WITH TEMPERATURE AND MOLECULAR WEIGHT

The Landau-Placzek ratio is the ratio of the integrated intensity of the central peak to the sum of the Brillouin intensities and is denoted J. It was determined for each liquid as a function of temperature and the values are listed in Table 40. This ratio was found to be relatively insensitive to both temperature and molecular weight. The large experimental error associated with the measurement, in conjunction with the very small spread of the data, prohibits more than a qualitative interpretation.

For a simple liquid the Landau-Placzek ratio is related to the heat capacity ratio by

$$J_{v} = C_{p}/C_{v} - 1$$
 [59]

The heat capacity ratios for several silicones were determined by Weissler (42) and ranged from 1.31 for MDM to 1.22 for  $MD_{11}M$ . These values are in good agreement with the Brillouin results. In addition, Wang and Huang found similar  $J_v$ values for liquid polypropylene glycol and noted the very slight decrease of  $J_v$  with temperature.

The high Landau-Placzek ratios of  $MD_9M$  and  $D_6$  are not consistent with the values for the other liquids in the series. Sample contamination by a small amount of high molecular weight polymer would account for this observation. The other spectral parameters would be influened only slightly since the principle effect would be to increase the intensity of the Rayleigh line and therefore,  $J_{y}$ .

т(°С)	MDM	MD <sub>2</sub> M	MD <sub>5</sub> M	MD_M 9
25	0.30	0.26	0.31	1.11
35	0.28	0.27	0.29	0.93
45	0.26	0.26	0.27	0.93
55	0.25	0.25	0.24	0.86
65	0.24	0.23	0.23	0.75
75	0.23	0.23	0.22	0.57
85	0.22	0.21	0.22	0.49
T(°C)	MD_M	MD <sub>13</sub> M	<sup>D</sup> 4	D 6
25	0.27	0.27	0.35	2.2
35	0.27	0.23	0.35	2.2
45	0.25	0.23	0.33	2.1
55	0.24	0.21	0.31	2.0
65	0.23	0.18	0.30	1.9
75	0.24	0.18	0.28	1.9
85	0.22	0.17	0.26	1.8

The relative uncertainty in the Landau-Placzek Ratios is ±5%.

Table 39. Landau-Placzek Ratio as a Function of Temperature

for the Silicones

CONCLUSIONS

Brillouin light scattering has been used to study the effect of molecular weight on spectral parameters in a homologous series of polydimethylsiloxane fluids. Each liquid behaved in the expected manner exhibiting linear relationships of refractive index, Brillouin shift, velocity of sound, adiabatic compressibility, Brillouin linewidth, and absorption coefficient with temperature. The high compressibilities and low sound velocities were evidence of the weak intermolecular forces in the silicones. Sound velocities agreed with those determined by ultrasonic methods.

The Brillouin shift, velocity of sound, Brillouin linewidth, and absorption coefficient were all found to vary in the same way with molecular weight. Each parameter increased rapidly to a molecular weight of about 1000 but increased only slightly as the molecular weight increased further. An empirical equation was found which described the given parameter as a linear function of reciprocal molecular weight. It has been pointed out that a chain length of eleven silicon atoms, corresponding to a molecular weight of approximately 1000, is just long enough to form a planar, unstrained ring (68). Since long polymer chains are known to be coiled, these steric considerations suggest that this does not occur below a molecular weight of 1000.

In summary:

- The first comprehensive Brillouin study of a homologous series of silicone fluids has been completed and the results are in agreement with reported ultrasonic data.
- 2. The acoustic properties of the cyclic fluids were distinctly different from those of the linear fluids. Sonic velocities and absorption coefficients in cyclic liquids were higher than in linear ones. This behavior was interpreted in terms of the more restricted motions of cyclic compared to linear molecules.
- 3. Adiabatic compressibilities for all the silicones were found to be unusually high, indicative of their weak intermolecular forces. The small ring liquids were less compressible than the corresponding linear ones but this difference disappeared for the higher molecular weight liquids.
- 4. Estimated activation energies for relaxation processes were found to be numerically the same as calculated barriers to rotation about the siloxane bonds.
- 5. The temperature coefficient of the sonic absorption coefficient was negative for all fluids, placing them in the category of associated and viscous liquids.
- 6. The classical prediction for absorption due to viscosity alone was found to be too large for all the silicones in contrast to most other liquids which

exhibit excess absorptions. This behavior has been attributed to a frequency-dependent viscosity.

7. The lack of velocity dispersion, absence of a Mountain line and low sonic absorptions indicate that the silicones behave as simple fluids in which there are no thermal or structural relaxations. CHAPTER V

LITERATURE CITED

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## LITERATURE CITED

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