COMPARISON OF THE TRANSVERSE VISCOELASTIC PROPERTIES OF BENZYI BENZOATE FROM ULTRASONIC AND LIGHT-SCATTERING MEASUREMENTS

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The results obtained from depolarised light scattering experiments as a function of temperature are compared with ultrasonic impedance measurements previously obtained by Barlow and Erginsav. At low temperatures (in the supercooled region) a depolarised propagating doublet is observed and the velocity thus obtained is concordant with Barlow's results. At higher temperatures the relaxation time, \( \tau_c \), is obtained from the width of the depolarised spectrum. Contrary to the suggestion of Barlow, there is little correspondence between \( \tau_c \) and the retardation time for viscous response.

1. Introduction

The longitudinal viscoelastic properties of liquids (velocity and attenuation of longitudinal sound waves) as obtained from ultrasonic measurements and from polarised light scattering (Brillouin scattering) have been compared some time ago for a number of viscous liquids [1-3]. However, similar comparisons for the transverse viscoelastic properties do not yet exist. Barlow and Erginsav [4] have recently tried to undertake such a comparison. Although they present a very complete set of ultrasonic measurements of the propagation and attenuation of shear waves in benzyl benzoate (from +3.85°C to -70°C) they were not able to carry out the corresponding experiments on the depolarised light scattering spectrum. Their comparison therefore is based on a single light-scattering measurement made at +22.4°C by Stegeman and Stoicheff [5]. This comparison involves a number of difficulties, firstly because it is made for a single point — thus excluding any comparison of temperature dependence; secondly because the ultrasonic measurements were made at a lower temperature and it was thus necessary to extrapolate Barlow's results from 3.85°C to +22.4°C. Barlow and Erginsav have analyzed their results in terms of the complex shear compliance \( J^*(j\omega) \) and suppose that the compliance contains in addition to the normal Maxwell term (viscous flow) a term describing the retarded response of the liquid. They suppose that the characteristic retardation time is described by a Cole–Davidson distribution and write:

\[
\frac{J^*(j\omega)}{J_\infty} = \left[ 1 + \frac{1}{j\omega \tau_m} \right] + \frac{J_\tau / J_\infty}{(1 + j\omega \tau_r)^{1/2}}.
\]

\( J_\infty \) is the infinite frequency limiting compliance, the term in square brackets describes the behaviour of a normal maxwellian-type fluid. The second term describes the retarded compliance, \( \tau_m = \eta / \mu \) (where \( \eta \) is the viscosity) is Maxwell's shear relaxation time. \( \tau_r \) is the largest time in the distribution of retardation times. \( J_\tau \) is the retarded part of the shear compliance, and

\[
G^\mu(j\omega) = 1/F^\mu(j\omega)
\]

is the complex shear modulus.

Stegeman and Stoicheff [5] have observed a narrow doublet structure in the depolarised VH spectrum and have analysed its spectrum in terms of Rytov's theory [6]. In this theory the lineshapes are functions of an infinite frequency shear modulus, \( \mu_\infty \), and two relaxation times which Stegeman calls \( \tau_\chi \) and \( \tau_\mu \) associated respectively with the relaxation of local anisotropy and local shear strain. We will assume, as suggested by Rytov that \( \tau_\chi = \tau_\mu \). This implies that the times obtained from analysis of the VH and HH spectra should be identical — this is generally found to be true within the experimental error. In agreement with Barlow's notation we
will call this relaxation time $\tau_c$.

In some of the more recent microscopic theories [8–11] the time $\tau_c$ is identified with the relaxation of molecular orientation rather than local shear.

Barlow concludes that $\tau_c$ and $\mu_\infty$ have values very different from $\tau_m$ and $G_\infty (=1/\eta_\infty)$ but are close to and possibly identical to $\tau_r$ and $G_r (=1/\eta_r)$. We have made measurements of the light scattering spectra of benzyl benzoate over a large range of temperatures in order to test Barlow's hypothesis.

2. Comparison of $\tau_c$, $\tau_r$, $\tau_m$

The experimental apparatus and the deconvolution procedure for the analysis of the spectra has been briefly described elsewhere [7]. For these measurements, we used a scattering angle of $90^\circ \pm 0.5^\circ$ and a Fabry–Perot etalon with a free spectral range of 25 GHz.

In our experiments, we preferred to measure the relaxation time $\tau_c$ from the linewidth of the HH spectra rather than from the VH spectra. This is for a number of reasons: firstly, although we observed the presence of the narrow doublet structure in the VH spectra at temperatures above room temperature, this structure was not sufficiently resolved with our apparatus to permit an accurate determination of the lineshape parameters. This fine structure is absent in the HH spectra and the fine structure arising from coupling with the longitudinal modes is sufficiently small to be negligible. The HH spectrum may then be supposed to be lorentzian in form. Secondly, the various theories proposed to explain the VH lineshape [6,8–10] contain the assumption that the liquid is at a temperature well above its melting point. As the melting point of benzyl benzoate is between 17 and 21°C, this assumption is therefore not verified at and below room temperature. It has already been noted that these theoretical lineshapes fail completely to describe the spectra of liquids supercooled to around the glass point [7]. This uncertainty in the effect of the coupling of the shear modes into the VH spectra below the melting point may be at the origin of an apparent discrepancy sometimes observed between the linewidths of the VH and HH spectra in this region [5].

Tsay and Kivelson [11] have recently published a calculation for the lineshape of VH spectra in which they retain terms of higher order in $k^2\eta/\rho$ ($k$ is the scattering wave vector, $\eta$ is the viscosity and $\rho$ the density). This term increases in value as the temperature decreases. They report good agreement with experimental lineshapes well below the freezing point.

We have measured $\tau_c$ down to 3°C. Below this temperature the depolarised line was not well resolved. The measured values of $\tau_c$ are shown in fig. 1 along with the values of $\tau_r$, $\tau_m$ and $\eta$ given by Barlow and Erginsav [4] and also the value of $\tau_c$ reported by Stegeman and Stoicheff [5]. The latter value of $\tau_c$ is in excellent agreement with our values. It can be seen that the temperature dependence of $\tau_c$ is very similar to that of $\eta$ (and hence also $\tau_m$) but is apparently quite different to that of Barlow's retardation time, $\tau_r$. Barlow does not give error limits on his values of $\tau_r$ but he considers that it is improbable that the extrapolated values of $\tau_r$ could pass through the value of $\tau_c$ at 22.4°C and suggests that a more likely extrapolation of $\tau_r$ would be asymptotic to a value of $5.5\tau_m$. This suggested extrapolation is shown by the dotted line in fig. 1. Our error limits on $\tau_c$ are upper limits, the probable error is somewhat smaller. Although a non-Arrhenius type of behaviour for $\tau_c$ is normal in supercooled liquids there is no evidence of the sudden change in slope that would be re-

![Graph showing the comparison of $\tau_c$, $\tau_r$, and $\tau_m$](image)

Fig. 1. $\tau_c$: ∙, our measurements. The error bars indicated are upper limits; ○, Stegeman and Stoicheff [5]. $\tau_r$, $\tau_m$ and $\eta$ are taken from ref. [4]. The dotted line is the extrapolation of $\tau_r$ proposed by Barlow.
quired if \( \tau_c \) were to follow \( \tau_r \). Moreover, such a change would be very unlikely, in our opinion. In other supercooled liquids the apparent activation energy for \( \tau_c \) is seen to increase only slowly below the freezing point [7,11]. In the case of acetophenone [13] which has a similar freezing point, viscosity and depolarised linewidth, we have measured \( \tau_c \) down to 40°C below the freezing point without finding any anomaly. It seems scarcely probable therefore that there is a direct connection between \( \tau_r \) and \( \tau_c \) in this temperature range.

3. Shear wave velocity at low temperatures

Fig. 2 shows the depolarised VH spectra at low temperatures in the supercooled liquid. The central depolarised peak is no longer resolved below 0°C and has the form of the instrumental function. About 45°C below the melting point a weak doublet, corresponding to propagating shear waves in the liquid, appears on the wings of the centre line. The doublet separation increases and the width decreases as the temperature is lowered. We have analysed these spectra using our convolution technique and supposing that the deconvoluted spectrum contains a central delta-function and pair of lorentzian-dispersion shaped lines in analogy with the Brillouin spectra [12]. The corresponding transverse velocities are shown in table 1 and fig. 3. In order to compare our results with Barlow's ultrasonic measurements we have plotted our results as a function of the reduced parameter, \( \omega \tau_m \), where \( \omega \) is the frequency of the shear waves and \( \tau_m \) is obtained from Barlow [4] at the corresponding temperature. Barlow states that in the region \( \omega \tau_m > 1 \) (our measurements are confined to this region) the ultrasonic measurements are described equally well by the simpler expression

\[
\frac{J^*(J\omega)}{J_\omega} = 1 + \frac{1}{J\omega\tau_m} + \frac{2}{(J\omega\tau_m)^{1/2}}
\]

from which we may calculate an expression for the shear wave velocity:

\[
V_T = \left( \frac{1}{J\omega\rho} \right)^{1/2} \frac{(\omega\tau_m)^{1/2}}{1 + (2\omega\tau_m)^{1/2}} \times \frac{1 + [1 + (2\omega\tau_m)^{1/2}]^2}{[1 + (\frac{1}{2}\omega\tau_m)^{1/2}]^2 + \frac{1}{2}\omega\tau_m}. \tag{3}
\]

The calculated values of \( V_T \), using Barlow's values of \( J_\omega \), \( \rho \) and \( \tau_m \), are also shown in fig. 3. The agreement between measured and calculated values is satisfactory although the low-temperature (high-frequency) limit-

### Table 1

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>Frequency shift (GHz)</th>
<th>Transverse velocity (ms(^{-1}))</th>
<th>Maxwell's shear relaxation time ( \tau_m ) (ns)</th>
</tr>
</thead>
<tbody>
<tr>
<td>248.15</td>
<td>2.475</td>
<td>533.0</td>
<td>0.395</td>
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<td>0.501</td>
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<tr>
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</tr>
<tr>
<td>229.65</td>
<td>3.602</td>
<td>771.2</td>
<td>10.11</td>
</tr>
<tr>
<td>217.95</td>
<td>4.085</td>
<td>871.6</td>
<td>90.7</td>
</tr>
</tbody>
</table>

Fig. 2. VH depolarised spectra of benzyl benzoate showing the presence of propagating shear waves.
ing velocity $(1/J_{\infty p})^{1/2}$ given by Barlow is only just within our error limits.

4. Conclusion

In the supercooled liquid well below the freezing point, we have observed the appearance of a weak doublet in the depolarised light scattering spectrum. This structure arises from a propagating transverse disturbance in the liquid and the velocity obtained from our spectra is in satisfactory agreement with the shear wave velocity deduced from the ultrasonic impedance measurements of Barlow and Erginsav [4]. As the temperature is increased towards the melting point the shear wave velocity decreases and this doublet structure is no longer resolved.

At higher temperatures (above and below the melting point), we have measured the relaxation time $\tau_r$. The evolution of $\tau_r$ as a function of temperature is very similar to that of $\eta$ (and also $\tau_m$) but seems quite different to that of $\tau_c$. It is doubtful that there exists a close relationship between $\tau_c$ and $\tau_r$, contrary to Barlow's suggestion.

It has recently been noted that Rylov's theory of the spectral lineshape of light scattered from viscous fluids does not describe the experimental spectra as accurately as the more recent hydrodynamic theories [13] do, particularly as the melting point is approached. Moreover, even these hydrodynamic theories fail at sufficiently low temperatures [7]. It seems hazardous therefore to try to compare the values of $G_r$ with the values of the parameter $\mu_m$ obtained by applying Rylov theory to spectra obtained at the melting point.

It is interesting to note, however, that the intermediate temperature range where light scattering spectra show that the shear disturbance exchanges its dissipative character for a propagative one is the same temperature range for which Barlow observed a very rapid variation in the value of $\tau_c$.

References