

# The complex shear modulus of polymeric and small-molecule liquids

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The complex shear moduli of some ordinary liquids and their dependence on the shear deformation angle have been measured by the resonance method at a frequency of 73.5 kHz. From the results obtained, it is concluded that liquids exhibit a low-frequency shear elasticity—a property unknown before—which is associated with collective interactions of liquid molecules.

(Keywords: complex shear moduli; shear deformation; liquids; viscoelasticity; shear elasticity)

## INTRODUCTION

The theory of the liquid state has conventionally been considered to be lagging considerably compared with the theories of gases and solids. This viewpoint remains valid in many respects at the present time, with the exception of the application of existing statistical theory to simple liquids. As regards multi-atomic liquids, the successes of theory are rather few, and the question of their true structure remains in many respects still to be resolved. That a low-frequency shear modulus of liquids has been detected<sup>1-3</sup> proves this, though, in accordance with existing concepts, it could only be detected at frequencies higher by 5–6 orders of magnitude.

The relaxation period  $\tau$ , i.e. the time of conservation of non-equilibrium states, in the theories of the liquid state of Frenkel<sup>4</sup> and others<sup>5,6</sup>, is estimated on the basis of the self-diffusion rate, by equating that period to the time of settled existence of separate molecules. In the case of low-viscosity liquids, such calculations give values of  $\tau$  of the order of  $10^{-10}$  s. However, in a number of cases collective effects may be of significance in condensed media, these effects depending on the mutual arrangement and interactions of groups of molecules. Relaxation of the non-equilibrium state of a configuration of a large number of particles requires the concordant displacement and variation in the orientation of many molecules. The probability of such a concordant displacement may be many times smaller than that of the displacement of one molecule for the same period of time. Therefore, the relaxation time of such collective non-equilibrium states may exceed by many orders of magnitude the time of the settled existence of individual molecules. That the modulus of elasticity of liquids has been detected at a shear vibration frequency of about  $10^5$  Hz is probably associated with just that circumstance.

The presence of shear elasticity at such low frequencies proves that in liquids there exists (up to now unknown) low-frequency, viscoelastic relaxation, which is probably associated with collective interactions. This property is inherent to all liquids, without exception, irrespective of their viscosity and polarity. This circumstance is obviously of great significance for understanding the proper nature of liquids, and thorough investigation of that property (which is in direct relation to their

structure) would seem to be very useful.

The shear elasticity of liquids has been investigated already. But those investigations concerned very viscous, supercooled liquids. For instance, in the work of Volarovich *et al.*<sup>7</sup>, the moduli of shear elasticity of colophony (rosin), guaiac gum and a number of other substances were measured within their softening range. Kornfeld<sup>8</sup> carried out a similar investigation.

In 1947–49, Mason and coworkers investigated the shear elasticity of liquids. They suggested two original measurement methods<sup>9</sup>. The first is based on the generation of torsional oscillations of a piezo-quartz cylinder immersed in a liquid, while the other is based on measuring the amplitude and phase of an elastic transverse wave as reflected by a solid–liquid interface. The second method, which is suitable for measuring the shear elasticity at high frequencies, has been developed to a larger extent. Mason *et al.*'s work mainly concerned investigation of the elastic properties of viscous polymers. Attempts to apply that method to low-viscosity liquids yielded negative results.

Litovitz and coworkers were the first to apply Mason's method to the investigation of the dynamic properties of ordinary high-viscosity liquids<sup>10</sup>. McSkimin and Andreatch<sup>11</sup> improved the method by enhancing its sensitivity through application of multiple reflections of pulses (momenta) of transverse waves by a solid–liquid interface. Those authors investigated a number of ordinary liquids at a frequency of shear waves of about 40 MHz, and obtained conflicting results. They also came to the conclusion that liquids such as water, carbon tetrachloride, dibutyl phthalate, etc., do not possess any shear modulus. Positive results were obtained when they investigated polymer solutions in different solvents. Of great interest also are the works of Barlow and Lamb and coworkers, who investigated the dynamic properties of different lubrication oils, liquid crystals and other liquids<sup>12-17</sup> at high frequencies. A review article<sup>18</sup> presents a detailed analysis of those research works. Further work<sup>19</sup> presents a theoretical consideration of different models of the viscoelastic behaviour of liquids.

All the above and subsequent works involving the investigation of the shear dynamic properties of liquids were carried out with highly viscous and supercooled

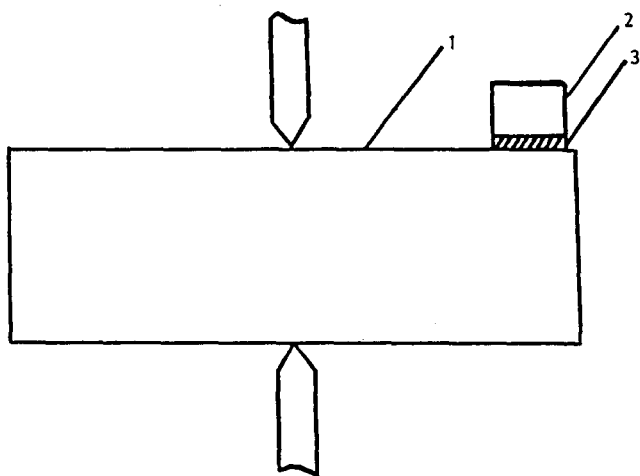


Figure 1 Piezo-quartz with an additional link: 1, piezo-quartz; 2, coverplate; 3, liquid film

liquids at frequencies of scores of megahertz. Those research works are connected with investigation of the viscoelastic relaxation associated with the character of thermal motion of individual molecules of a liquid. In particular, Barlow and Erginsav<sup>20</sup> give a comparison of the viscoelastic properties of benzyl benzoate with its dielectric properties, as well as with data on light scattering. Gray *et al.*<sup>21</sup> investigated the viscoelastic behaviour of fused polystyrene at different frequencies within the vitrification temperature range. At low frequencies, a technique based on torsional oscillations was applied. The authors have shown that the viscoelastic behaviour of low-molecular-weight polystyrene solutions is the same as that of polymeric liquids.

A method of reflection of high-frequency transverse waves by a solid-liquid interface was applied to investigate low-viscosity liquids and yielded negative results. This can be explained by the low sensitivity of the method, which depends on the relative values of the shear elasticity of the solid and the liquid investigated differing by many orders of magnitude.

A resonance measurement method was used elsewhere<sup>1-3</sup> to detect the low-frequency shear elasticity of liquids. The method is based on investigation of the influence of a liquid film in contact with a horizontal lateral surface of piezo-quartz at one of its ends (Figure 1) and covered by a solid coverplate on the crystal oscillation parameters. When the piezo-quartz is oscillating longitudinally, the liquid film undergoes shear deformation. At this juncture, the coverplate, in view of the weak bond due to the liquid film, is considered to be practically at rest, and the thickness of the liquid interlayer is considered to be much smaller than the length of a shear wave.

Under these conditions, if the liquid possesses the shear bulk modulus, the piezo-quartz resonance frequency should increase, doing this inversely proportional to the liquid film thickness. Just this behaviour was detected<sup>1-3</sup>. However, subsequent experiments have demonstrated that the shear moduli measured are influenced very strongly by a number of factors, such as electrical induction (sighting) and the existence of a normal oscillation component on the working surface, as well as the cleanliness of the latter. The last two factors cause a considerable underestimation of the shear moduli being measured; therefore, in later research<sup>22,23</sup> taking into

account the aforesaid factors, higher shear moduli of liquids that are closer to the true ones have been obtained.

The dependence of the effective shear modulus of liquids on the deformation has been investigated<sup>23</sup>, and it has been shown that the elasticity retains its constant value at small shear angles. The existence of a low-frequency shear elasticity of liquids presupposes the possibility of shear waves propagating in those liquids. It has been shown<sup>24</sup> that the shear elasticity of a number of liquids can be measured under conditions of complete decay of shear waves in a sufficiently thick layer of liquid. Finally, the shear elasticity has been determined by measuring the length of shear waves<sup>25</sup>. The present work deals with the measurement of the complex shear modulus of liquids and its dependence on the shear deformation angle.

### THEORY

Below, we shall briefly discuss the derivation of a general formula expressing the complex shift of the resonance frequency of piezo-quartz under the action of an additional bond provided by a liquid film covered by a coverplate. For this purpose, it is necessary to determine the acoustic impedances of liquid  $Z_l$  and piezo-quartz  $Z_q$  by considering the interaction forces in the given system, and to equate them to one another, which is possible in the case of a weak bond provided by a liquid film. Owing to the weakness of this bond, the piezo-quartz coverplate almost does not undergo any shear deformations.

We shall set the origin of coordinates in the middle of the horizontal lateral surface of the piezo-quartz and we shall confine our consideration to one half of it.

The impedance of piezo-quartz is equal to the ratio between the force exerted by piezo-quartz and acting on the liquid, and the velocity of piezo-quartz particles at its end:

$$Z_q = \frac{(\lambda + 2\mu)Q(\partial u/\partial x)|_{x=l}}{(\partial u/\partial t)|_{x=l}} \quad (1)$$

Here  $\lambda$  and  $\mu$  are the Lamé coefficients,  $Q$  is the cross-section of piezo-quartz,  $l$  is its half-length, and  $u$  is the displacement of quartz particles as a function of time  $t$  and distance  $x$  from the piezo-quartz centre (see Figure 1). Assuming  $u = u_0 \sin(K^*x)l^{i\omega t}$ , where  $u$  is the cyclic frequency,  $u_0$  is the amplitude of piezo-quartz oscillations at its end, and  $K^*$  is its complex wavenumber, we have for the impedance of piezo-quartz the expression:

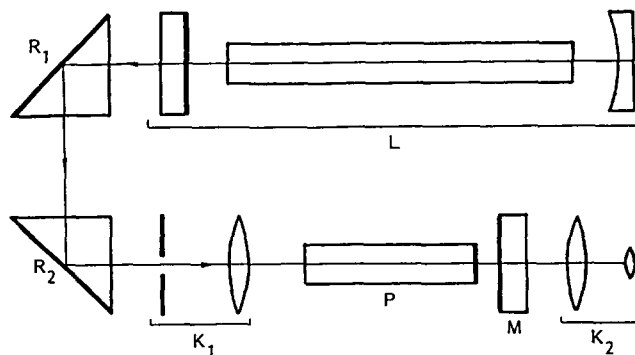


Figure 2 Schematic diagram of the set-up for determination of the piezo-quartz oscillation amplitudes: L, gas laser; R<sub>1</sub> and R<sub>2</sub> turnable prisms; K<sub>1</sub>, collimator; P, piezo-quartz; M, second mirror; K<sub>2</sub>, autocollimator

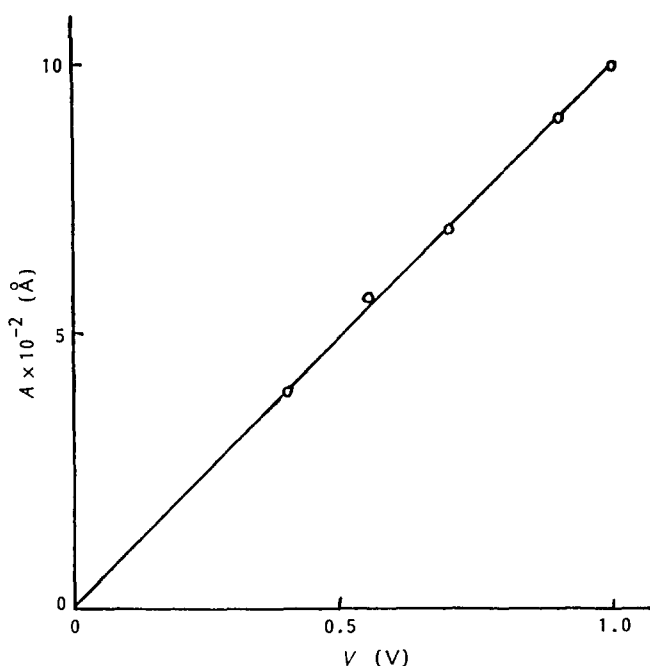


Figure 3 Dependence of the amplitude of oscillations of the piezo-quartz on the voltage taken off it

$$Z_q = icQ\rho \cot(K^*l) \quad (2)$$

where  $c$  is the velocity of longitudinal waves in piezo-quartz and  $\rho$  is its density.

The impedance of liquid is equal to the ratio between the force exerted by liquid and acting on piezo-quartz, and the velocity of liquid particles at  $z=0$ , where  $z$  is the distance from the piezo-quartz surface:

$$Z_l = \frac{SG^*[\partial\xi(z,t)/\partial z]|_{z=0}}{[\partial\xi(z,t)/\partial t]|_{z=0}} \quad (3)$$

where  $S$  is the contact area (the area of the coverplate base) and  $G^*$  is the complex shear modulus of the liquid.

The expression for the horizontal shift of liquid particles  $\xi(z,t)$ , which is the sum of the direct wave and that reflected from the coverplate, is as follows:

$$\xi(z,t) = A(l^{-i\kappa^*z} - l^{-i[\kappa^*(2H-z) - \varphi^*]})l^{-i\omega t} \quad (4)$$

where  $\kappa^*$  is the complex wavenumber of the liquid,  $H$  is the interlayer thickness and  $\varphi^*$  is the complex phaseshift when the wave is reflected from the liquid-coverplate interface. It follows from the boundary conditions that the amplitude  $A$  is:

$$A = \frac{u_0}{1 - l^{-i(2H\kappa^* - \varphi^*)}}$$

From the equation of motion of the coverplate of mass  $m$  under the action of the force exerted by liquid, we obtain:

$$\varphi^* = i \ln \frac{m\omega^2 - iS\kappa^*G^*}{m\omega^2 + iS\kappa^*G^*} \quad (5)$$

whence it follows that the phaseshift depends on the coverplate mass and the properties of the liquid.

Determining the derivatives with respect to  $z$  and  $t$  from formula (4) and substituting them into (3), we obtain for the impedance of liquid the expression:

$$Z_l = \frac{S\kappa^*G^*}{\omega} \frac{1 + l^{-i(2\kappa^*H - \varphi^*)}}{1 - l^{-i(2\kappa^*H - \varphi^*)}} \quad (6)$$

Equating (2) and (6) and bearing in mind that

$$(K^* - \Delta\omega^*/c)l = \pi/2$$

we obtain for the complex frequency shift  $\Delta\omega^*$  the expression:

$$\Delta\omega^* = \frac{2S\kappa^*G^*}{M\omega} \frac{1 + \cos(2\kappa^*H - \varphi^*)}{\sin(2\kappa^*H - \varphi^*)} \quad (7)$$

where  $M = 2lQ\rho$  is the piezo-quartz mass.

Expression (7) is simplified to the utmost by assuming that, owing to the weakness of the bond provided by the liquid film, when piezo-quartz is oscillating, the coverplate is practically at rest, and that the film thickness is much smaller than the length of the shear waves in the liquid. Under the conditions of our experiments the validity of these assumptions was assured. Taking into account that the contact area is only at one end of the horizontal surface of piezo-quartz, we shall obtain from (7), when passing over to a linear frequency  $f$  and complex frequency shift  $\Delta f$ , the following expression for the complex shear modulus:

$$G^* = 4\pi^2 M f \Delta f^* H / S \quad (8)$$

It follows from this formula that, when the liquid has a bulk shear modulus, both real  $\Delta f'$  and imaginary  $\Delta f''$  frequency shifts should be proportional to the reciprocal of the film thickness. The imaginary frequency shift is equal to the variation in the damping of the oscillating system:

$$\Delta f'' = \Delta\alpha/2 \quad (9)$$

where  $\Delta\alpha$  is the variation in the width of the resonance curve of piezo-quartz. The mechanical loss tangent is equal to:

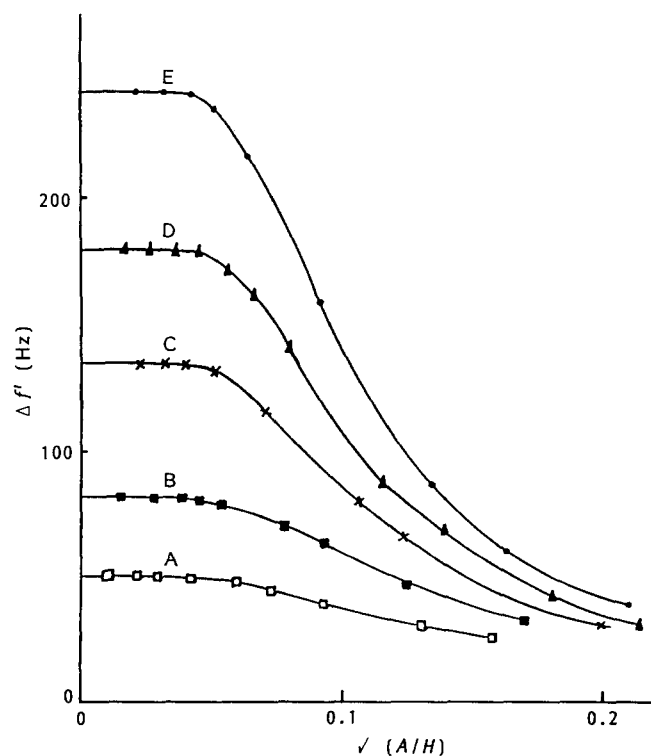


Figure 4 Dependence of the real piezo-quartz frequency shift on the shear deformation angle for diethylene glycol films of different thicknesses: A, 4.75  $\mu\text{m}$ ; B, 3.05  $\mu\text{m}$ ; C, 1.173  $\mu\text{m}$ ; D, 1.37  $\mu\text{m}$ ; E, 1.05  $\mu\text{m}$

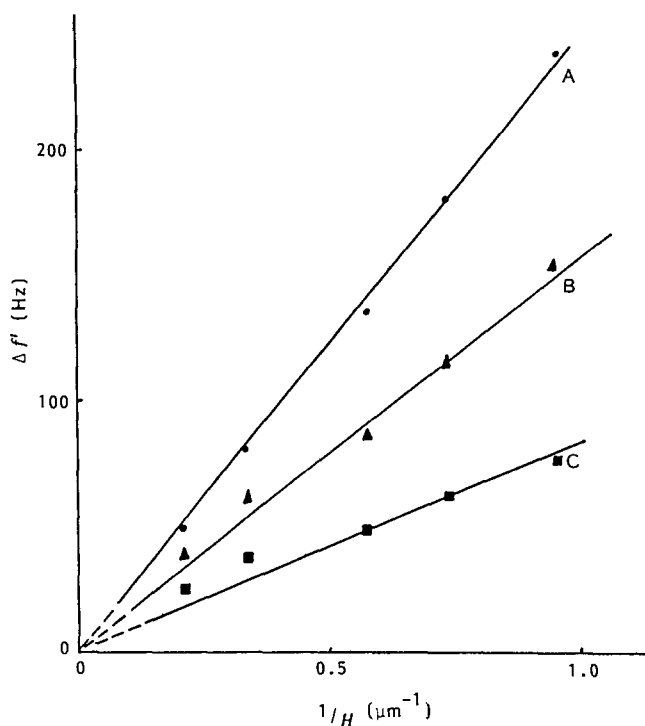


Figure 5 Dependence of the real piezo-quartz frequency shift on the inverse film thickness for different shear deformation angles: A, 0 and 10°; B, 34°; C, 1°24'

$$\tan \theta = \frac{G''}{G'} = \frac{\Delta f''}{\Delta f'} = \frac{\Delta \alpha}{2 \Delta f'} \quad (10)$$

## EXPERIMENTAL METHODS

When investigating the shear modulus of liquids as a function of the shear deformation angle, it is important to measure the absolute values of the oscillation amplitudes of piezo-quartz as a function of the voltage taken off it. This dependence is determined by the given experimental conditions, in particular by the dimensions of the electrodes, the size of the air gap between the electrodes and the piezo-quartz, etc. To determine that dependence, we used the Fabry-Perot interferometer method. A silver film having a high reflection coefficient was applied to the right-hand end face of the piezo-quartz, which served as one of the mirrors of the interferometer. The second mirror of the interferometer, in the form of a flat glass plate, was coated with silver by thermal evaporation *in vacuo*, using the technique of producing films for multiple-beam interferometry. A Ne-He gas laser with wavelength  $\lambda = 6328 \text{ \AA}$  was used as a monochromatic light source. Figure 2 represents the set-up for determining the oscillation amplitude of piezo-quartz. The gas laser L emits light which, after two reflections on prisms  $R_1$  and  $R_2$  and having passed through the collimator  $K_1$ , impinges on the Fabry-Perot interferometer consisting of piezo-quartz P and flat mirror M.

Having passed through the interferometer, the light beam falls on the autocollimator  $K_2$ , by means of which it is possible to observe visually the interference pattern and to measure directly the angles  $\varphi$  between the normal to the interferometer mirror and the beam forming light-coloured rings. The angles  $\varphi$  satisfy the condition:

$$2h = m\lambda \cos \varphi \quad (11)$$

Here  $h$  is the spacing between the interferometer mirrors and  $m$  is the interference order.

The second mirror of the interferometer is secured in a special mounting provided with micrometer screws that allow adjustment of the mirror into a plane-parallel position with regard to the piezo-quartz end face. The quartz holder is rigidly attached to the holder of the second mirror mounting, to eliminate any vibrations.

When the piezo-quartz is oscillating, the distance  $h$  varies periodically, so that the interference rings widen in proportion to the piezo-quartz amplitude. It follows from (11) that, under conditions in which the angle  $\varphi$  is sufficiently small, the piezo-quartz amplitude is determined by the expression:

$$A = \frac{1}{2} m \lambda \varphi \Delta \varphi \quad (12)$$

where  $\Delta \varphi$  is the increase in the width of an interference ring of order  $m$ , expressed in radians.

Figure 3 shows the dependence of the piezo-quartz amplitude upon the voltage taken off it, obtained by the method described. The dependence, as it should be, is linear and converges towards the origin. The graph shown in Figure 3 allows the piezo-quartz oscillation amplitude to be known at any desired moment.

In the present work we used a piezo-quartz crystal of 18.5° cut, which practically oscillates only lengthwise. Moreover, crystals of the above mentioned type possess a particularly small value of the normal-directed component of vibration on the active horizontal face, whose presence does not have an appreciable effect upon the experimental results. The piezo-quartz mass was equal to 6.7 g and the resonance frequency was 73.5 kHz. The area of the coverplate base was equal to 0.2 cm<sup>2</sup>, and its mass was 0.25 g.

Piezo-quartz is mounted in a special holder between two steel needles along a nodal line passing through its middle. Since piezo-quartz frequently requires special cleaning, we used electrodes with an air gap.

To excite the piezo-quartz to the main (basic) resonance frequency, a stabilized generator was used, whose frequency could be controllably varied. The range

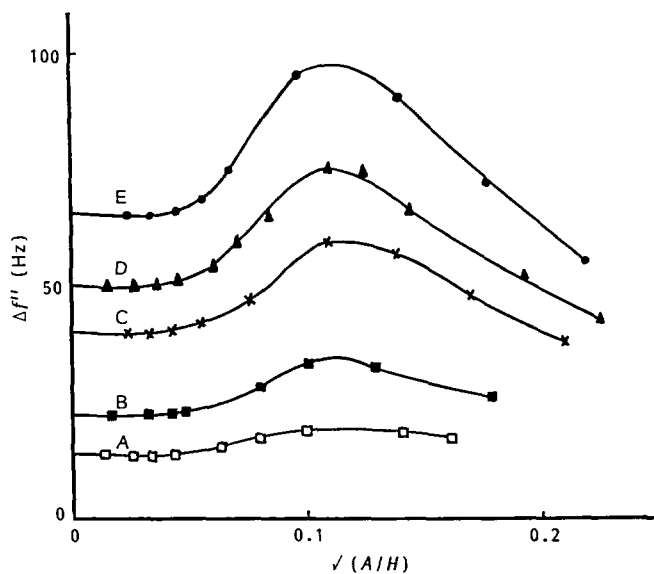
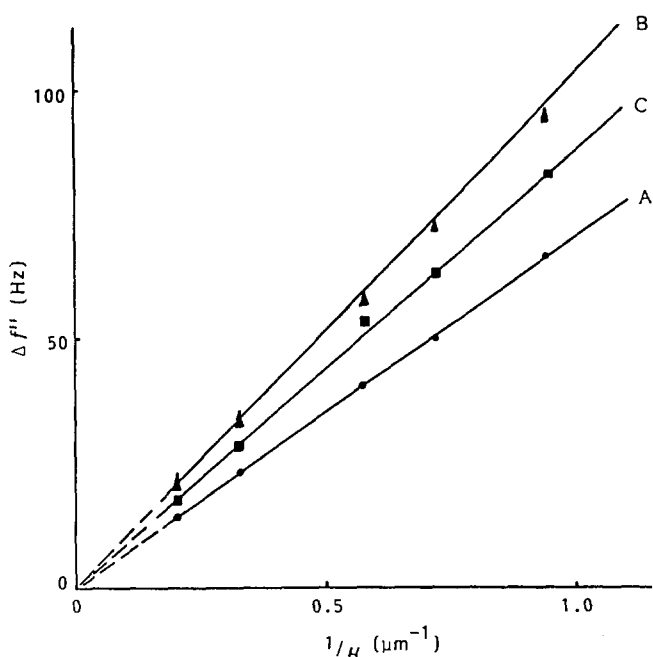


Figure 6 Dependence of the imaginary piezo-quartz frequency shift on the shear deformation angle for the same thicknesses of diethylene glycol films: A, 4.75 μm; B, 3.05 μm; C, 1.73 μm; D, 1.37 μm; E, 1.05 μm



**Figure 7** Dependence of the imaginary piezo-quartz frequency shift on the inverse film thickness for different shear deformation angles: A, 0 and 10°; B, 34°; C, 1°24'

of its gradual variation was fairly wide, so that the complex shift of the piezo-quartz resonance frequency could be measured.

Special attention was given to the cleanliness of the active surfaces and the purity of the liquids being investigated. The surfaces of piezo-quartz and coverplate were previously washed in organic solvents, treated in a chromic mixture and then subjected to cleaning in a glow discharge. A lengthy steaming of the surfaces was also resorted to. The liquids to be investigated were thoroughly cleaned by known methods.

The measurement technique was as follows. Immediately after cleaning, the liquid to be investigated in the form of a small droplet was applied to the active piezo-quartz surface by means of a clean glass rod and carefully covered with the coverplate. After fixing the piezo-quartz together with the coverplate in the quartz holder, the film thickness in the gap was determined by an optical method. During the experiment, the film thickness was controlled by repeated measurements. A uniform film thickness was achieved by using a special device for rotating the coverplate about its own vertical axis.

After determining the film thickness, we measured the dependence of the piezo-quartz resonance frequency on the voltage taken off it, and simultaneously the width of the resonance curve. We repeated this procedure for various thicknesses of liquid film being investigated. The film thickness was varied by displacing part of the liquid from the gap. The frequency shift measurement error did not exceed about 1 Hz. The accuracy of the measurement of the thickness of a liquid interlayer was equal to 0.02  $\mu\text{m}$ . If the shear deformation angle amplitude has a small value, it is proportional to the ratio between the piezo-quartz amplitude and the thickness of the liquid film. In the present experiments the deformation angle did not exceed 3° to 4°. Therefore, the ratio  $A/H$  may serve as a measure of angular shear deformation amplitude  $\Psi$ . However, to facilitate plotting we will present the experimental results as a function of the

square root of that ratio.

## EXPERIMENTAL RESULTS

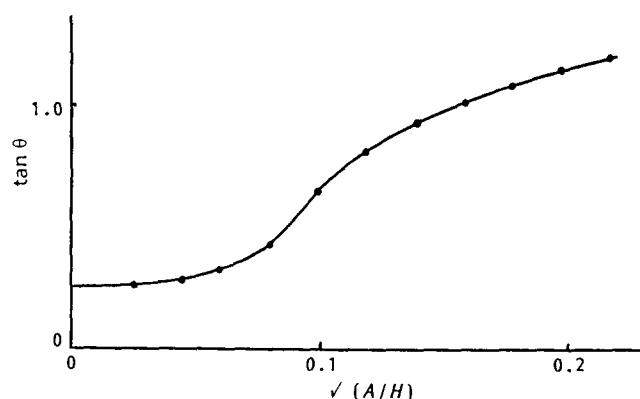
Now, let us discuss the experimental results. *Figure 4* shows the dependence of the real shift of the piezo-quartz frequency on the shear deformation angle for various thicknesses of a diethylene glycol film. These dependences have several peculiar features. First, at small shear angles they show horizontal sections corresponding to the linear elasticity of liquid. In this region, the shear stress is proportional to the shear deformation. The second peculiar feature is that the violation of the proportionality between the elastic stress and the shear deformation value does not depend upon the film thickness, and is observed at the same shear angle  $\Psi_K$ , which will be termed the critical shear angle and corresponds to a certain critical shear stress. Another peculiarity of the curves shown in *Figure 4* is that the limit of linear elasticity is rather sharp. And finally, all the curves possess inflection points corresponding to the same shear deformation angle. At this angle, the steepness of the variation in the real frequency shift is maximum and, hence, so is the steepness of variations in the shear elasticity of liquid.

*Figure 5* shows the dependences of the real frequency shift upon the inverse thickness of films for various shear angles. Curve A corresponds to the linear elasticity region. It is evident that the frequency shift is proportional to the inverse thickness of the film. This indicates that the liquid possesses bulk shear elasticity which does not depend upon the film thickness (at least with the thickness used in the present work).

Similar dependences, but having smaller slopes, are obtained with other shear deformation angles. Consequently, a definite value of shear elasticity corresponds to each shear angle.

*Figure 6* shows the dependences of the imaginary frequency shift of piezo-quartz upon the shear deformation angle for various thicknesses of diethylene glycol films. It is evident that the damping within the linear region also remains constant. The maximum damping is observed at the same shear angle for all film thicknesses, this angle being equal to the angle of the greatest steepness of the variation in the real frequency shift. That angle is characteristic of every liquid and will, therefore, be designated by  $\Psi_p$ . For diethylene glycol  $\Psi_p \approx 42^\circ$ .

*Figure 7* shows the dependences of the imaginary frequency shift upon the inverse thickness at various shear



**Figure 8** Dependence of the mechanical loss tangent on the shear deformation angle for diethylene glycol

**Table 1** Basic experimental results for the liquids investigated here

Liquids	$t$ ( $^{\circ}\text{C}$ )	$G' \times 10^{-6}$ ( $\text{dyn cm}^{-2}$ )	$\tan \theta$	$\Psi_K$	$\Psi_P$
Ethylene glycol	24	0.91	0.27	12'	1 $^{\circ}$ 46'
Diethylene glycol	23	1.22	0.30	10'	0 $^{\circ}$ 42'
Triethylene glycol	21	1.27	0.27	9'	0 $^{\circ}$ 59'
Butyl alcohol	21	1.06	0.10	7'	0 $^{\circ}$ 34'
Octyl alcohol	23	1.34	0.16	7'	0 $^{\circ}$ 58'
Cyclohexanol	24	1.12	0.30	9'	1 $^{\circ}$ 06'
Dimethylphthalate	23	0.97	0.10	12'	1 $^{\circ}$ 50'
Water	22	0.31	0.30	—	—

deformation angles. Curve A corresponds to the region of linear elasticity, curve B to the shear deformation angle equal to 34', and curve C to angle 1 $^{\circ}$ 24'. We see that the dependences are linear and converge to the origin, and that a quite definite value of the complex shear modulus corresponds to every shear angle.

Figure 8 shows the dependence of the mechanical loss tangent on the shear deformation value. We can see that  $\tan \theta$  increases with deformation angle, exhibiting an inflection point at a certain angle. Such a dependence of  $\tan \theta$  is characteristic of almost all the liquids investigated. The inflection point is also observed on this curve at the angle  $\Psi_P$ . Figures 9 and 10 show the dependences of the real and imaginary shear moduli upon the shear deformation angle for butyl alcohol and dimethylphthalate. We see from Figure 9 that the shear modulus decreases more sharply for butyl alcohol (curve A) than for dimethylphthalate (curve B). In the latter case (Figure 10) the maximum imaginary shear modulus is observed at a much larger shear deformation angle (curve B).

We have also measured the complex shear modulus of water. Unfortunately, we have not succeeded in studying its dependence on the deformation angle, because of the comparatively great volatility of water, which does not allow us to maintain the experimental conditions, viz. film thickness constant for a long period of time. Approximately similar results are obtained with all the liquids investigated in the present work.

Table 1 presents basic experimental results for the liquids investigated. The first column gives the temperatures of the experiments. The next two columns give the values of the real shear modulus and of the mechanical loss tangent within the linear elasticity region. Then the values of critical angles  $\Psi_K$  are given. The last column lists the angles  $\Psi_P$  which vary within a fairly wide range.

It should be stressed that, for all the liquids investigated, up to a certain limiting shear angle or a critical stress, both the real and the imaginary parts of the complex shear modulus are constant, viz. we have detected the region of linear complex elasticity (the generalized Hooke's law). Within this region, dissipative processes may be treated phenomenologically on the basis of the Boltzmann integro-differential equations of elastic after-effect.

## DISCUSSION

The molecular aspects of these processes should probably be analogous to Maxwell relaxation, where, owing to the rearrangement of molecules, the rate of disappearance of

elastic stress is proportional to the shear stress value. When passing beyond the 'elastic limit', the dissipative processes are accelerated, which accounts for an increase in the mechanical loss tangent.

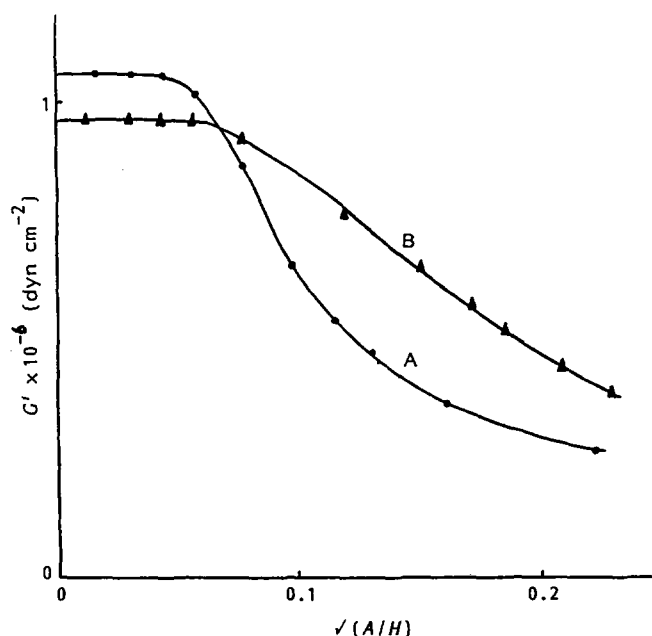
Apparently at large deformations the excess free energy of deformation is able to overcome the activation barriers, leading to other rearrangements of liquid molecules, thus increasing the intensity of dissipative processes. The consumption of the deformation energy in overcoming those barriers and subsequent energy dissipation explain the decrease in the effective dynamic shear modulus with increasing shear angle.

All the liquids investigated have elongated molecules. We may suppose that the mutual arrangement and interactions of liquid molecules change significantly under the action of progressively increasing shear deformations. In particular, the elongated liquid molecules may become oriented along the direction of piezo-quartz oscillations.

It should be stressed that the shear elasticity measured is connected with the low-frequency mechanism of viscoelastic relaxation, which was unknown before. In fact, if we were to measure the low-frequency tail of a high-frequency viscoelastic relaxation connected with the mechanism of thermal motion of separate liquid molecules, we would find the mechanical loss tangent to be much greater than unity. But it is clear from Table 1 that, for all the liquids investigated,  $\tan \theta < 1$  and in several cases  $\tan \theta \ll 1$ .

The method of measuring the shear elasticity described in the present work may be applied to the examination of liquids within a wide range of varying viscosity. Thus we have additionally determined  $G'$  and  $\tan \theta$  values for three polymeric liquids of very different viscosity<sup>25</sup>.

For poly(diethylsiloxane), having a viscosity of about 260 cS, the following data were obtained:  $G' = 5.5 \times 10^5 \text{ dyn cm}^{-2}$ ,  $\tan \theta = 1.65$ . In the case of two liquid poly(methylsiloxanes) having viscosities of 52 000 and 509 000 cS, the following results were obtained, respectively:  $G' = 2.7 \times 10^6 \text{ dyn cm}^{-2}$ ,  $\tan \theta = 0.5$ , and



**Figure 9** Dependence of the real shear modulus on the shear deformation angle for butyl alcohol (A) and dimethylphthalate (B)

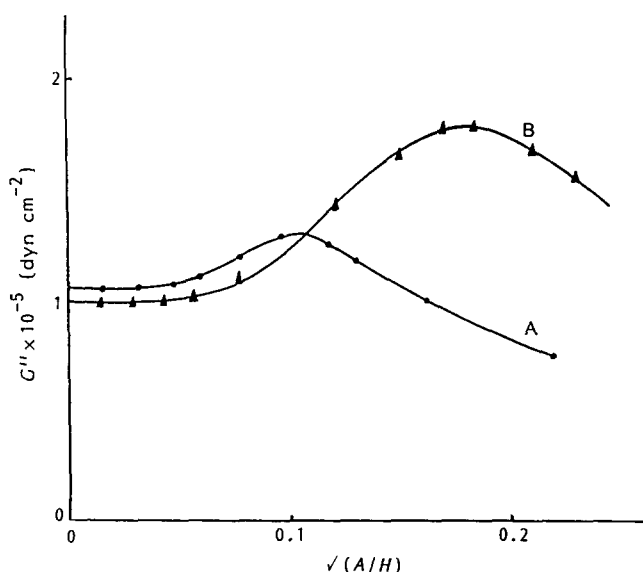


Figure 10 Dependence of the imaginary shear modulus on the shear deformation angle for butyl alcohol (A) and dimethylphthalate (B)

$$G' = 6.7 \times 10^6 \text{ dyn cm}^{-2}, \tan \theta = 0.15.$$

References 16 and 17 described research into the viscous and elastic properties of a number of liquid poly(methylsiloxanes) within a wide frequency range.

Comparison of the above data with the results of the cited references gives a good qualitative agreement, if the differences between the liquids examined and in their viscosities are considered. Thus, for example, according to the data<sup>16,17</sup> for the liquid poly(dimethylsiloxanes) having viscosity of 1 000 000 cS,  $G' = 1.7 \times 10^6 \text{ dyn cm}^{-2}$  and  $\tan \theta = 0.6$  at the frequency of our experiment (73.5 kHz).

In conclusion, it will be pointed out that, in the case of low-viscosity liquids examined in the present work, the nature of the viscous and elastic relaxation is essentially

different from that of polymers.

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