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Measurement of Shear Elasticity and Viscosity of Liquids at Ultrasonic Frequencies

W. P. Mason, W. O. Baker, H. J. McSkimin, and J. H. Heiss
Bell Telephone Laboratories, Murray Hill, New Jersey

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It has long been suspected that if liquids were sheared sufficiently rapidly they would exhibit a shear elastic effect as well as a viscous effect. This supposition was verified recently by one of the writers (see reference 8) by employing a torsionally vibrating crystal and measuring the mechanical loading for the shear wave by observing the increased resistance at resonance and the change in the resonant frequency. By this method it was shown that long chain polymer liquids had shear configurational elasticities in the order of 10^7 dynes/cm^2.

The use of a torsional crystal is limited in frequency to about 2 to 3×10^6 cycles on account of the small sizes needed. In the present paper the range of shear wave measurements in liquids has been extended up to 60 megacycles by observing the effect, on a series of shear waves in a fused quartz rod, of terminating the rod by a thin layer of a liquid. The shear wave in the rod is altered in magnitude and phase by the boundary layer impedance of the liquid. By observing the reflection loss and the change in phase caused by the liquid layer, a measure is obtained of the shear impedance of the liquid. By employing a fused quartz rod for which the shear wave strikes the reflecting surface at an angle from the normal of about 79 degrees, the effect of the shear wave impedance on the boundary is greatly enhanced and a more accurate measurement obtained.

Both the torsional crystal and high frequency shear wave techniques applied to polyisobutylene and poly-α-methylstyrene liquids, show that there are two main relaxation frequencies in these liquids. At frequencies under 100 kc, the shear stiffness is in the order of 3×10^7 dynes/cm^2, while in the high megacycle range it has increased to 5×10^9 dynes/cm^2. The low shear elasticity appears to be associated with a composite motion of molecular rotation and translation that allows a configurational change to occur from the most probable chain shape. When the shear stress is removed, the molecule quickly returns to its most probable shape. This results in a low shear stiffness. At high frequencies this motion cannot take place, and the shear stiffness is determined by motions within single potential wells, and the value approaches that for a crystal. It is shown that the dispersion for longitudinal waves measured recently (see reference 11) is primarily due to the shear mechanisms investigated.

I. INTRODUCTION

IT HAS long been suspected that if liquids were sheared sufficiently rapidly, they would exhibit a shear elastic effect as well as a viscous effect. In fact, Maxwell,[1] on the basis of a gas model, predicted that an instantaneous shear distortion would have a relaxation time τ and a relaxation frequency f_r given by the formulas

$$\tau=\eta/\mu;\ f_r=1/(2\pi\tau)=\mu/(2\pi\eta), \tag{1}$$

where η is the shear viscosity and μ the shear elasticity. A similar result has recently been obtained by Frenkel[2] by assuming that a liquid has a short range order similar to a solid, and identifying the relaxation time τ as the mean life in a sedentary state. For ordinary light liquids, assuming a shear elasticity similar to a loosely knit crystal—about 10^{10} dynes per square centimeter—and a viscosity of about 0.01 poise, the relaxation frequency is in the order of 10^{11} cycles, which is considerably above any present day ultrasonic equipment.

However, if we use long chain polymer liquids, certain significant new effects appear. Long chain molecules are flexible, and can take up many different shapes. Certain coiled-up shapes are more probable than others and if a molecule is distorted from this shape, the molecule tends to return to it in a very short time when the stress is removed. This type of elasticity is called configurational elasticity, and the rapidity of regain of its most probable shape determines the relaxation time for such configurational elasticities.

When a shearing stress is put on such a molecule, segments of the molecule 20 to 30 chain atoms long are displaced from one configuration to another configuration which coincides with an empty space or hole in the liquid. A single segmental jump will have two effects on the polymer molecule. First, the shape of the molecule will be slightly altered by the motion of the segment, and second, the center of gravity of the molecule will be slightly shifted. The result of a large number of successive segmental jumps will likewise be twofold. First, the molecule will wriggle about from one shape to another, and second, the center of gravity will undergo a slow wandering. When these segment jumps are caused by the application of a shearing stress, the wandering of the center of gravity produces the viscous flow, while the change of shape from the most probable shape produces the shear configurational elasticity.

The flow of segments has to occur over certain energy barriers W, and hence the temperature variations of the viscosity of some polymers such as linear polyesters have been shown to satisfy an equation of the type

$$\eta_1=Ae^{BZ^{\frac{1}{2}}}e^{W/RT}, \tag{2}$$

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[1] J. Clark Maxwell, "On the Dynamical Theory of Gases," Phil. Trans. Roy. Soc. **157**, 49–88 (1867).

[2] J. Frenkel, *Kinetic Theory of Liquids* (Oxford University Press, London, 1946), Chapter IV, pp. 196–200.

where W is the free energy barrier, R the gas constant, and T the absolute temperature. The probability of the center of gravity of the molecule as a whole moving in a given direction depends on the probability of a number of successive segmental jumps occurring in the same direction, and hence decreases with the increasing molecular weight Z. Equation (2) is an equation proposed by Flory[3] and justified on a theoretical basis by Kauzmann and Eyring.[4] A more general equation which has a similar segmental flow justification[5] is

$$\log\eta = A\log Z + W/RT, \tag{3}$$

and this equation holds for the liquids investigated.

When the stress is removed from the molecule, the molecule returns to its most probable position by a series of segmental jumps. It has been proposed by Alfrey[6] that the activation energy should be the same as for viscous flow, and that there should be no chain length effect or

$$\eta_1 = A' e^{W/RT}. \tag{4}$$

Actual experiments given here and in a previous paper on longitudinal measurements[2] show, however, that the average activation energy is only $\frac{3}{4}$ of that for viscous flow, and there is a chain length effect which is considerably smaller than that for viscous flow.

If we go to still higher frequencies so that single chain segments do not have time to rearrange in the time of a single cycle, the configurational elasticity cannot be excited, but a shear elasticity caused by changing the relative positions of the segments of the molecules in single potential wells can still occur and this is a crystalline type of elasticity which should be of the order of 10^9 to 10^{10} dynes/cm^2. This type of elasticity also occurs at low temperatures for which η_1 and η_2 become so large that the shear stiffness is the dominant impedance. All of these effects can be represented by the equivalent electrical circuit of Fig. 1. The flow viscosity is represented by η_1, the configurational elasticity by μ_2, the configuration viscosity which determines the rate at which the configurational elasticity is relaxed is given by η_2, while μ_3 represents the high frequency crystalline elasticity. Another relation that is equivalent to this is shown by Fig. 1B. The constants of this circuit are related to those of circuit 1A by the equations

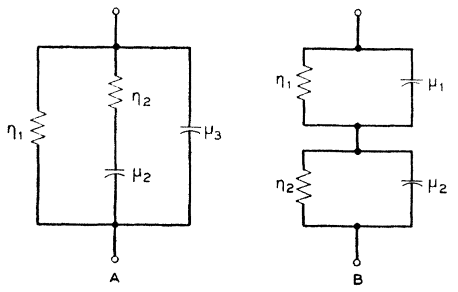

FIG. 1. Equivalent electrical circuits.

$$\begin{aligned}
\eta_1{}^A &= \eta_1{}^B + \eta_2{}^B,\\
\eta_2{}^A &= \frac{\eta_1{}^B\eta_2{}^B(\eta_1{}^B+\eta_2{}^B)(\mu_1{}^B+\mu_2{}^B)^2}{(\eta_1{}^B\mu_2{}^B-\eta_2{}^B\mu_1{}^B)^2},\\
\mu_2{}^A &= \frac{(\eta_1{}^B+\eta_2{}^B)^2(\mu_1{}^B+\mu_2{}^B)\mu_1{}^B\mu_2{}^B}{(\eta_1{}^B\mu_2{}^B-\eta_2{}^B\mu_1{}^B)^2},\\
\mu_3{}^A &= \mu_1{}^B+\mu_2{}^B.
\end{aligned} \tag{5}$$

Considerable study has been given to the configurational type of elasticity and it has been shown that under equilibrium conditions, the "kinetic" theory of elasticity describes the elastic retractive force, for example as[7]

$$F = -T(\partial S/\partial L) = (kT\nu/L_0)[\alpha - (1/\alpha^2)], \tag{6}$$

where T = absolute temperature, L = length of sample, S = entropy, L_0 = length of unstretched sample, ν = number of chains in the volume V, and $\alpha = L/L_0$. Here this theory accounts nicely for the widely observed shear modulus of 10^6 dynes/cm^2 and for its increase with temperature. It is, however, an equilibrium theory and requires time for equilibrium to be established before it is valid. For the torsional crystal measurements reported in the next section, the elasticity is higher than that of Eq. (6), and increases with a decrease in temperature. It appears likely that it is determined by nearest neighbor interaction, rather than an equilibrium between all elements of the chain, and

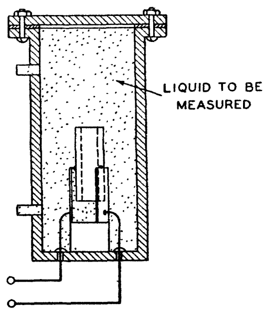

FIG. 2. Experimental arrangement.

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[3] P. J. Flory, J. Am. Chem. Soc. 62, 1057 (1940).

[4] Walter Kauzmann and Henry Eyring, J. Am. Chem. Soc. 62, 3113–3125 (1940).

[5] Baker, Fuller, and Heiss, J. Am. Chem. Soc. 63, 2142 (1941).

[6] Turner Alfrey, Jr., *Mechanical Behavior of High Polymers* (Interscience Publishers, Ind., New York, 1948), p. 115.

[7] F. T. Wall, J. Chem. Phys. 10, 132 (1942); 10, 485 (1942); 11, 1527 (1943); P. Flory, Chem. Rev. 35, 51 (1944).

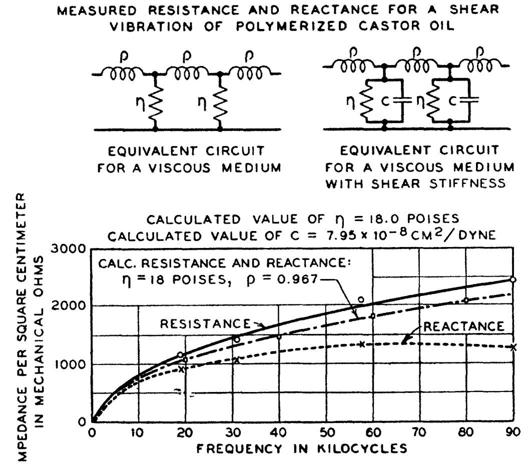

FIG. 3. Equivalent circuits and measured values for castor oil.

has been designated as a quasi-configurational elasticity.

II. USE OF TORSIONAL CRYSTAL IN MEASURING CONFIGURATIONAL ELASTICITIES AND FLOW VISCOSITIES

Since the configurational elasticity of long chain molecule liquids is in the order of 10^7 dynes/cm^2 while the associated shear viscosities may range from 10 to millions of poises, the relaxation frequencies of such liquids will be in the order of 10^5 to a few cycles, and should be in the range of easily measured frequencies. In fact, by employing a torsionally vibrating crystal whose motion is tangential to the surface, one of the writers[8] showed that the shear viscosity and elasticity of polymer liquids could be measured. In light liquids the method gives directly the viscosity of the liquids. Under temperature-controlled conditions the method is accurate to within a percent.

The method consists of using a torsional quartz crystal, measuring the change in resonant resistance, and change in frequency caused by immersing the crystal in the liquid. Figure 2 shows the experimental arrangement. These measured quantities determine the resistance and reactance components of the liquid for a pure shearing motion. If the liquid is a purely viscous liquid the wave is propagated by having layers of mass ρdx coupled to adjacent layers by the viscosity η/dx of the liquid layer. An equivalent circuit is shown by the left side of Fig. 3. One can readily show[1] that the so-called characteristic impedance Z_0, which is the impedance of an infinitely thick layer, is equal to

$$Z_0 = (\pi f \eta \rho)^{\frac{1}{2}}(1+j), \tag{7}$$

and hence the resistance and reactance terms are equal.

It was shown in a reference[8] that when a polymer liquid such as polymerized castor oil was measured, the resistance and reactance terms were no longer equal, but the resistance term was larger than the reactance by increasing amounts as the frequency increased. The curves of Fig. 3 show the measured values for castor oil, while the dot-dash line shows the theoretical value if the liquid were a purely viscous liquid. This divergence can be accounted for if the liquid has a configurational shear elasticity as shown by the equivalent circuit on the right of Fig. 3. The impedance of a liquid with a single relaxation time was calculated[1] and is given by the formula

$$\left.\begin{aligned} R_M &= (\rho\mu)^{\frac{1}{2}}\left[\frac{(f^2/f_1{}^2)+(f^4/f_1{}^4+f^2/f_1{}^2)^{\frac{1}{2}}}{2[1+f^2/f_1{}^2]}\right]^{\frac{1}{2}}; \\ X_M &= (\rho\mu)^{\frac{1}{2}}\left[\frac{(-f^2/f_1{}^2)+(f^4/f_1{}^4+f^2/f_1{}^2)^{\frac{1}{2}}}{2[1+f^2/f_1{}^2]}\right]^{\frac{1}{2}} \end{aligned}\right\} \tag{8}$$

where f_1 is the relaxation frequency $f_1 = \mu/(2\pi\eta)$. A plot of this equation is shown in Fig. 4 (by solid lines). At low frequencies, i.e. for frequencies much less than the relaxation frequency, the resistance and reactance terms are equal, and increase proportionally to the square root of the frequency. As the frequency approaches the relaxation frequency, the resistance becomes larger than the reactance, and at very high frequencies the resistance approaches $(\rho\mu)^{\frac{1}{2}}$ while the reactance approaches zero. By fitting the theoretical curves of Fig 4. to the measured curve of Fig. 3 it is found that the viscosity is equal to the value measured by a falling ball method, namely 18 poises, while the configurational stiffness is $\mu = 1/C_s = 1.26 \times 10^7$ dynes/cm^2.

Further measurements[2] by this method have been made for a series of polyisobutylene polymer liquids A', B, C, and D, having the viscosity average molecular weights 1060, 3520, 4550, and 5590. The results are shown by Fig. 5. The viscosities agree quite well with those measured by falling ball methods, while the configurational shear elasticities

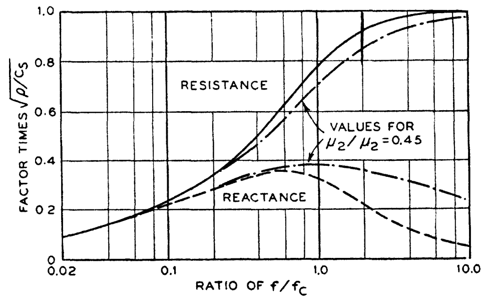

FIG. 4. Plot of Eq. (8).

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[8] W. P. Mason, "Measurement of the Viscosity and Shear Elasticity of Liquids by Means of a Torsionally Vibrating Crystal," Proc. A.S.M.E., May 1947.

have values ranging from 6×10^6 dynes/cm^2 to 5×10^7, depending on the temperature and molecular weight. These shear elasticities do not follow the temperature relations established for the "kinetic" theory indicating that equilibrium is not established and that this quasi-configurational elasticity is controlled by the reaction of nearest neighbors. Further measurements by this method have been made and are reported in a previous paper.[9]

III. MEASUREMENTS OF SHEAR ELASTICITIES OF LIQUIDS AT VERY HIGH FREQUENCIES

The measurements made with the torsional crystal can be satisfied by a single relaxation frequency, whereas the discussion in the introduction indicates that polymer liquids should have two main relaxation frequencies, the latter one determined by the high frequency or crystalline elasticity of the liquid. Rough calculations indicated that the second relaxation frequency should come in the upper megacycle range. In order to measure this relaxation frequency it was necessary to devise a different method since the torsional crystal method is limited to about 500 kilocycles on account of the small sizes of the crystal. Consideration was given to the use of a thickness vibrating shear crystal of the *AT* or *BT* type, but it was found that the shear motion was too closely coupled to other modes of motion, such as flexure modes, to give reliable results. Hence another method had to be used.

Previous studies[10] had shown that it was possible to set up very pure shear waves in a fused quartz rod by attaching a *Y* cut or *AT* shear vibrating crystal to the quartz rod. For permanent connection, silver paste was baked to the quartz rod and the crystal soldered on by a very thin layer of solder. However, for experimental purposes the joint could be made of wax, or preferably, a very thin layer of one of the polyisobutylene liquids. The success of this joint shows that the shear elasticity of this liquid is becoming quite high. By sending a pulse down the rod and picking up the series of pulses by the sending crystal or a receiving crystal on the far end, the purity of the shear motion can be tested. Any longitudinal wave will travel with nearly twice the velocity of the shear wave, and will appear on the cathode-ray oscillograph at a point intermediate between the sent pulse and the first shear pulse. In this way it is found that any longitudinal pulse is at least 50 db down from the received shear pulse, and is entirely negligible.

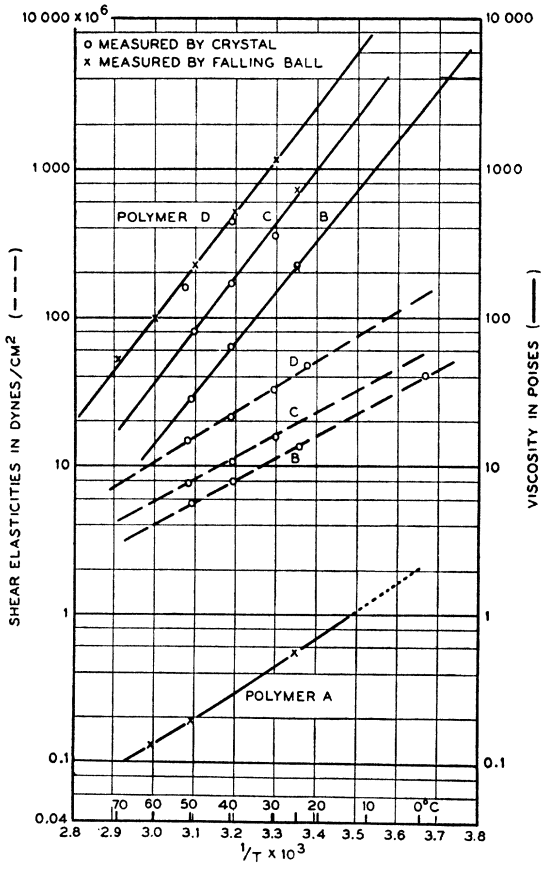

FIG. 5. Shear elasticities and viscosities for polyisobutylene polymer liquids.

By using a short length of fused quartz rod which is accurately made parallel and polished on both ends, and using a single crystal for sending and receiving, a series of shear wave pulses was set up in the rod and their relative amplitudes and positions were shown on the cathode-ray oscillograph as shown by Fig. 6. Then a layer of liquid to be studied was put on the polished free end and the difference in the received pulses noted. At 10 megacycles, for example, it was found that the first received pulse was decreased by 1.10 db, the second which had been reflected twice from the fused quartz-liquid joint, by 2.2 db, etc. It was found by experiment that the thickness of the liquid layer did not make any difference until the thickness was extremely small, i.e., less than .001 cm. Hence the liquid layer can be considered an infinite medium, and the effect is only on the reflection coefficient which is given by the formula

$$R_F=(Z_Q-Z_L)/(Z_Q+Z_L), \tag{9}$$

where Z_Q is the characteristic impedance of the quartz and Z_L, the characteristic impedance of the liquid. The fused quartz having no dispersion and a very small attentuation ($Q>50{,}000$) can be considered a pure resistance within less than 1 part in 50,000. However, the liquid impedance Z_L

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[9] W. P. Mason, J. Coll. Sci. **III**, No. 2 (May 1948).

[10] W. P. Mason and H. J. McSkimin, J. Acous. Soc. Am. **19**, 464 (1947).

will certainly have a phase angle. Hence the reflection factor R_F will have a phase angle and can be represented by

$$R_F = Re^{-i\theta}, \tag{10}$$

where R is the absolute value of the reflection coefficient, and θ, the phase angle. Solving for Z_L we find

$$Z_L = R_L + jX_L = 8.3\times10^5\left[\frac{1-R^2+2jR\sin\theta}{1+R^2+2R\cos\theta}\right], \tag{11}$$

where 8.3×10^5 is the shear impedance per square centimeter for a fused quartz rod. Now, since the impedance Z_L for all these liquids is less than $0.1(1+j)$, that for the fused quartz, it can be shown that the phase angle θ will not be greater than 5°, and the reduction in amplitude measures the resistance term R_L quite accurately by using the formula

$$R_L = 8.3\times10^5\left[\frac{1-R}{1+R}\right]. \tag{12}$$

A series of measurements was made for the polyisobutylene liquids shown by Fig. 5 for 25°C, and the resistance components of the shear impedance are shown plotted by Fig. 7. The resistances of the longer chain polymers show a marked rise with frequency which tends to approach an asymptotic value of about 75,000 mechanical ohms per square centimeter. The shorter chain polymers tend to approach a somewhat lower value.

To see if this impedance tends to approach that which should exist for a liquid with two relaxation frequencies, calculations have been made for the case of a liquid with a series element $j\omega\rho dx$ and a shunt element shown by Fig. 1B. The B form is taken since the two relaxation frequencies are easily calculated from it. Introducing the values

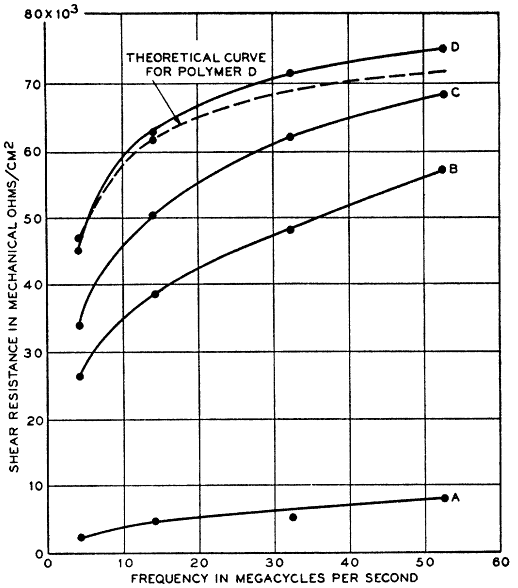

FIG. 7. Resistance components of the shear impedance for the polyisobutylene liquids.

$$Z_1 = j\omega\rho dx;$$

$$Z_2 = \left[\frac{(-j\mu_1\eta_1)/\omega}{\eta_1-(j\mu_1/\omega)} + \frac{(-j\mu_2\eta_2)/\omega}{\eta_2-(j\mu_2/\omega)}\right](1/dx) \tag{13}$$

into the formula

$$Z_0 = (Z_1Z_2)^{\frac{1}{2}},$$

we find

$$Z_0 = \left[\rho(\mu_1+\mu_2)\frac{\left[\dfrac{f^4}{f_1^2f_2^2}+f^2\left[\dfrac{\mu_2}{\mu_1+\mu_2}\times\dfrac{1}{f_2^2}+\dfrac{\mu_1}{\mu_1+\mu_2}\times\dfrac{1}{f_1^2}\right]\right] + jf\left[\dfrac{2\pi(\eta_1+\eta_2)}{\mu_1+\mu_2}+\dfrac{f^2}{f_1f_2}\left[\left(\dfrac{\mu_1}{\mu_1+\mu_2}\right)\dfrac{1}{f_2}+\left(\dfrac{\mu_2}{\mu_1+\mu_2}\right)\dfrac{1}{f_1}\right]\right]}{[1+(f^2/f_1^2)][1+(f^2/f_2^2)]}\right]^{\frac{1}{2}}, \tag{14}$$

where f_1 and f_2, the two relaxation frequencies, are given by

$$f_1 = \mu_1/(2\pi\eta_1); \quad f_2 = \mu_2/(2\pi\eta_2). \tag{15}$$

To illustrate the form of the impedance, use is made of the data obtained for the liquid polyisobutylene, polymer D at 26°C. The low frequency viscosity and torsional crystal measurements show that the flow viscosity is 1600 poises, and the configurational shear elasticity is 4×10^7 dynes per square cm. The high frequency longitudinal measurements given in a previous paper[11] show that there is a dispersion in the longitudinal velocity which requires a compressional stiffness of 1.17×10^{10} dynes/cm² higher at an infinite frequency than the stiffness at zero frequency. Compressional stiffnesses are controlled by the Lamé elastic constants $\lambda+2\mu$, and compressional measurements do not

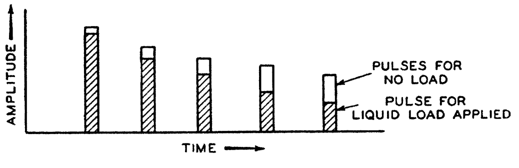

FIG. 6. Series of shear wave pulses.

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[11] Mason, Baker, McSkimin, and Heiss, Phys. Rev. **73**, 1074–1091 (1948); **74**, 1873–1874 (1948).

distinguish whether the dispersion comes in the λ-constant or the μ-constant. By means of the shear measurements presented here, it becomes obvious that the dispersion occurs in the μ-constant.

With the values of the Fig. 1A constants as $\mu_3{}^A=(1.17\times 10^{10}/2)=5.85\times 10^9$ dynes/cm²; $\mu_2=4.5\times 10^7$ dynes/cm²

$$\eta_1{}^A=1600 \text{ poise}; \quad \eta_2{}^A=200 \text{ poise}. \tag{16}$$

This results in the elements of the 1B network being

$$\eta_1{}^B=1425 \text{ poises}; \quad \eta_2{}^B=175 \text{ poises}; \quad \eta_1{}^B=4\times 10^7 \text{ dynes/cm}^2; \quad \mu_2{}^B=5.81\times 10^9 \text{ dynes/cm}^2. \tag{17}$$

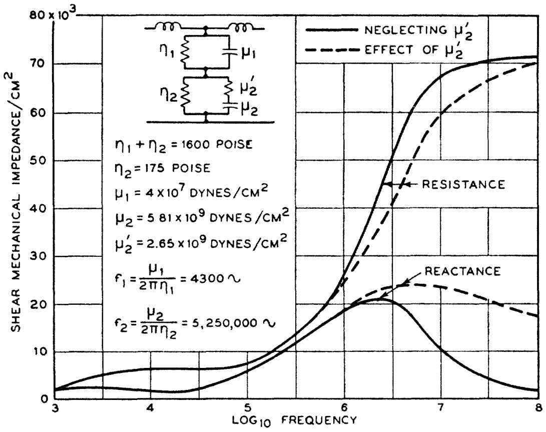

FIG. 8. Resistance and reactance for the *D* polymer liquids.

Since the 1B constants are separated out in the form of two relaxation frequencies, these constants are more easily evaluated than the constants in the form 1A. For example, at the very high frequencies, $\eta_1{}^B$ is relaxed out by the stiffness $\mu_1{}^B$ and the measurement of the second shear viscosity of Fig. 14, reference 11, divided by two, gives directly $\eta_2{}^B=175$ poise. $\eta_1{}^B+\eta_2{}^B$ is the "steady" flow viscosity, 1600 poises. $\mu_1{}^B$ is the measured shear elasticity of 4×10^7 dynes/cm². Substituting these values in Eq. (14), the resulting resistance and reactance terms for the *D* polymer liquid are shown by Fig. 8. There are two plateaus, one in the region below 100 kc and the other above 100 megacycles. Hence the measurements with the torsional crystal in which the constants were evaluated as though only one relaxation frequency existed, give very closely the correct results for the lowest relaxation frequency. For the high frequency range, the theoretical values of Fig. 8 are somewhat too high to agree with the measured curves of Fig. 7. This divergence is mostly due to the fact that the stiffness $\mu_2{}^B$ has a hysteresis component, as shown in the previous paper,[11] and this is not taken account of in the solid lines of Fig. 8. By introducing a series component $\mu_2{}'$ such that the stiffness impedance is

$$(\mu_2{}'-j\mu_2)/\omega$$

the effect of a hysteresis component is taken care of. This results in an input impedance for a long line of

$$Z_0=\left[\rho(\mu_1+\mu_2)\frac{\begin{array}{r}\left[\left[\dfrac{\mu_1}{\mu_1+\mu_2}\left(\dfrac{f^2}{f_1{}^2}\right)\left[1+\left(\dfrac{\mu_2{}'}{\mu_2}+\dfrac{f}{f_2}\right)^2\right]+\dfrac{\mu_2}{\mu_1+\mu_2}\left(\dfrac{f^2}{f_2{}^2}\right)\left(1+\dfrac{f^2}{f_1{}^2}\right)\right]\right. \\ \left.+jf\left[\dfrac{\mu_1}{\mu_1+\mu_2}\left(\dfrac{1}{f_1}\right)\left[1+\left(\dfrac{\mu_2{}'}{\mu_2}+\dfrac{f}{f_2}\right)^2\right]+\left(\dfrac{\mu_2}{\mu_1+\mu_2}\right)\left(\dfrac{1}{f_2}\right)\left[1+\dfrac{\mu_2{}'}{\mu_2}\left[\dfrac{\mu_2{}'}{\mu_2}+\dfrac{f}{f_2}\right]\right]\right]\right]\end{array}}{\left(1+\dfrac{f^2}{f_1{}^2}\right)\left(1+\left(\dfrac{\mu_2{}'}{\mu_2}+\dfrac{f}{f_2}\right)^2\right)}\right]^{\frac{1}{2}}. \tag{18}$$

The effect of this is to raise the effective relaxation frequency as shown by the dashed line of Fig. 8. These values were calculated for a ratio of $\mu_2{}'/\mu_2=0.45$ as found in the previous paper.[11] This tends to make the theoretical and experimental values agree closely as shown by the dashed line of Fig. 7, and hence all the evidence points to a relaxation in the shear elasticity as the cause of the relaxation measured in the longitudinal velocity.

IV. MORE SENSITIVE METHOD FOR MEASURING RESISTANCE AND REACTANCE COMPONENTS OF SHEAR IMPEDANCES OF LIQUIDS

The method discussed previously for measuring the shear impedance of liquids by their effects on the reflection coefficient at normal incidence suffers from the fact that the limiting impedances of the liquids are only about 0.1 that of the fused quartz, and hence the effects on the reflection factor and reflection phase are very small. It has been found[12] that an enhanced effect can be obtained by re-

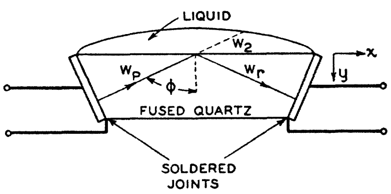

FIG. 9. Arrangement for measuring the shear impedance of liquids by reflection at low angle of incidence.

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[12] This idea was suggested and developed by H. J. McSkimin.

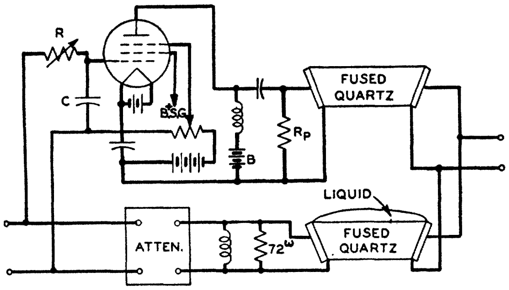

FIG. 10. Circuit connections.

flecting the shear wave off the liquid-solid interface at a low angle of incidence. An exact solution for the reflected wave has been obtained by H. T. O'Neil and will be published in a companion paper. It appears, however, that for all the liquids considered here, the effect of this low angle in determining Z_2 is given by the equation

$$Z_2 = R_2 + jX_2 = \cos\varphi Z_Q \left[\frac{1 - R^2 + 2jR \sin\theta}{1 + R^2 + 2R\cos\theta} \right], \quad (19)$$

where R is the absolute value of the reflection factor, and θ, the phase angle. Hence the effect of the low angle is to transform the shear impedance of the liquid up by an impedance transformation ratio $1/\cos\varphi$, where φ is the angle of incidence from the normal.

In order to make the device a reasonably short length—approximately four inches as shown by Fig. 9—and have it still radiate the whole surface by the directive shear wave, the angle φ was chosen as 79°, giving an impedance transformation ratio of 5.25 to 1. The solution given by Eq. (19) depends on the particle motion of the surface being at right angles to the surface normal. This is secured by putting the x-crystallographic axis of the quartz crystal parallel to the reflecting surface for both sending and receiving crystals.

The method for obtaining the resistance and reactance components is to determine the reflection loss per reflection and the phase change per reflection. The reflection loss is obtained by comparing any one of the reflections with a clear reflecting surface with the same reflection, with the reflecting surface covered by the liquid, and dividing by the number of times this particular component has suffered reflection from the solid liquid interface. To measure phase, two identical fused-quartz rods were constructed with two input and two receiving crystals. These are connected in the circuit shown by Fig. 10. Here the upper reference bar is connected through a pentode vacuum tube with an R-C phase shifting network in the input. Since we are comparing two received pulses occurring at the same time, one has to balance the amplitude and make the phase 180° different. When the variable resistance, R, is equal to zero, the phase shift introduced by the phase shifting network is zero and 180° is introduced by the tube. If we make R_p low so that the gain through the tube is zero, the two received pulses can be balanced out when no liquid is placed on the lower rod. Now, when a liquid is placed on this reflecting surface, the amplitude is reduced and the phase is changed for the pulse received from the lower unit. To balance it out now, the gain of the tube is reduced by introducing a negative bias on the suppressor grid. By comparison methods it is shown that this changes the phase of the upper pulse by less than 1°. Then, to balance out the phase shift introduced in the first reflection by the liquid, the variable resistance R is increased, until the two adjustments annul the received pulse. By calibrating the phase of the adjustable circuit, the reflection phase shift can be measured within a degree. Only a very moderate amount of temperature and frequency stability are required for this system.

A few measurements have been made with this system. Figure 11 shows the resistance and reactance at 10 megacycles and 25°C of a number of polyisobutylene liquids graduated according to molecular weight. The lighest liquid, having a flow viscosity of 0.55 poises, acts nearly like a purely viscous liquid with only a small amount of shear elasticity. As the molecular weight increases, the divergence between resistance and reactance increases, and above a molecular weight of 10,000 the shear elasticity is a very slowly increasing function of the molecular weight.

A number of these liquids have been measured at the three frequencies: 4.5 megacycles, 14 megacycles, and 24 megacycles, over a temperature range. The measurements for three of these liquids

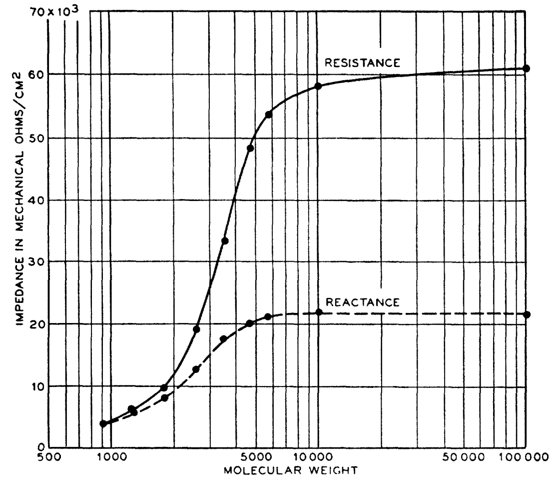

FIG. 11. Resistance and reactance at 10 megacycles and 25°C of polyisobutylene liquids.

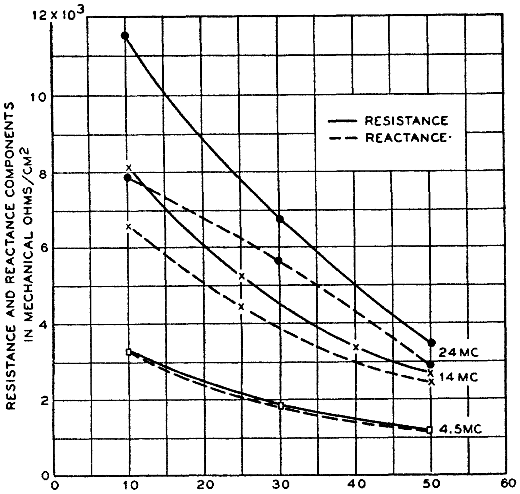

FIG. 12. Resistance and reactance curves at various frequencies for liquids having viscosity average molecular weight of 1060.

having viscosity average molecular weights of 1060, 3520 and 5560 are shown by Figs. 12, 13, and 14. The highest molecular weight material shows a stiffness at all three frequencies that increases with a decrease in temperature. The lowest molecular weight material, on the other hand, appears to be a viscous liquid at 4.5 mc and only shows a stiffness at 24 mc, or at low temperatures.

The measured results can be fitted by an equivalent circuit having the elements shown by Fig. 1B. Here the sum of η_1 and η_2 equals the low frequency viscosity, which for these liquids is shown by Fig. 5. μ_1, the quasi-configurational shear stiffness for a number of liquids, is also shown by Fig. 5. If we plot these as a function of density, it appears that all of the stiffnesses can be plotted on one curve as shown by Fig. 15. If we extrapolate this down to

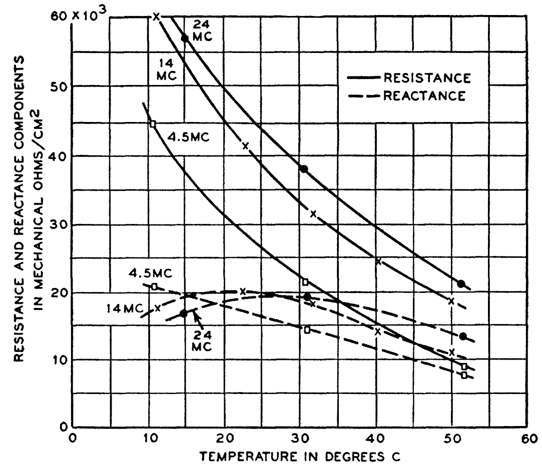

FIG. 13. Resistance and reactance curves at various frequencies for liquids having viscosity average molecular weight of 3520.

the density of the lowest molecular weight liquid (0.826 at 25°C), the shear stiffness for configurational conditions will have dropped to 2×10^5 dynes/cm² for this liquid. At the same time the viscosity as measured by the reflection coefficient of the shear wave nearly coincides with the static measurements shown by Fig. 5. Hence it appears that the first relaxation mechanism of Fig. 1 can be neglected, and the impedance accounted for by a single mechanism. For the other two liquids, the relaxation frequency of μ_1, η_1 is much less than the measured frequency, and as shown by Fig. 8, the impedance measured can be accounted for by a single relaxation mechanism having the constants μ_2 and η_2.

In order to evaluate these constants, μ_1 is set equal to zero, and f_1 to infinity. Solving for the resistance and reactance terms we find.

$$R=(\rho\mu_2)^{\frac{1}{2}}\left[\frac{\dfrac{f^2}{f_2^{\,2}}+\left(\dfrac{f^4}{f_2^{\,4}}+\dfrac{f^2}{f_2^{\,2}}\left[1+\dfrac{\mu_2'}{\mu_2}\left(\dfrac{\mu_2'}{\mu_2}+\dfrac{f}{f_2}\right)\right]^2\right)^{\frac{1}{2}}}{2\left[1+\left(\dfrac{\mu_2'}{\mu_2}+\dfrac{f}{f_2}\right)^2\right]}\right]^{\frac{1}{2}}, \tag{20}$$

$$X=(\rho\mu_2)^{\frac{1}{2}}\left[\frac{\dfrac{-f^2}{f_2^{\,2}}+\left(\dfrac{f^4}{f_2^{\,4}}+\dfrac{f^2}{f_2^{\,2}}\left[1+\dfrac{\mu_2'}{\mu_2}\left(\dfrac{\mu_2'}{\mu_2}+\dfrac{f}{f_2}\right)\right]^2\right)^{\frac{1}{2}}}{2\left[1+\left(\dfrac{\mu_2'}{\mu_2}+\dfrac{f}{f_2}\right)^2\right]}\right]^{\frac{1}{2}}. \tag{21}$$

A plot of these values for a value of $\mu_2'/\mu_2=0.45$ (the value found from longitudinal measurements) is shown by the dot-dash lines of Fig. 4.

Fitting the reactances and resistances measured and shown by Figs. 12, 13, and 14 to these curves, the asymptotic value of $R_\infty=(\rho\mu_2)^{\frac{1}{2}}$ and the relaxation frequencies f_2 can be determined for the different temperatures and different molecular weights.

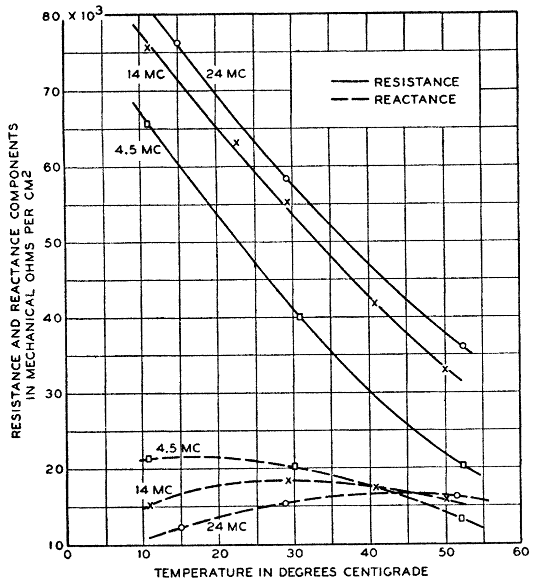

FIG. 14. Resistance and reactance curves at various frequencies for liquids having viscosity average molecular weight of 5560.

Then knowing the density ρ, the value μ_2 can be determined from the equation

$$\mu_2 = R_\infty^2/\rho. \tag{22}$$

The second shear viscosity, η_2, can be determined from the formula

$$\eta_2 = \mu_2/2\pi f_c, \tag{23}$$

where f_c is the relaxation frequency.

The high frequency shear elasticity μ_2 is shown plotted on Fig. 15 as a function of the density. Since over this range the change in density is roughly proportional to the change in temperature, it is seen that the variation in high frequency shear elasticity parallels quite closely the variation in quasi-configurational elasticity as a function of temperature. However, the difference due to molecular weight change does not even approximately follow the variation in density, unlike the quasi-configurational elasticity. The viscosities η_2 are shown plotted as a function of $1/T$ by Fig. 16. All the slopes are approximately parallel, and indicate an activation energy of about 12 kilocalories. The low frequency viscosities, shown by Fig. 5, have an activation energy of 16 kilocalories for molecular weights of 3500 and above, but for the lowest molecular weight of 1060 the slope is less and the indicated activation energy is about 12 kilocalories. Since a molecular weight of 1060 corresponds to a repeating chain of 19 links, i.e., perhaps about the size of an Eyring segment, it may be that an activation energy of 12 kilocalories is the value for the motion of a single segment. The values of η_2 plotted on Fig. 16 then represent the motion of individual segments caused by a chain retraction. There is a chain length effect due to the fact that there is an increased improbability of all the segments moving in the same direction as the chain increases in length.

Since both quasi-configurational (in the sense of relaxation times leading to apparent stiffness for shape changes), and crystalline elasticities in all probability are determined by nearest neighbors, the action of any segment may be represented as

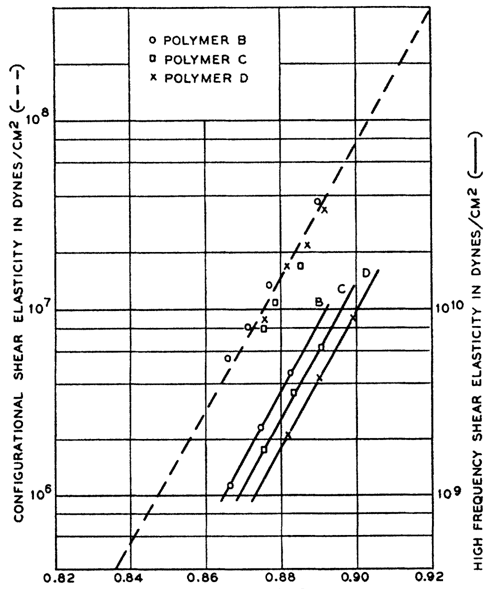

FIG. 15. Shear elasticities plotted as a function of density.

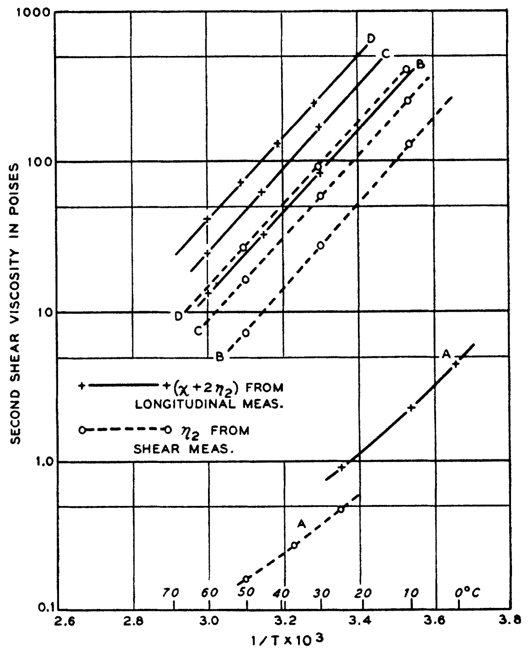

FIG. 16. Second shear viscosity as a function of $1/T$.

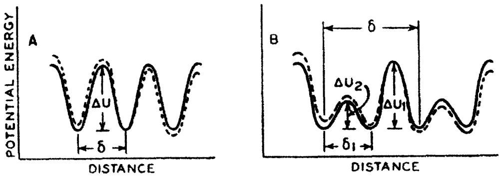

FIG. 17. Potential well distributions.

due to the potential well distribution shown in Fig. 17B. The viscous flow of the molecule requires a translation and rotation and hence occurs over the free energy barrier ΔU_1. On the other hand, an extension or contraction of the chain as a whole, which occurs when configurational elasticity occurs, requires no change in the center of gravity of the chain, and probably results in a lower over-all free energy barrier ΔU_2. When a shearing stress is put on the liquid, one well is lowered compared to the other, as shown by the dotted line. At low frequencies, sufficient time is given so that a viscous flow occurs over the high energy barrier. As the frequency increases there is not time for an actual transfer of the center of gravity in the time of a single cycle, but a local distortion still can occur across the lower energy barrier. This is a reversible process and results in the quasi-configurational elasticity since entropy changes tending always toward most probable chain shapes are concurrently happening. Since the motion that can occur is large, the configurational stiffness is small. At still higher frequencies, even the local distortion cannot occur and the only effect is the displacement of the segment from its equilibrium position. This results in a very high shear stiffness of the crystalline type. According to the measurements, the height of the flow viscosity activation energy barrier is 16 kilocalories per mole, whereas the local distortion energy barrier is 12 kilocalories. The same relative slope of the configurational and crystalline stiffnesses with temperature shown by Fig. 15, indicates that there is a correspondence between the shape of the bottom of the two potential wells and the complete free energy curve. As the chain length decreases, the distinction between a local distortion and a true flow motion disappears, and for liquids having a chain length in the order of one Eyring unit or less, the two potential wells become equal and the potential well distribution is similar to that for a light liquid as shown by Fig. 17A. Under these circumstances the quasi-configurational elasticity disappears.

Another interesting result is obtained by comparing the values of viscosity η_2 measured by the high frequency shear technique with the value measured in longitudinal measurements of Fig. 14, reference 2. The longitudinal measurements, which determine the sum of the compressional viscosity χ plus twice the shear viscosity η_2, are shown plotted by the solid lines of Fig. 16. For the lowest molecular weight (polymer A) the longitudinal viscosity is about 2 times η, indicating a negligible compressional viscosity. The longer chains have a compressional viscosity which is, however, a considerable fraction of the shear viscosity. Evidently com-

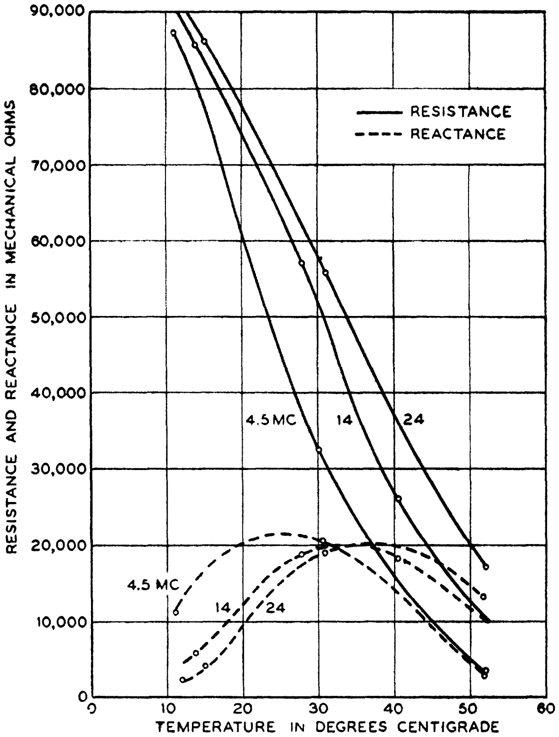

FIG. 18. Resistance and reactance for a poly-α-methyl styrene liquid.

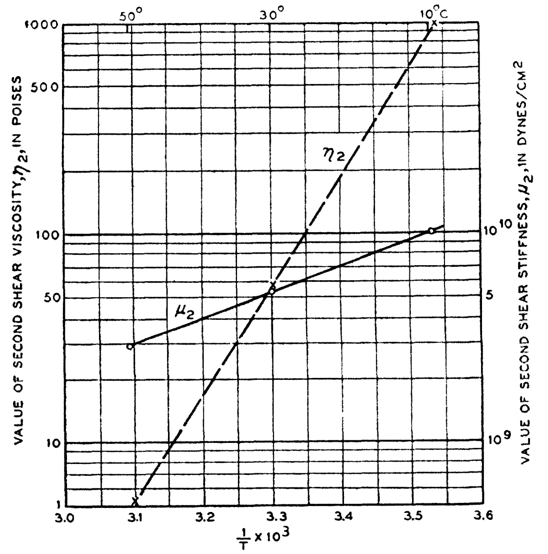

FIG. 19. Second shear viscosity and stiffness for a poly-α-methyl styrene liquid.

pressional viscosity is a steep function of average chain length. As nearly as can be judged from the relative slopes of the viscosities measured by longitudinal and shear waves, the activation energy of the compressional viscosity is equal to that of the second shear viscosity.

Some measurements were also made for a poly-α-methyl styrene liquid and the results are shown by Fig. 18 for three frequencies over a temperature range. One interesting difference is at once obvious, namely, that any hysteresis effects are small, since at low temperatures the ratio of reactance to resistance becomes greater than 50, whereas it did not exceed 8 for polyisobutylene. This correlates also with the fact that the high frequency losses of solid polystyrene are much less than those of high molecular weight polyisobutylene at ordinary temperatures. Analyzing the data of Fig. 18, using the solid curves of Fig. 4, one obtains the shear elasticity μ_2 and the shear viscosity η_2 shown by Fig. 19. The shear elasticity is somewhat higher than that for a 5560 molecular weight polyisobutylene but has about the same change with temperature. The variation of η_2, however, is much larger for poly-α-methyl styrene than for polyisobutylene, and corresponds to an activation energy of 23.6 kilocalories.

Some measurements were also made of very light liquids such as water and cyclohexane. By observing the fifth and seventh reflection for both amplitude and phase changes, measurable results were obtained. For both cases within the experimental error, the values agreed with the steady flow measurements. Hence in agreement with Eq. (1), they are considerably below their relaxation frequencies, and indicate that no configurational type elasticities exist for these liquids. These measurements show that the enhanced losses for longitudinal waves for these liquids must be due to compressional viscosities.

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Ultrasonic Measurements on Rochelle Salt Crystals*

W. J. Price
*Physics Department, Rensselear Polytechnic Institute, Troy, New York***

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A pulse technique at 10 Mc/sec. has been used to study the anomalous elastic properties of rochelle salt single crystals at temperature around the upper Curie temperature. The temperature dependence of foiled crystal constant S_{44}^E and of the attenuation of waves which contain a component of shear strain in the X crystallographic plane is reported. The attenuation measurements are formulated in terms of the interaction theory.

The dependence of the velocity in 45° X cut crystals of rochelle salt on a d.c. field in the X crystallographic direction shows a marked unipolarity. This change in velocity which is caused by the bias field arises from the two following sources: one is the usual saturation on effect which produces a change in velocity that is independent of the polarity; the other is the morphic effect which results from the induced monoclinic constants, and which produces a velocity change, the sign of which is dependent on the polarity.

I. INTRODUCTION

It is well known that rochelle salt exhibits extraordinary elastic, dielectric, and piezoelectric properties: Several experimental and theoretical studies of these properties have been made.[1]

In the past the data on the elastic properties have been obtained principally by the self-resonance method. Recently Huntington[2] has used a pulsed ultrasonic technique for determining a complete set of elastic moduli for rochelle salt at room temperature. The present paper reports the use of the ultrasonic method to study further certain interesting aspects of rochelle salt.

In the self-resonance experiments the wave-length of the sound waves in the specimen is of the order of the specimen dimensions, while in the pulsed ultrasonic method the frequency is sufficiently high that the specimens are essentially infinite compared to the wave-length of the sound. The boundary conditions for the two cases lead to expression for the velocity in terms of the elastic compliance coefficients S_{ij} and of the elastic moduli C_{ij}, respectively.

The interesting elastic phenomena in Rochelle salt center around the anomalous temperature dependence and the saturation effects (both

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** Now at Battelle Memorial Institute, Columbus, Ohio.

[1] For a review of the investigations of rochelle salt, see W. G. Cady, *Piezoelectricity* (McGraw-Hill Book Company, Inc., New York, 1946).

[2] H. B. Huntington, Phys. Rev. **72**, 321 (1947).