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Mechanical Properties of Long Chain Molecule Liquids at Ultrasonic Frequencies

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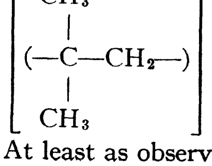
Measurements have been made of the mechanical properties of long chain molecule liquids of the polyisobutylene type by means of shear and longitudinal waves in the ultrasonic frequency range. The shear waves show that these liquids behave as Maxwell relaxing liquids. The viscosity measurements in the range around 14 kilocycles check the viscosities measured by falling ball measurements within the experimental error. As the temperature decreases or the frequency increases, the reaction of the liquid shows that a shear elasticity of the Maxwell type comes into play with a shear elastic constant of from 5×10^6 dynes/cm^2 to 5×10^7. This elasticity increases with decreasing temperature and increases with chain length, and represents an intermediate type to the "frozen" type of elasticity or the "kinetic theory" type in that it has the high compliance of the "kinetic theory" type but the temperature variation of the "frozen" type of elasticity. It is suggested that this type of elasticity may be due to a composite motion of the chains, including hindered rotation within chains, as well as interaction of segments between chains. At very high frequencies this composite motion disappears and the shear stiffness becomes very high.

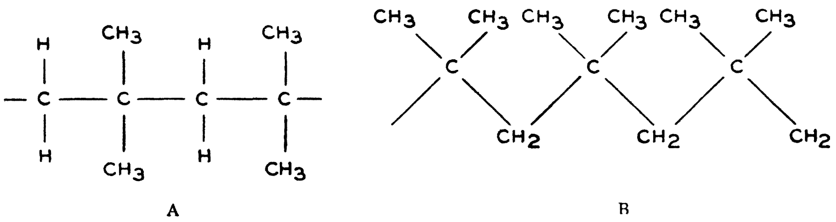
Above about 30 kilocycles for these liquids, some shear viscosity is relaxed by the shear elasticity. Measurements with longitudinal ultrasonic waves show, however, a dispersion of velocity and an associated attenuation curve. From very low frequencies to very high frequencies the velocity increases by about 25 percent, while the attenuation has the high value of 0.7 neper per wave-length at a frequency for which the velocity is a mean between the two extremes. These measurements show that a relaxation occurs in either the shear elasticity, μ, or the Lame constant, λ. Current investigations show this to be in the shear constant, μ. However, the measured attenuation frequency curve is broader than that of a single relaxation frequency and moreover indicates that the attenuation reaches a constant value per wave-length at high frequencies. A simple explanation of this is that the rearrangement compliance has a hysteresis component. Calculations of the velocity and attenuation on this basis agree very well with the measured curves.

I. INTRODUCTION

VELOCITY dispersion and associated sound absorption caused by molecular process are very hard to locate and measure in ordinary liquids because they come at frequencies higher than can be utilized with present day ultrasonic equipment. If, however, we use liquids containing long chain molecules, the frequencies of the relaxing effects are low enough to be measurable by ordinary ultrasonic equipment. This is because the shear and compressional viscosities are high enough to lower the relaxation frequencies to easily measurable ranges.

In order to study these effects, shear and longitudinal measurements have been made for a number of samples of polyisobutylene of viscosity average molecular weight ranging from 900 to 5600. This is a molecule composed of chains of  $\left[\begin{array}{c} CH_3 \\ | \\ (-C-CH_2-) \\ | \\ CH_3 \end{array}\right]$ groups without cross linkages. At least as observed when crystallized, this chain occurs in a spiraled zigzag form, as shown in Fig. 1. It turns all the way around in the direction of its length probably once in every 9 pairs of CH_3 groups. In the liquid state some less regular twisted form is likely. The different average chain lengths used result in a range of viscosities from 0.3 to 1700 poises at 25°C. By measuring the shear properties of these liquids with a torsionally vibrating crystal, it is shown that they act as a Maxwellian relaxing liquid with a shear elasticity as well as a shear viscosity. The shear elasticity depends on the chain length, and if one plots the logarithm of the elasticity against the inverse of the temperature, one obtains a straight line having less than half the slope of the logarithm of the viscosity *versus* inverse temperature curve. Although the different chain length liquids have different elasticities, it is found that all of their elasticities for different temperatures and chain lengths can be represented by a single curve when plotted against density.

At frequencies so high that the shear viscosity is relaxed, the shear viscosity cannot be contributing to the loss of a longitudinal wave.



$$-\overset{\displaystyle \mathrm{H}}{\underset{\displaystyle \mathrm{H}}{\mathrm{C}}}-\overset{\displaystyle \mathrm{CH_3}}{\underset{\displaystyle \mathrm{CH_3}}{\mathrm{C}}}-\overset{\displaystyle \mathrm{H}}{\underset{\displaystyle \mathrm{H}}{\mathrm{C}}}-\overset{\displaystyle \mathrm{CH_3}}{\underset{\displaystyle \mathrm{CH_3}}{\mathrm{C}}}-$$

A

B

FIG. 1. Molecular structure and chain form for polyisobutylene.

Torsional crystal measurements show that the first marked relaxation frequencies for all of these liquids are less than 30 kilocycles. Measurements by a pulsing technique show however that there are other components of the shear elasticity that are not relaxed until the high megacycle region, and these are the most likely cause of the relaxation phenomenon so far observed for longitudinal waves. By measuring the initial slope of attenuation-frequency curves, these secondary components of the shear viscosity can be determined.

The logarithm of this second component of the shear viscosity for all chain lengths was directly proportional to the inverse absolute temperature with a slope about $\frac{3}{4}$ as large as that for the lower frequency or "primary" shear viscosity. All the different molecular weight liquids had the same slope, indicating that the element that was rearranged was a segment of the molecule rather than the whole molecule. As with the low frequency shear viscosity, an increase in molecular weight of the chain causes a marked increase in viscosity.[1] Measurements over a wide frequency range show that the attenuation increases to a maximum and falls off at higher frequencies. At the same time the velocity increases with frequency and then levels off for higher frequencies. This agrees with the prediction of a relaxation theory. However, when plotted on a logarithmic scale the attenuation is not symmetrical about the frequency of highest attenuation, but indicates that the loss comes down to a constant value per wave-length independent of the frequency. This deviation from the relaxation theory can be explained if the molecular rearrangement compliance has a hysteresis[2] component. When calculated, attenuation and velocity curves fit the measured values very well. Since the hysteresis component appears only at high frequencies for which the secondary shear viscosity is relaxed, it appears to be due to a twisting up of chain segments which cannot quite jump from one stable potential well to a neighboring one by untwisting.

II. MEASUREMENTS OF SHEAR VISCOSITY AND SHEAR ELASTICITY FOR POLYISOBUTYLENE

Polyisobutylene is a polymer molecule that occurs in a long chain. It has the formula shown by Fig. 1A and the (non-planar) zigzag form shown by Fig. 1B. This chain in an ordered, stretched state appears to rotate about the direction of its length once in every 9 pairs of CH_3 groups. Accordingly, non-planar zigzag segments can be expected in the liquid state. The specimens used were designated *A*, *B*, *C*, and *D*, which had, respectively, average molecular weights of 903, 3520, 4550, and 5590.

Measurements of the viscosity of these four samples were made by the falling ball method (b) over a range of temperatures and are shown plotted as the logarithm of the viscosity *versus* the inverse temperature by Fig. 2. All of these liquids have the same slope, which indicates according to Eyring's theory[3] that the element which moves from one potential well to an adjacent one is a segment of the chain of 20 submolecules or so, whose length is essentially independent of the total chain length. The large decrease in viscosity for any one temperature as a function of chain length has been explained as the increased probability that the chain as a whole will jump to a new position as the chain length gets shorter. Measurements have also been made of the density of these liquids, and

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[1] (a) P. J. Flory, J. Am. Chem. Soc. 62, 1057 (1940); (b) W. O. Baker, C. S. Fuller and J. H. Heiss, *Ibid.* 63, 2142 (1941). The molecular weight-melt viscosity relation seems to be linear in a log-log plot rather than in the simpler forms in the references.

[2] By elastic hysteresis we mean a stress-strain loop (usually nearly an ellipse) that does not vary with frequency. For elastic hysteresis for small strains, the area of the loop is proportional to the square of the maximum strain.

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

the data are shown plotted on Fig. 3 as a function of the temperature.

According to classical theory, longitudinal waves have an attenuation which is determined by both the shear and compressional viscosity, but recent experiments by one of the writers[4] have shown that shear viscosities of viscous liquids are often relaxed at relatively low frequencies by the shear elasticities of the liquids, and the low frequency shear viscosities do not contribute to the attenuation of a longitudinal wave. Both the shear elasticities and the shear viscosities can be measured by means of the resistance and reactance loading that the liquids impress upon a torsionally vibrating crystal. In order to demonstrate that the low frequency shear viscosities were relaxed at frequencies well below the frequencies used for longitudinal measurements, torsional crystals were used to measure the shear viscosities and shear elasticities.

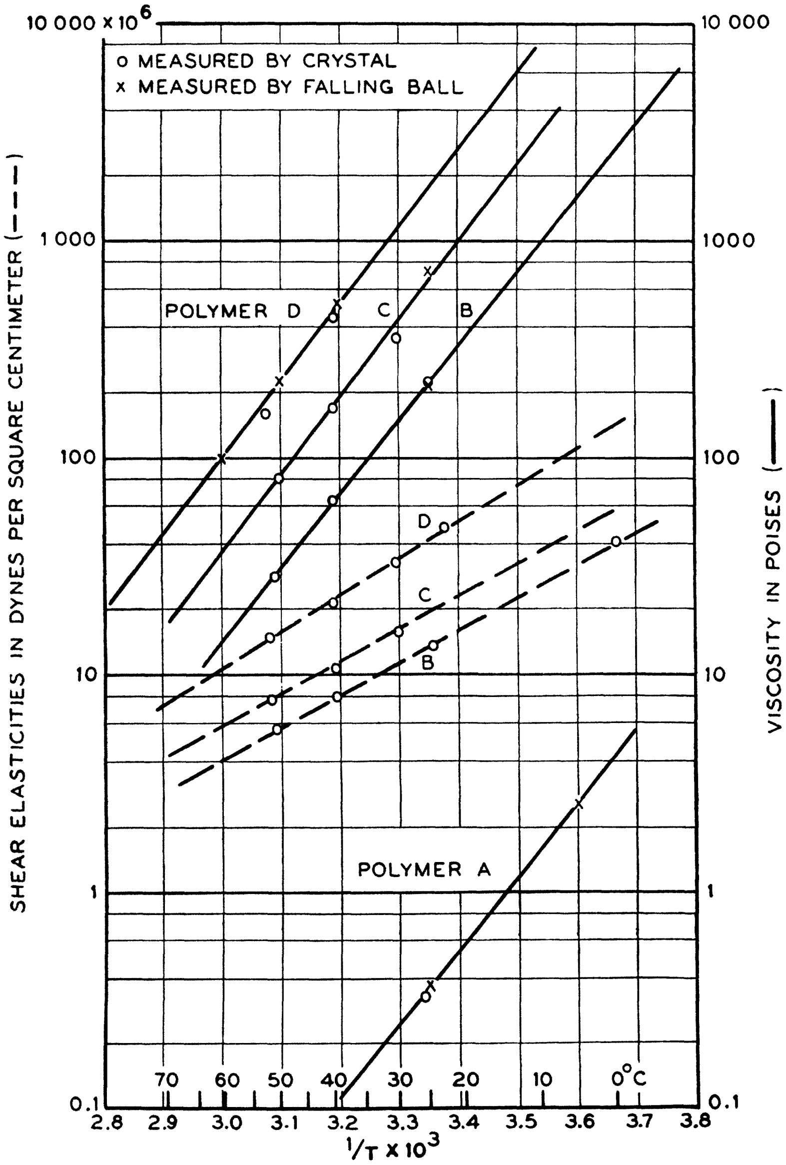

FIG. 2. Shear viscosity and shear elasticity of polyisobutylene liquids.

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[4] 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).

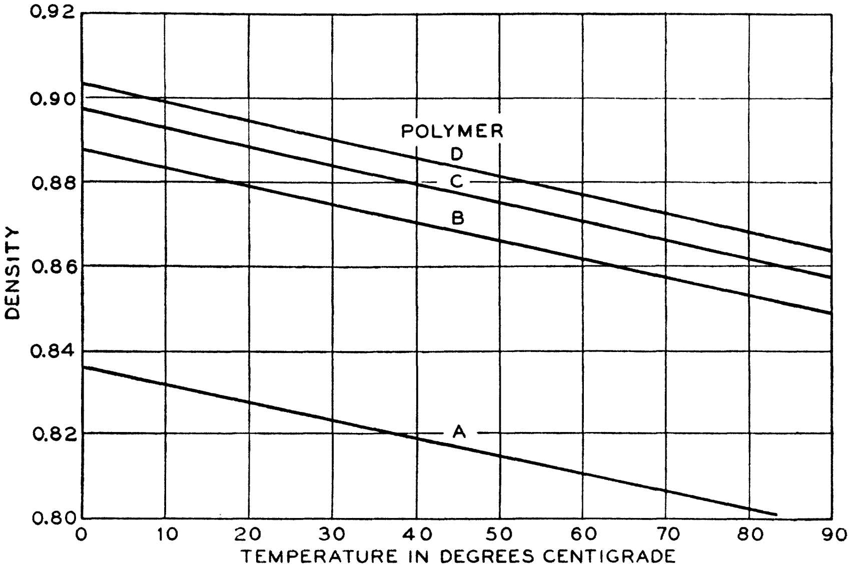

FIG. 3. Density of polyisobutylene liquids as a function of the temperature.

The experimental arrangement is shown by Fig. 4. A torsional crystal of ADP (ammonium dihydrogen phosphate) was gold-plated by the evaporation process and suspended from its nodal plane by three wires glued to the surface by Bakelite cement. The resonant frequency, the antiresonant frequency, the resistance at resonance, and the capacity at 1000 cycles were all measured, and the results are shown by Eq. (1)

$$\text{Crystal length}=5.0\text{ cm};\ \text{O.D.}=2R=0.472\text{ cm};\ \text{I.D.}=2R_0=0.30\text{ cm};\ \rho=1.804;\ f_R=19615\text{ cycles};\ f_A=19835;\ C_0=100\ \mu\mu\text{f};\ R=500\text{ ohms}. \tag{1}$$

From these data the ratios between the shear resistance and reactance and the increase in electrical resistance and decrease in resonant frequency can be calculated by formulae developed in the previous paper. These are given by the equations

$$\Delta R_E=K_1R_M;\quad \Delta f=-K_2X_M, \tag{2}$$

where ΔR_E is the increase in electrical resistance, Δf the decrease in resonant frequency, R_M the mechanical resistance loading of the shear wave per square centimeter, X_M the mechanical reactance loading of the crystal per square centimeter, and K_1 and K_2 are constants of the crystal. These are related to the above measurements by the formulae

$$\begin{aligned} K_1&=\frac{1}{2\pi^2 f_R(\Delta f_R)C_0\rho}\left[\frac{R^3+R_0^3}{R^4-R_0^4}+\frac{1}{l}\right];\\ K_2&=\frac{1}{\pi\rho}\left[\frac{R^3+R_0^3}{R^4-R_0^4}+\frac{1}{l}\right], \end{aligned} \tag{3}$$

where Δf_R is the separation f_A-f_R. With the above values, at 25°C

$$K_1=425,\quad K_2=1.15. \tag{4}$$

The value of K_1 changes slightly with temperature and at 50°C was evaluated as 455.

It was found that the resistance values at resonance gave the most reliable results since it was difficult to locate accurately the resonant frequency of the crystal in a viscous liquid. The measurements were made in a balanced electrical bridge and data similar to Fig. 7 of the previous paper[4] were used to evaluate the resistance loading. Measurements were made at the first, third, and fifth harmonic of the crystal. For the harmonics, the same value of K_1 holds as for the fundamental. Typical data for the resistance loading per square centimeter in terms of the frequency and temperature are shown for the polymer "B" liquid by Fig. 5. To interpret this data in terms of shear viscosity use is made of a calculation of the resistance and reactance loading of a liquid having shear viscosity and

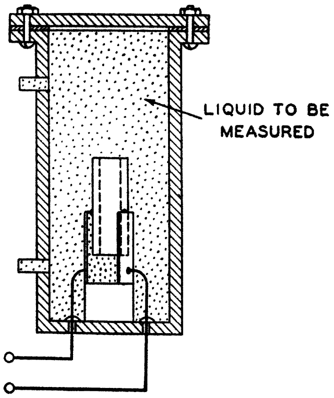

FIG. 4. Torsional crystal and container, used for measuring shear viscosity and shear elasticity of liquids.

TABLE I. Polyisobutylene "*B*."

Temperature	f/f_c	R at high frequency mech. ohms	μ dynes cm²	Relaxation frequency f_c cycles	Value of shear viscosity in poises
0°C	—	6100	42×10^6	—	—
24°C	1.8	3500	14×10^6	9700	230.0
40°C	0.9	2650	8×10^6	19400	65.8
50°C	0.6	2200	5.6×10^6	29200	30.5

shear elasticity given in the previous paper.[4] This is reproduced in Fig. 6 of this paper. Comparing this with the data of Fig. 5, we see, for example, that at 0°C, the loading is nearly independent of frequency, which means that the relaxation frequency is considerably below the lowest measuring frequency of 17.5 kilocycles. The curves for 24°, 40°, and 50°, however, show enough bending with frequency to allow one to fit them to the theoretical curve. From this data, one can find that the ratio of the lowest frequency (about 17.5 kc) to the relaxation frequency is given by the second column of Table I, while the asymptotic value of the loading resistance at very high frequencies is given by the third column. Since the shear elasticity is related to the resistance loading at high frequencies by the formula

$$(\rho\mu)^{\frac{1}{2}}=R \quad \text{or} \quad \mu=R^2/\rho, \tag{5}$$

the shear elasticity μ is shown by the fourth column. The fifth column shows the calculated relaxation frequency, while the sixth column shows the shear viscosity η which can be calculated from the formula

$$\eta=\mu/(2\pi f_c). \tag{6}$$

The values of viscosity measured by the crystal are shown plotted by the circles of Fig. 2 for all three liquids and, as is evident, they agree with the values measured by the falling ball method within 5 percent, which is probably the accuracy of measurement by the present method.

The values of shear elasticity measured for the three polymer liquids, *B*, *C*, and *D* are shown plotted by the dashed lines of Fig. 2. They lie nearly on straight lines of uniform slope when plotted as logμ *versus* $1/T$, at least within the temperature range shown. If we plot all of these

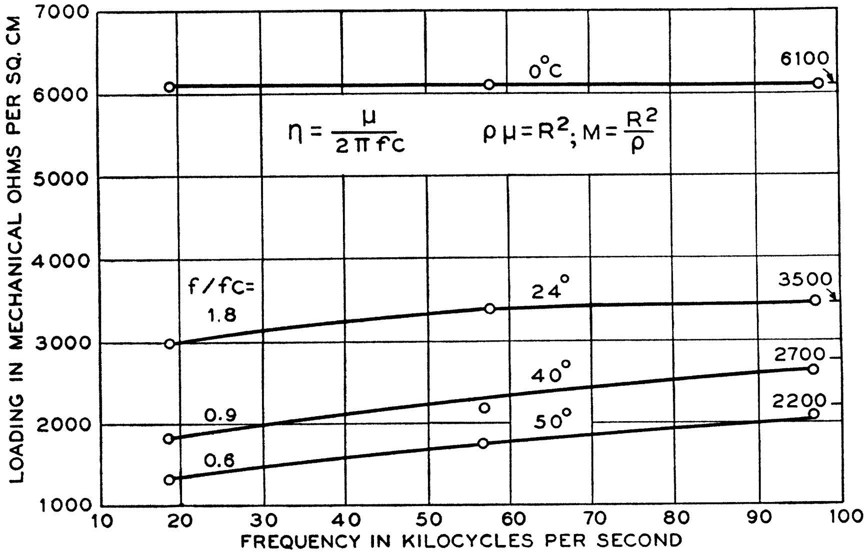

FIG. 5. Resistance loading of torsional crystal for polymer *B* plotted as a function of frequency and temperature.

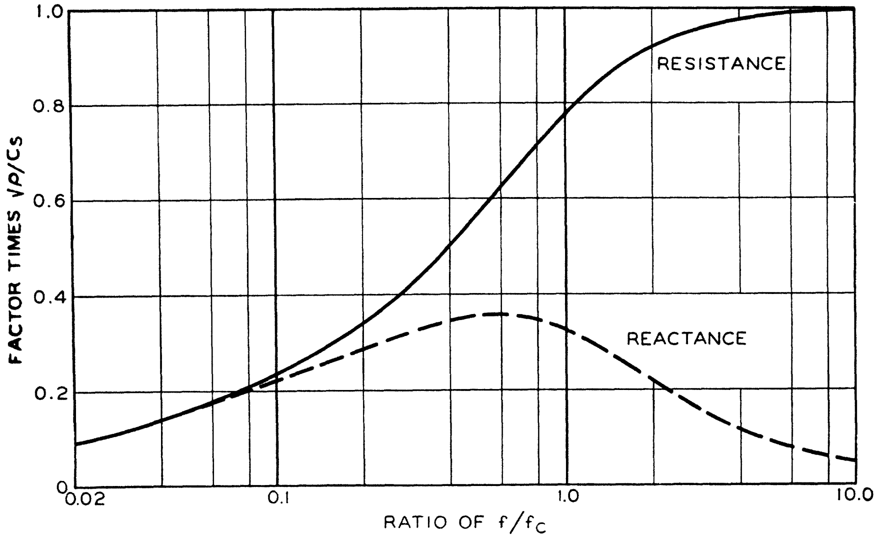

FIG. 6. Resistance and reactance values for a Maxwellian relaxing liquid plotted as a function of the frequency to the relaxation frequency.

shear elasticities as a function of density alone, which can be done using the data of Fig. 2 and Fig. 3, the points of Fig. 7 result. It appears likely, within the experimental error, that all of these points can be represented by a single curve.

III. VELOCITY AND ATTENUATION FOR LONGITUDINAL WAVES

In the last section it was shown that the first components of shear viscosities of these polyisobutylene liquids were relaxed at frequencies from several kilocycles to 30 kilocycles. Measurements made by terminating a rod of fused quartz, which is carrying shear wave pulses, by a layer of these liquids have shown that there are other components of the shear viscosity which are the causes of the dispersion measured with longitudinal waves. These measurements will be discussed in another paper. The losses in these materials run as high as 300 db per centimeter in the eight megacycle region and have necessitated new experimental means for measuring the attenuation and velocity. The experimental method chosen is a combination of pulsing and steady-state methods and is shown schematically by Fig. 8. Here a source of high frequency is fed to an amplifier-rectifier through two parallel paths. One is through an amplifier that is gated by a direct-current pulse. The pulse of a.c. current is impressed on a transmitting crystal which sends a pulse of alternating longitudinal waves into the liquid. This wave is picked up by a second crystal accurately parallel to the sending crystal which is placed at a variable distance from the sending crystal. The voltage generated by the receiving crystal is sent through a wide band amplifier, is rectified, and actuates the vertical set of electrodes of the oscilloscope. The sweep circuit of the horizontal set is controlled by the same synchronizing oscillator that controls the d.c. pulse generator so that the pulse received always occurs in the same position on the fluorescent screen. The second path from the high frequency oscillator is a steady state one through an attenuation box to the amplifier rectifier and oscilloscope. The attenuation box has carbon film resistors that are stable in value up to a frequency of 10 megacycles. Attenuation measurements are made by comparing the output of the receiving crystal with the output of the attenuator (connection shown by dotted line). If the loss in the liquid is 15 db or more, the pulse length does not make any difference and comparisons can be made by steady-state methods. However, if the loss between the two crystals is small, trouble is experienced with standing waves. To get around this difficulty a very short pulse length is used, and the first received pulse, which is free from standing wave complications, is used. Figure 9 shows a typical measurement of attenuation *versus* change in path length for polymer *D*. A change of 38 db occurs in a path difference of 0.1465 cm, indicating an attenuation of

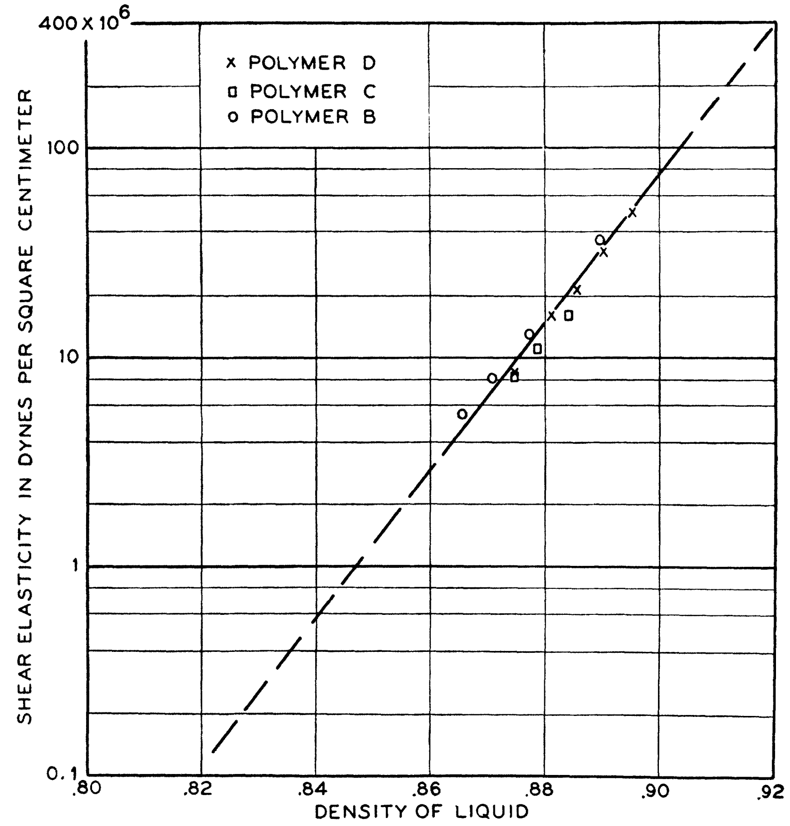

FIG. 7. Shear elasticity of polyisobutylene liquids plotted as a function of the density.

259 db per cm for a frequency of 8 megacycles and a temperature of 31°C. From the straightness of the attenuation-distance line it appears likely that the attenuation can be measured within ±2 percent for a high loss material and ±5 percent for a low loss material.

A measurement of the velocity for such a high loss material is more difficult by conventional methods. The path length is so short that a comparison of the position of received pulse with transmitted pulse does not give an accurate measurement of the velocity. On the other hand, the attenuation is too high to utilize the standing wave properties of the liquid as is done with the acoustic interferometer. The method adopted was to compare the phase of the received pulse with the phase of the steady-state transmission. For this purpose both paths were connected simultaneously to the amplifier-rectifier, and the attenuation in the db box was adjusted to be approximately equal to that through the liquid. As the path length was changed, the output from the pulse alternately added and subtracted from that through the box. By plotting the positions of the maxima, the wave-length in the liquid can be obtained. Figure 10 shows a typical measurement for the same liquid polymer *D*, plotting the number of wave-lengths change against the separation in centimeters. A very good straight line can be drawn through these points, and it is estimated that the velocity can be measured about ±1 percent. By this method velocities can

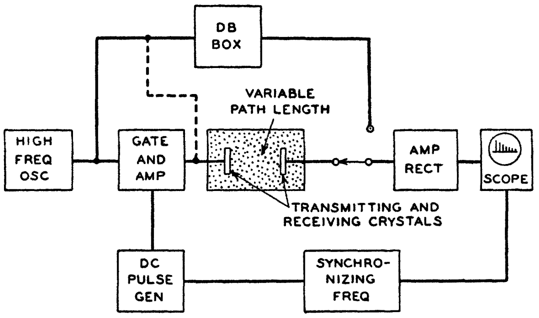

FIG. 8. Experimental arrangement for measuring the velocity and attenuation of a liquid at ultrasonic frequencies.

be measured even though the liquid path has 50 db or more attenuation.

Employing these methods a series of measurements were made for these three liquids at the frequencies 2 mc, 5 mc, and 8 mc and over a wide temperature range. The data on the attenuation for polymer *D* is shown plotted by Fig. 11, while the velocities for the same conditions are plotted on Fig. 12. The attenuation is plotted in terms of nepers (1 neper equals 8.68 db) per wavelength, since the theoretical attenuation is most easily calculated for that quantity. It is obvious from the data that an attenuation and associated velocity dispersion is occurring for this liquid.

In order to classify the measured results and to obtain parameters in terms of which they can be expressed, use is made of the calculated value of the attenuation and phase shift due to a relaxation theory. The effect can be represented by the equivalent circuit of Fig. 13, in which the series arm is the density times the length of the section *dx* considered, and the shunt arm consists of a stiffness κ_1/dx in parallel with a second shear viscosity divided by *dx* and the two in series with a second stiffness κ_0/dx. At very low frequencies this will reduce to the impedance of the stiffness κ_0, so that κ_0 represents the compressibility of the liquid measured by static methods. At very high frequencies, the impedance of the shunt arm reduces to that of the two stiffnesses in series. Hence, κ_0 = low frequency compressibility; κ_1 = difference between high frequency

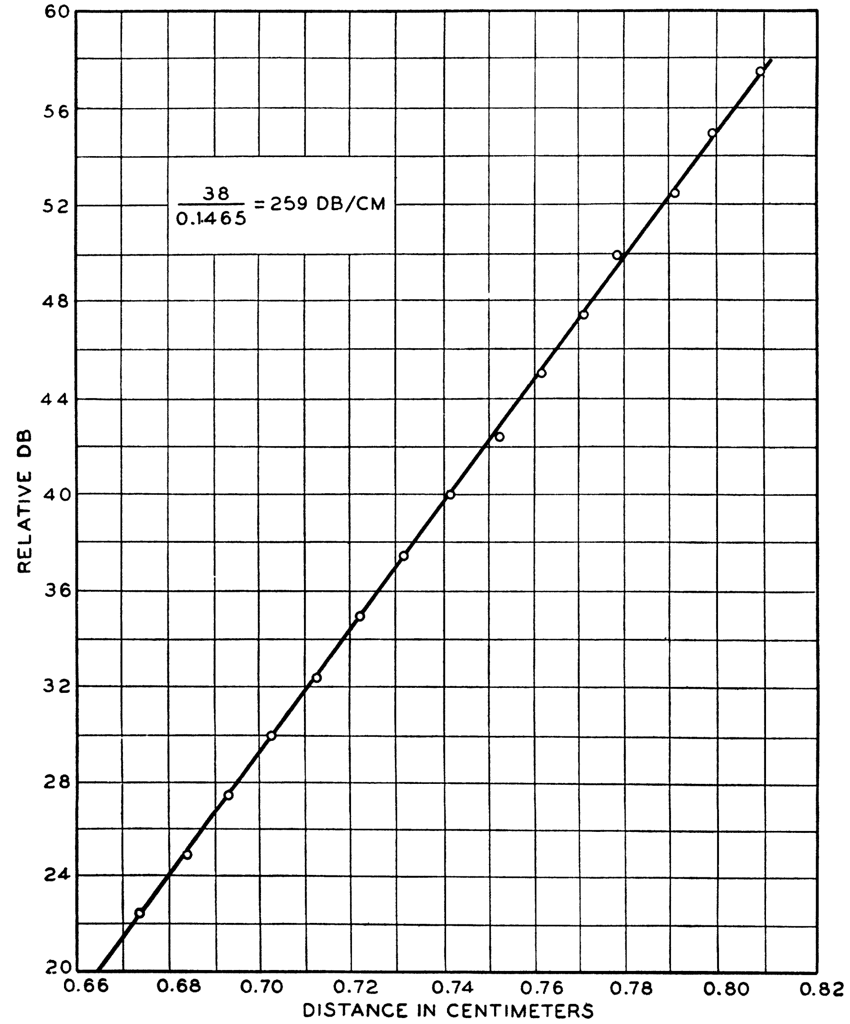

FIG. 9. *DB* attenuation plotted as a function of crystal separation for polymer *D*. Temperature 31°C, frequency 8 megacycles.

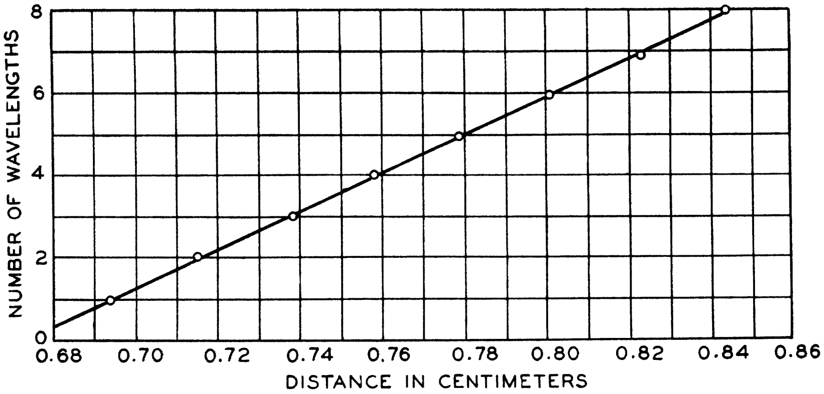

FIG. 10. Number of wavelengths plotted as a function of crystal separation for polymer D. Temperature 31°C, frequency 8 megacycles.

and low frequency compressibility. The resistance λ represents the viscosity. The attenuation and velocity can be calculated from the formula

$$Pdx=(A+jB)dx$$

$$=\left(\frac{Z_1}{Z_2}\right)^{\frac{1}{2}}=\left[\frac{j\omega\rho(dx)^2}{\dfrac{-j\kappa_0}{\omega}+\dfrac{\lambda(-j\kappa_1/\omega)}{\lambda-j\kappa_1/\omega}}\right]^{\frac{1}{2}}, \tag{7}$$

where $Z_1=j\omega\rho dx$ is the series arm and

$$Z_2=\left[\frac{-j\kappa_0}{\omega}+\frac{\lambda(-j\kappa_1/\omega)}{\lambda-j\kappa_1/\omega}\right]\times\frac{1}{dx}$$

is the shunt arm.

If we solve for the attenuation A (expressed in nepers per cm) and B the phase shift (expressed in radians per cm), we have

$$B=\omega\left(\frac{\rho}{\kappa^0}\right)^{\frac{1}{2}}\left(\frac{1+\lambda^2\omega^2(\kappa_0+\kappa_1/\kappa_0\kappa_1^2)}{1+\lambda^2\omega^2(\kappa_0+\kappa_1/\kappa_0\kappa_1)^2}\right)^{\frac{1}{2}}$$

$$=\frac{\omega}{\left(\dfrac{k^2v_0^2+\omega^2v_\infty^2}{k^2+\omega^2}\right)^{\frac{1}{2}}}. \tag{8}$$

$$\frac{A}{B}=\frac{1}{2}\,\frac{\omega\lambda/\kappa_0}{1+\lambda^2\omega^2\left(\dfrac{\kappa_0+\kappa_1}{\kappa_0\kappa_1^2}\right)}=\frac{1}{2}\left(\frac{v_\infty^2-v_0^2}{v_0v_\infty}\right)\frac{k\omega}{k^2+\omega^2},$$

where

$$v_0=\left(\frac{\kappa_0}{\rho}\right)^{\frac{1}{2}};\quad v_\infty=\left(\frac{\kappa_0+\kappa_1}{\rho}\right)^{\frac{1}{2}};$$

$$k=\frac{1}{\lambda(\kappa_0+\kappa_1/\kappa_0\kappa_1^2)^{\frac{1}{2}}}=\frac{(v_\infty^2-v_0^2)\rho v_0}{v_\infty}.$$

v_0 is the velocity at low frequencies, v_∞, the velocity at high frequencies, and $k/2\pi$ is the relaxation frequency f_0. If we multiply the ratio A/B by 2π, we obtain the attenuation A_w in nepers per wave-length, which is the quantity measured and expressed in Fig. 11. This becomes

$$A_w=\frac{\pi\omega\lambda}{\rho v_0^2}\times\frac{1}{1+\lambda^2\omega^2\left[\dfrac{v_\infty^2}{\rho^2v_0^2(v_\infty^2-v_0^2)^2}\right]}. \tag{9}$$

For very low frequencies this reduces to

$$A_w=2\pi^2f\lambda/(\rho v_0^2), \tag{10}$$

and the attenuation should initially be proportional to the frequency. This agrees with the measurements of Fig. 11 for high temperatures where the initial slopes of the attenuation frequency curves can be obtained. Equation (8) gives a method for determining the second component of the shear viscosity for

$$\lambda=A_w\rho v_0^2/(2\pi^2f). \tag{11}$$

Since all these quantities are known, λ can be determined and for poymer D is shown plotted as $\log\lambda$ *versus* $1/T$ by Fig. 14. The points lie on a straight line having a slope of $\frac{3}{4}$ that for the first component of the shear vicosity. The initial slopes have been determined for the other three liquids and are shown by Fig. 14. All the curves are parallel, indicating, as for the first component of shear viscosity, that the temperature dependent jump occurs by chain sections that are the same for all average molecular weights. The viscosity increases with molecular weight, although the spread is not nearly as large as that for the low frequency shear viscosity.

To correlate all the measurements of Fig. 11, over temperature and frequency ranges we plot the product

$$A_w \rho v_0^2/(\rho v_0^2)_S \qquad (12)$$

against the product of frequency times second shear viscosity, where $(\rho v_0^2)_S$ is the product of density times v_0^2 for polymer D at 20°C. All these viscosities are determined by the curves of Fig. 14, while the zero frequency velocities can be obtained by extrapolating the data of Fig. 12 and are shown by Fig. 15. Within the experimental error all these points lie on one curve shown by Fig. 16. Also the measured attenuation per wave-length of the polymer C liquid and the polymer B liquid can be plotted on the same curve. From the equation for the phase shift (6) since $B=\omega/v$, we see that the ratio of v/v_0 should also be a function of the product of the frequency by the secondary shear viscosity. From the data of Fig. 12, showing the measured velocity, the data of Fig. 14, showing the viscosity, and the data of Fig. 15 for the zero frequency velocity, the ratio of v/v_0 can be evaluated and is shown plotted by Fig. 17 as a function of the product frequency times

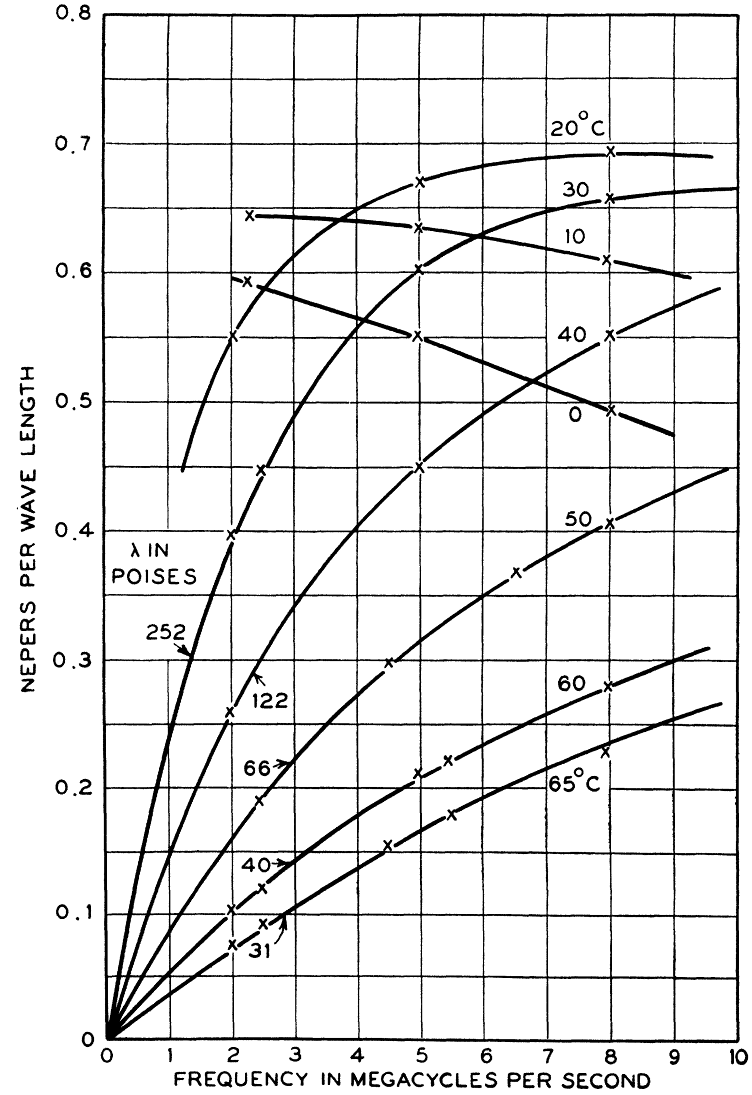

Fig. 11. Measurement of the attenuation per wave-length for polymer D plotted as a function of frequency and temperature.

viscosity. A single curve suffices for all the temperatures and for the other two polyisobutylene liquids.

IV. DISCUSSION OF LONGITUDINAL VELOCITY AND SOUND ABSORPTION IN LIQUIDS

A traditional concept of the liquid state regards a liquid as a solid substance for which the long-range order between the molecules has broken down. Alternately, if we regard a liquid as being a very dense gas as far as the interchange of energy between translational and internal vibrational modes is concerned, the natural method for accounting for the velocity dispersion and attenuation dispersion of a gas is to generalize the Herzfeld-Rice-Kneser[5] theory so that it applies for a liquid. This has recently been done by Kittel,[6] using the Tonks equation

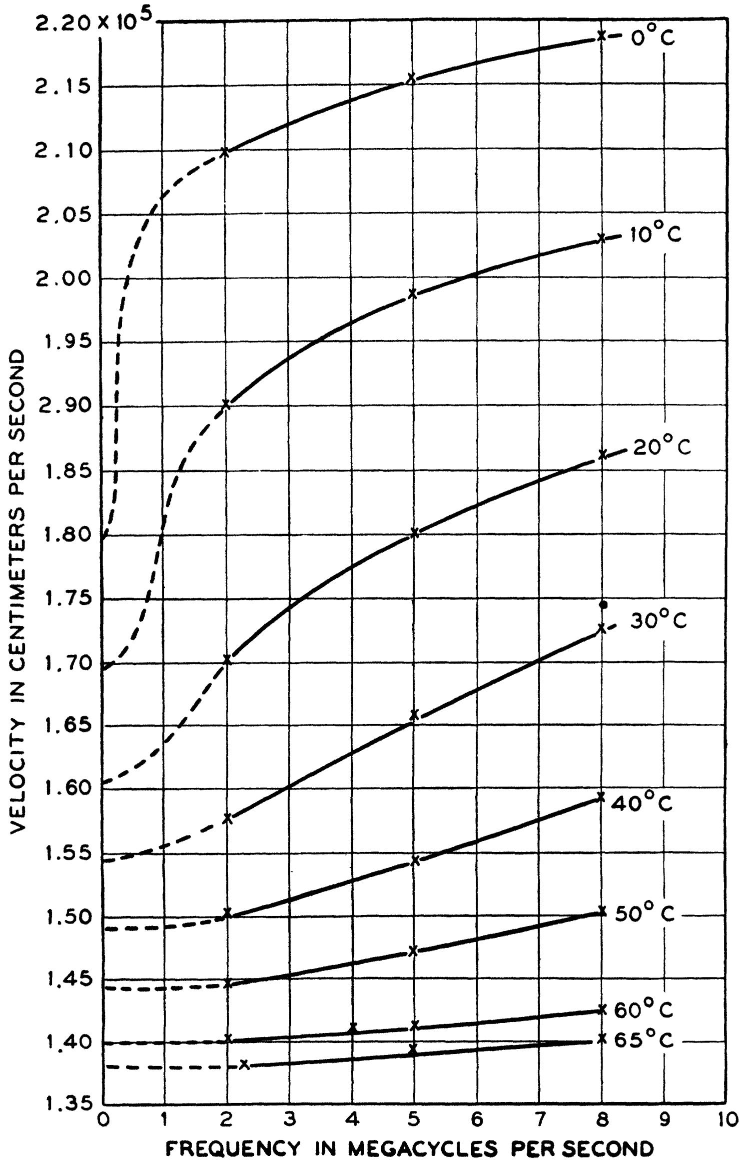

Fig. 12. Measured velocity of polymer *D* plotted as a function of frequency and temperature.

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[5] K. F. Herzfeld and F. O. Rice, Phys. Rev. **31**, 691 (1928); H. O. Kneser, Ann. d. Physik **11**, 761, 777 (1931); 16, 347 (1933).

[6] Charles Kittel, J. Chem. Phys. **14**, 614 (1946).

of state, and he finds that the attenuation A is given by

$$A=\left(\frac{\pi f^2}{v_0}\right)\left(\frac{3RC_i}{C_p^\infty C_v^0}\frac{f_0}{f_0^2+f^2}\right), \tag{13}$$

where C_p^∞ is the specific heat at constant pressure for an infinite frequency, i.e., with no internal modes of vibration of the molecules excited, C_v^0, the specific heat at constant volume and zero frequency, $3R=C_p-C_v$, C_i the specific heat associated with internal modes of vibration, f, the frequency, and $f_0=1/2\pi\tau$, where τ is the relaxation time which corresponds to the average lifetime of the excited vibration. On account of the larger number of collisions at higher absolute temperatures, this relaxation time is inversely proportional to the absolute temperature in degrees K. Since the attenuation per wave-length at low frequencies is

$$A_w=\frac{Av_0}{f}=\frac{2\pi^2 f\lambda}{\rho v_0^2}=2\pi^2 f\tau\left[\frac{3RC_i}{C_p^\infty C_v^0}\right] \tag{14}$$

by Eqs. (8) and (11), a "compressional" viscosity on the gas-like theory should be

$$\lambda=\left(\frac{3RC_i}{C_p^\infty C_v^0}\right)\rho v_0^2\tau. \tag{15}$$

When a liquid is regarded as being a solid in which the long range order between molecules has broken down, another method of explaining a compressional viscosity is the rearrangement process, after perturbation. This was first suggested by Debye[7] and has been further developed by Frenkel.[8] On this theory the compressibility is due to two components, the increase in potential energy caused by decreasing the distance between molecules, and a change in the degree of local order in the arrangement of the particles, in the sense of a more compact arrangement when the liquid is compressed, and a more open distribution when it is expanded. This change in the degree of local order must, in general, lag with respect to the variation of the pressure, since it is connected with a rearrangement of the particles or a redistribution of their mutual orientations, i.e., with processes requiring a certain activation energy, and proceeding accordingly with a finite velocity only. This time lag of the arrangement with respect to the volume must coincide with the mean lifetime of vibrations about the same equilibrium positions which determine the shearing viscosity of the liquid. By developing this point of view Frenkel shows that the reaction of an infinitesimal volume to a compression can be represented by the network of Fig. 13, and this theory results in the variation of velocity and attenuation given by Eqs. (8) and (9). Since an activation energy U is involved in the change from one degree of order to another, the viscosity should vary with temperature according to the form

$$\lambda=Ae^{U/kT}, \tag{16}$$

and when one plots the log of the viscosity against the inverse of the absolute temperature a straight line should result.

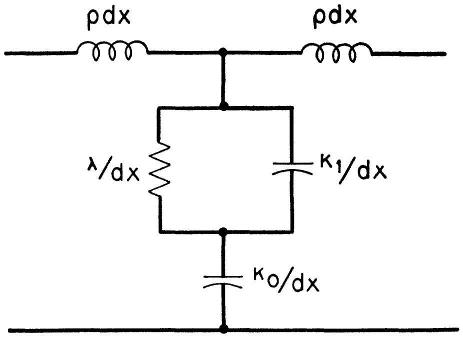

FIG. 13. Equivalent circuit for the propagation of a longitudinal wave in a liquid having an elastic compliance controlled by a relaxation mechanism.

The longitudinal measurements, however, do not distinguish between a change in λ, which would be caused by either the H-R-K mechanism, or the Debye-Frenkel mechanism, and a change in the shear elasticity, μ, which can be caused by a secondary relaxation of the shear term. Measurements that will be described in a forthcoming paper have shown that the increase in shear elasticity with frequency is the cause of this increase in longitudinal velocity.

However, this theory does not account entirely for the measured attenuation and velocity curves

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[7] See H. O. Kneser, Physik. Zeits. **39**, 800 (1938).

[8] J. Frenkel, *Kinetic Theory of Liquids* (Oxford University Press, New York, 1946), p. 208.

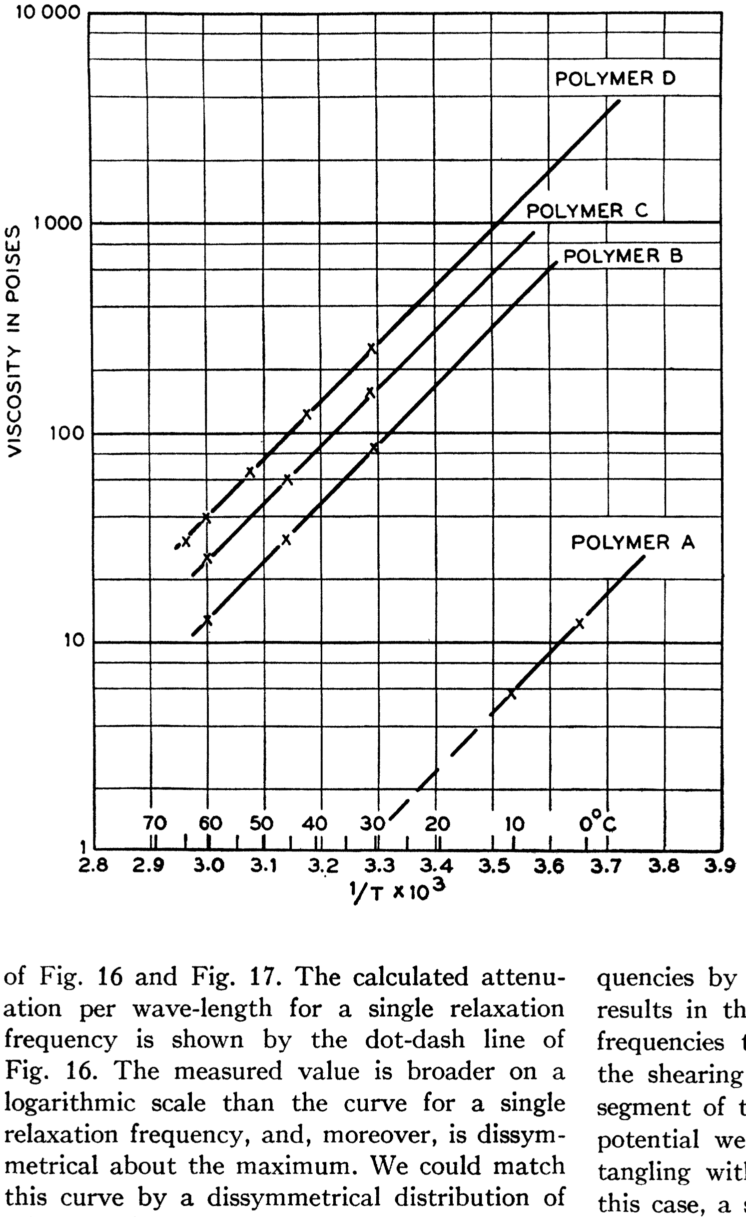

Fig. 14. Second shear viscosity of polyisobutylene liquids plotted as a function of temperature.

of Fig. 16 and Fig. 17. The calculated attenuation per wave-length for a single relaxation frequency is shown by the dot-dash line of Fig. 16. The measured value is broader on a logarithmic scale than the curve for a single relaxation frequency, and, moreover, is dissymmetrical about the maximum. We could match this curve by a dissymmetrical distribution of relaxation frequencies.

However, a simpler explanation of this effect is that a hysteresis occurs in the stress-strain relationship which introduces a constant loss per cycle. In order to get an agreement with experiment, this hysteresis loss has to be introduced in series with the elastic stiffness κ_1, giving this arm the impedance

$$(\lambda' - j\kappa_1)/\omega. \qquad (17)$$

Since this arm is shunted out at very low frequencies by the second shear viscosity λ, this results in the following interpretation. At low frequencies the local order change caused by the shearing of the liquid takes place by one segment of the chain jumping from one stable potential well to another with no appreciable tangling with other chains. There is even, in this case, a small amount of hysteresis loss, as is shown by Fig. 18, which shows the measured attenuation of the lightest liquid, the polymer *A* liquid. The attenuation values measured at 2, 5, and 8 megacycles lie on straight lines that do not go through the origin at zero frequency but have intercepts of about 0.0025 neper per wave-length, indicating the presence of a slight amount of hysteresis loss. As the frequency increases, fewer and fewer of the chains accumulate enough heat energy in the time of a single cycle to rearrange to adjacent stable potential wells, and the liquid becomes less compressible. It appears, however, that they can be displaced to intermediate potential minima. The displacement probably consists of an internal twisting. The steric restrictions imposed by the close packed methyl groups on the flexibility of individual chain then tend to hold the new twisted position. The chain segments then are not released until a later part of the cycle, and hence the strain lags behind the applied stress. It is supposed that the wave traveling through the polymer exerts such torque on certain portions of the convolved chains that an extreme biasing force for pairs twisting occurs. Thus the normally considerable activation energy for internal rotation of pairs of methyl groups past each other, in polyisobutylene, is effectively reduced to zero. Accordingly, since this potential barrier that the chains have to surmount to reach the twisted positions is so small compared, for instance, to that for proceeding to the next stable position (the latter process requires both twisting and translation), the hysteresis type of loss should continue to a very high frequency. This mechanism seems concordant with the general principles of hysteresis.

The network of Fig. 19 represents the effect of the hysteresis loss component. If we solve this network to obtain the velocity and attenuation, we have

$$Pdx=(A+jB)dx=\left(\frac{Z_1}{Z_2}\right)^{\frac{1}{2}}$$

$$=\left[\frac{j\omega\rho(dx)^2}{\dfrac{j\kappa_0}{\omega}+\left[\dfrac{\lambda((\lambda'-j\kappa_1)/\omega)}{\lambda+((\lambda'-j\kappa_1)/\omega)}\right]}\right]^{\frac{1}{2}}, \tag{18}$$

where Z_1 the series arm is $j\omega\rho dx$, and Z_2 the shunt arm is

$$Z_2=\frac{-j\kappa_0}{\omega}+\frac{\lambda[(\lambda'-j\kappa_1)/\omega]}{\lambda+(\lambda'-j\kappa_1)/\omega}. \tag{19}$$

Solving for the attenuation A and the phase shift B, we find

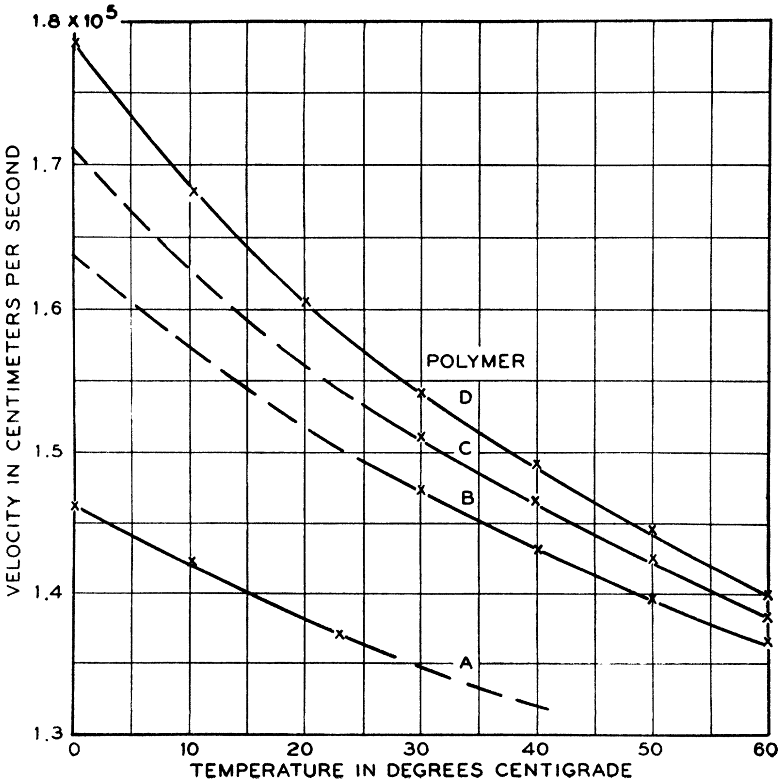

FIG. 15. Low frequency velocities for polyisobutylene liquids plotted as a function of temperature.

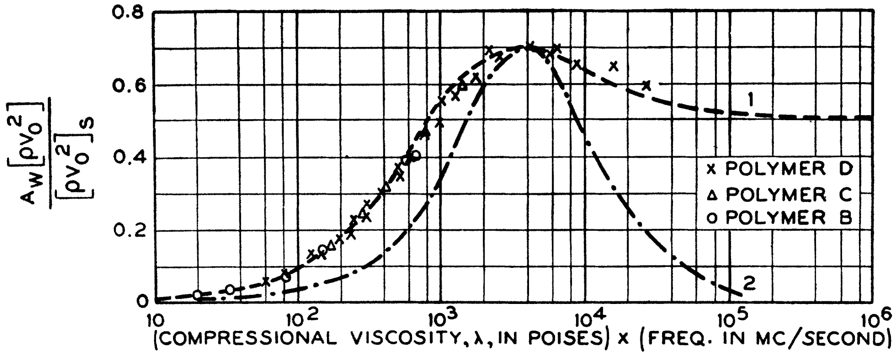

FIG. 16. Attenuation per wave-length for polyisobutylene liquids plotted as a function of secondary shear viscosity times the frequency. Dashed line calculated value assuming $\kappa_0=2.28\times10^{10}$ dyne/cm²; $\kappa^9=1.17\times10^{10}$; $\lambda'=0.53\times10^{10}$. Dashed dot line, calculated value for a single relaxation frequency. (The adjective "compressional" at the bottom of the figure should be deleted.)

$$A^2=\frac{\omega^2\rho}{2\kappa_0}\left[\frac{(\lambda'^2+\kappa_1{}^2)+2\omega\lambda\lambda'+\omega^2\lambda^2[(\kappa_0+\kappa_1)/\kappa_0]}{[\lambda'+\omega\lambda((\kappa_0+\kappa_1)/\kappa_0)]^2+[(\omega\lambda\lambda'/\kappa_0)-\kappa_1]^2}\right]$$

$$\times\left[-1+\left(\frac{1+(\omega^2\lambda^2/\kappa_0{}^2)[\lambda'^2+\kappa_1{}^2+\omega\lambda'\lambda]^2}{\lambda'^2+\kappa_1{}^2+2\omega\lambda\lambda'+\omega^2\lambda^2((\kappa_0+\kappa_1)/\kappa_0)^2}\right)^{\frac{1}{2}}\right]. \quad (20)$$

$$B^2=\frac{\omega^2\rho}{2\kappa_0}\left[\frac{(\lambda'^2+\kappa_1{}^2)+2\omega\lambda\lambda'+\omega^2\lambda^2[(\kappa_0+\kappa_1)/\kappa_0]}{[\lambda'+\omega\lambda((\kappa_0+\kappa_1)/\kappa_0)]^2+[(\omega\lambda\lambda'/\kappa_0)-\kappa_1]^2}\right]$$

$$\times\left[1+\left(1+\frac{(\omega^2\lambda^2/\kappa_0{}^2)[\lambda'^2+\kappa_1{}^2+\omega\lambda\lambda']^2}{\lambda'^2+\kappa_1{}^2+2\omega\lambda'\lambda+\omega^2\lambda^2((\kappa_0+\kappa_1)/\kappa_0)}\right)^{\frac{1}{2}}\right].$$

These can be written quite closely as

$$B=\omega\left(\frac{\rho}{\kappa_0}\right)^{\frac{1}{2}}\left(\frac{(\lambda'^2+\kappa_1{}^2)+4\pi\lambda'(f\lambda)+(4\pi^2/\kappa_0{}^2)[(\kappa_0+\kappa_1)/\kappa_0](f\lambda)^2}{(\lambda'^2+\kappa_1{}^2)+4\pi\lambda'(f\lambda)+4\pi^2[(\kappa_0+\kappa_1)^2+\lambda'^2/\kappa_0{}^2](f\lambda)^2}\right)^{\frac{1}{2}},$$

$$\frac{2\pi A}{B}=A_W=\frac{(2\pi^2/\kappa_0)(f\lambda)[\lambda'^2+\kappa_1{}^2+2\pi\lambda'(f\lambda)]}{[(\lambda'^2+\kappa_1{}^2+4\pi\lambda^2(f\lambda)+4\pi^2((\kappa_0+\kappa_1)/\kappa_0)(f\lambda)^2]}. \quad (21)$$

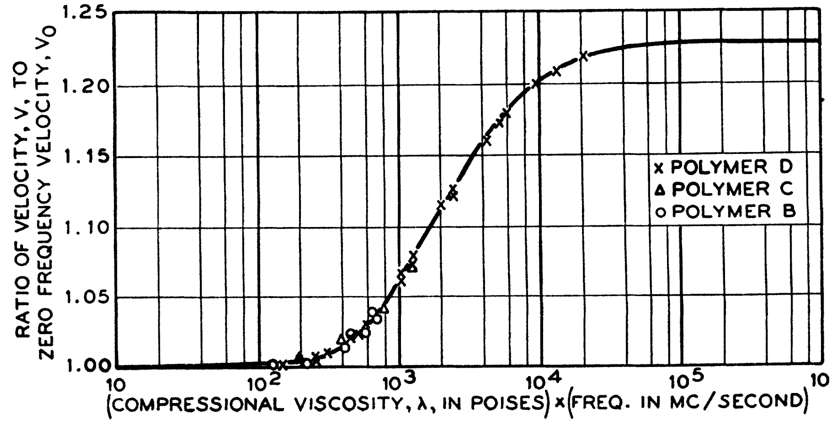

FIG. 17. Ratio of velocity to zero frequency velocity v_0 plotted as a function of secondary shear viscosity times the frequency. Solid line is calculated value assume $\kappa_0=2.28\times10^{10}$ dynes/cm²; $\kappa_1=1.17\times10^{10}$ dynes/cm²; $\lambda'=0.53\times10^{10}$ dynes/cm². (The adjective "compressional" at the bottom of the figure should be deleted.)

Several limiting cases are of interest. At low frequencies, the attenuation per wave-length and the velocity v_0 become

$$A_{w0}=\frac{2\pi^2}{\kappa_0}(f\lambda)=\frac{2\pi^2 f\lambda}{\rho v_0^2},\quad v_0=\left(\frac{\kappa_0}{\rho}\right)^{\frac{1}{2}}. \tag{22}$$

For very high frequencies the attenuation per wave-length and the velocity become

$$A_{w_\infty}=\frac{\pi\lambda'}{\kappa_0+\kappa_1}\quad\frac{\pi\lambda'}{\rho v_\infty^2},$$

$$v_\infty=\left(\frac{\kappa_0+\kappa_1}{\rho}\left(1+\frac{\lambda'^2}{(\kappa_0+\kappa_1)^2}\right)\right)^{\frac{1}{2}}. \tag{23}$$

Hence with a hysteresis type of loss the attenuation per wave-length at high frequencies remains constant and independent of the frequency. This is the type of attenuation[9] found for solid bodies of the glass type, and it appears that the polyisobutylene liquids approach this condition at high frequencies.

Introducing these values in Eqs. (19), the velocity, which is ω/B, and the attenuation per wave-length can be written in the form

$$v=v_0\left(\frac{1+2A(f\lambda)+B(v_\infty^2/v_0^2)(f\lambda)^2}{1+2A(f\lambda)+B(f\lambda)^2}\right)^{\frac{1}{2}};$$

$$A_w=\frac{2\pi^2}{\kappa_0}\frac{(f\lambda)[1+C(f\lambda)]}{1+2C(f\lambda)+D(f\lambda)^2}, \tag{24}$$

where

$$C=\frac{2\pi\lambda'}{\lambda'^2+\kappa_1^2};\quad D=\frac{4\pi^2(\kappa_0+\kappa_1)}{\kappa_0(\lambda'^2+\kappa_1^2)}.$$

Hence if C, D and v_∞^2/v_0^2 are relatively constant with temperature, the velocity and attenuation per wave-length are functions of the product frequency times second shear viscosity. As indicated by the data of Fig. 16 and Fig. 17, this assumption appears to be justified.

The measured curves of Fig. 16 and Fig. 17 can be fitted quite closely by taking

$$\kappa_0=2.28\times10^{10}\ \text{dynes/cm}^2;$$
$$\kappa_1=1.17\times10^{10}\ \text{dynes/cm}^2; \tag{25}$$
$$\lambda'=0.53\times10^{10}\ \text{dynes/cm}^2.$$

This gives a zero frequency velocity of 1.6×10^5

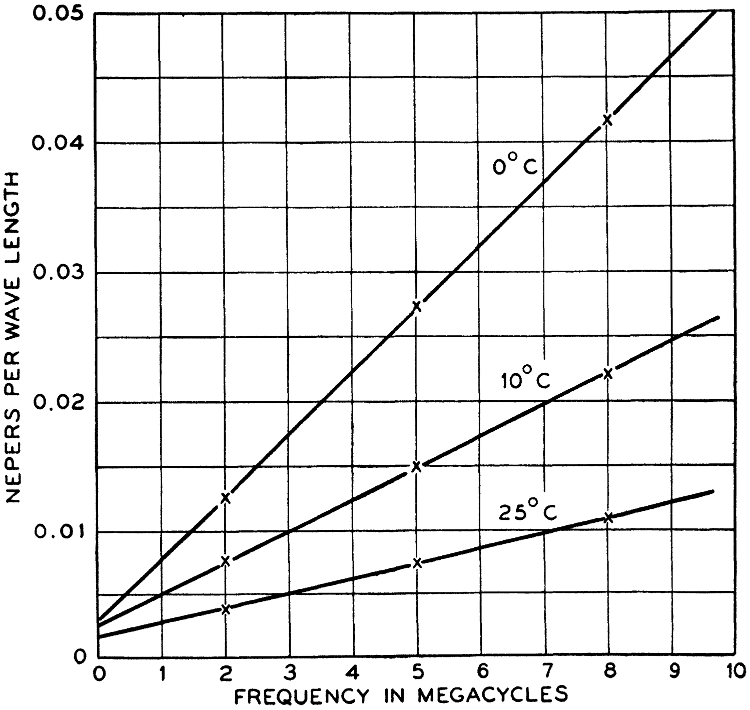

FIG. 18. Measured attenuation of polymer *A* polyisobutylene liquid plotted as a function of frequency.

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

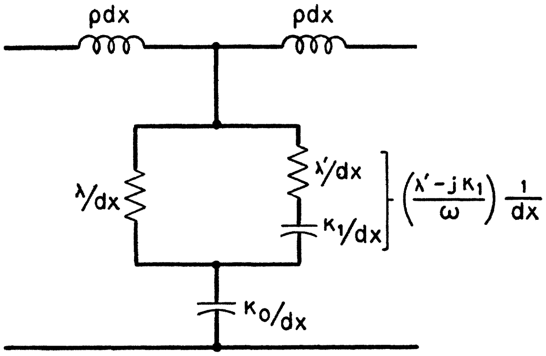

FIG. 19. Equivalent circuit for the propagation of a longitudinal wave in a liquid having an elasticity controlled by a relaxation mechanism and a hysteresis component in the rearrangement compliance.

corresponding to a temperature of 20°C, the standard condition of Fig. 16. The dashed line shows the calculated attenuation per wave-length which agrees very well with the measured points. The solid line of Fig. 17 is a plot of the ratio of velocity to zero frequency velocity, using Eq. (24) and the constants of Eq. (25). The agreement with the measured points is very good. The theoretical curve of Fig. 16 indicates that at high frequencies, polyisobutylene liquids should have an attenuation per wave-length of 0.5 neper, independent of frequency.

V. ORIGIN OF SHEAR ELASTICITY IN LIQUIDS

The present study should apply to the dynamic properties of all chain polymers, i.e., systems without cross linkage. One interesting result is that they show a shear modulus which decreases with increase in temperature contrary to that found for the "kinetic theory."

On the "kinetic theory" we have become accustomed to the unique high compliance of these substances (polymer networks held by secondary forces as well as from vulcanization), a particularly spectacular property at high amplitudes of motion. Here the "kinetic theory" of elasticity describes the elastic retractive force, F, for example as [10,11]

$$F=-T\left(\frac{\partial S}{\partial L}\right)=\left(\frac{kT\nu}{L_0}\right)\left(\alpha-\frac{1}{\alpha^2}\right),$$

where T = absolute temperature, L = length of sample, S = entropy, L_0 = length of unstretched sample, ν = number of chains in a volume V, and $\alpha = L/L_0$. Here the 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.

Most polymers show in addition to this "ideal" elasticity, several other elastic effects, portions of which have been extensively reported in earlier literature. For instance, at suitably low temperatures, ordinary supercooled organic liquids (glasses) become hard, as also do all kinds of rubbers and plastics. In this low temperature range, however, rubbery materials usually exhibit a really high shear modulus, of the order of 10^8 to 10^{10} dynes/cm^2. This is approximately the same whether the chains are cross linked into networks or not[12–14] and does not depend much on average length of chains or segments between cross links above a certain limit.[12] Accordingly, the displacement process here can be imagined as the biasing of the positions of small chain elements in potential wells defined by their interaction with neighboring chain elements. Thus, as expected, there is a steep decline in this modulus with increase in temperature, even for static measurements.

With increasing temperature, however, true "kinetic" theory elasticity rapidly comes into play for static or slowly varying measurements. However, the present results emphasize that all typical chain systems should also be examined for an intermediate type of elastic behavior in which the shear modulus of the order of 10^6 dynes/cm^2, which has the opposite temperature dependence to the kinetic theory phenomenon. This type of elasticity is markedly dependent on chain length and indeed the data are qualitatively similar to the recent conclusion[15] of the effect of average molecular weight on the *rate* of deformation of polyisobutylene, which is also notably dependent on molecular weight.

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[10] F. T. Wall, J. Chem. Phys. **10**, 132 (1942); **10**, 485 (1942); **11**, 1527 (1943).

[11] P. J. Flory, Chem. Rev. **35**, 51 (1944).

[12] W. O. Baker and N. R. Pape, Report to Rubber Reserve Company May 27, 1943.

[13] J. W. Liska, Ind. Eng. Chem. **36**, 40 (1944).

[14] F. S. Conant and J. W. Liska, J. App. Phys. **15**, 767 (1944).

[15] J. Rehner, J. Polymer Sci. **2**, 225 (1946).

Hence, new causes besides kinetic theory behavior (which of course remains fundamental to rubber-like elasticity if enough time is given to establish equilibrium) must be sought to explain this intermediate type of low shear moduli in the order of 10^6 dynes/cm^2, whose presence must be regarded as well established. It may be that a composite movement, including hindered rotation *within* chains, as well as interaction of segments *between* chains, is the basis for this sort of elasticity. Such motion would be affected by chain length, through a chain articulation effect. Study of cellulose derivatives and other polymers, involving alteration of interchain forces without great changes in intrachain stiffness, will elucidate further this possibility. It is always striking that a degree of softness and high compliance may be imparted to virtually any chain system by sufficient amounts of plasticizer. Yet this does not much change the barriers to internal chain flexing, and, it is suspected, does not always directly introduce kinetic theory elasticity, but perhaps the other type of elasticity of this report.

Finally, at very high frequencies, the data on the velocity dispersion together with the shear measurements showing that the increase in longitudinal velocity is caused by an increase in shear elasticity indicate that this composite motion is relaxed and the shear elasticity is then determined by single potential wells and approaches that of a crystal. The data of Eq. (25) show that the shear elasticity equals 5.85×10^9 dynes/cm^2 and the liquid is similar to a solid having a Poisson's ratio of 0.4.

ACKNOWLEDGMENTS

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