

Discussion

H. BLOK.¹¹ It is important to check whether a drop in viscosity, which might be expected at high rates of shear,¹² has occurred in Mr. Mason's experiments.

In this connection, an estimate should be made of the highest rates of shear and shearing stresses attained in the various liquids tested. It is appreciated that the amplitude of the vibrating motion was very small indeed, but, on the other hand, the frequencies of vibration were excessively high.

L. BRILLOUIN.¹³ The experimental method described in this paper should be extended to a variety of liquids and for the whole range of frequencies. The author is absolutely correct in emphasizing the necessity to use two viscosity coefficients, λ and η , since Stoke's relation must be abandoned as unjustified, especially for ultrasonic waves. The results obtained by the author's method should be compared with those derived from the attenuation of ultrasonic waves, where many results have been obtained and are not clearly understood now.¹⁴

The possible role of transverse elastic waves of hypersonic frequency in thermal agitation of liquids was suggested by the writer in a paper of 1936,¹⁵ and further investigations, both theoretical and experimental were carried on by R. Lucas,¹⁶ who discovered some very strange mechanical effects in liquids ununiformly heated. These effects again seem to be closely related with transverse elastic waves in liquids.

J. H. RAMSER.¹⁷ According to the author, the penetration of a viscous wave from the vibrating crystal into a liquid is only a few thousandths of a centimeter. The friction brought about by the rapidly moving liquid layers must cause a rise of temperature in the film of liquid in which the viscous wave exists. Since the temperature in the film tends to equalize itself to the temperature of the remainder of the liquid, a steady-state temperature distribution will exist in the film as long as the crystal is vibrating. Therefore it may be expected that the observed values of viscosity as determined by this method are lower than the values corresponding to the ambient temperature. This seems to be partly supported by the data listed in Table 1 of the paper, which show that the observed viscosities are lower than the viscosities anticipated on the basis of ambient temperature in 6 out of 8 cases. However, the deviations between viscosities, as determined by the flow method and by the vibrating-crystal method, respectively, may also be due partly to the fact that the coefficient of viscosity depends upon the rate of shear.

The author states that better temperature control is required. In view of the existence of a steady-state temperature gradient in the liquid film adjacent to the vibrating crystal, it would seem to be difficult to control the temperature in the film by a control of the ambient temperature alone since the "effective temperature" in the film should also depend upon other factors, such as the heat conductivity of the liquid under investigation. The

accuracy with which the effective temperature in the film is known will determine the accuracy with which viscosities can be measured by this very interesting method.

CHARLES KITTEL.¹⁸ The author's work reported in this paper promises to find wide practical application in the measurement of viscosity, particularly in connection with small samples. The work is also of fundamental interest to physicists concerned with the structure of the liquid and solid states as it offers a direct and clear-cut method for determining the relaxation time of the shear elasticity in viscous liquids.

The general study of relaxation or time-lag phenomena is of increasing importance in many fields at the present time. Experimental and theoretical work on mechanical, thermal, and dielectric relaxation, and on the relaxation of electronic and nuclear magnetic moments is contributing to the understanding of the basic properties of matter. The study of relaxation processes in liquids has caused a revision of the classical picture of a liquid as a medium which will not support shearing stress and which is perfectly elastic with respect to compression. It is now fairly well established that there are time lags in the motion of liquids under high-frequency shear or pressure.

It was suggested first by Poisson¹⁹ that liquids may react elastically to shearing stresses, provided that these are applied sufficiently rapidly. This conception was put into a convenient mathematical form by Maxwell.²⁰ The propagation of shear waves in liquids was looked for originally at low frequencies by Reiger,²¹ but without success. Recently Ferry²² has measured the velocity of shear waves in solutions of high polymers and Raman and Venkateswaran²³ have found an effect of the shear elasticity in optical scattering experiments.

It should be noted that simple liquids are not expected to behave elastically with respect to shear until very high frequencies are attained. The relaxation frequency is given by $f_r = \mu/2\pi\eta$, according to Equation [12] of this paper. For $\eta = 10^{-2}$ poises, and the value $\mu \sim 10^{+10}$ dynes per sq. cm, characteristic of simple crystals, one estimates $f_r \sim 10^{11}$ cycles per sec. Optical experiments²⁴ at 10^9 cycles per sec have given no indication of shear elasticity in simple liquids.

C. M. LARSON.²⁵ The author has presented a new tool which should make it possible to extend our knowledge of viscosity into new fields, i.e., those of viscosity under pressure, high rate of shear, and viscosity separated from oiliness.

Viscosity is one of the most important characteristics in a lubricant. The rate-of-flow and the falling-ball methods have been quite practical but have limited our knowledge to physical

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¹² "Sur les Équations Générales de l'Équilibre et du Mouvement des Corps Solides, Élastiques, et Fluides," by S. D. Poisson, *Journal de l'École Polytechnique*, vol. 20, 1831, p. 139.

¹³ "On the Dynamic Theory of Gases," by J. C. Maxwell, *Philosophical Transactions of the Royal Society of London*, vol. 157, 1867, pp. 49-88.

¹⁴ "Über die Ausbreitung Scherender Deformationen im Flüssigkeiten," by R. Reiger, *Annalen der Physik*, vol. 31, 1910, pp. 51-92.

¹⁵ "Mechanical Properties of Substances of High Molecular Weight. II. Rigidities of the System Polystyrene-Xylene and Their Dependence Upon Temperature and Frequencies," by J. D. Ferry, *Journal of the American Chemical Society*, vol. 64, 1942, pp. 1323-1329.

¹⁶ "Rigidity of Liquids," by C. V. Raman and C. S. Venkateswaran, *Nature*, vol. 143, 1939, pp. 798-799.

¹⁷ "Interferometric Studies of Light Scattering in Viscous Liquids and Glasses," by C. S. Venkateswaran, *Proceedings of the Indian Academy of Sciences, Series A*, vol. 15, 1942, pp. 362-370.

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¹⁹ "Delft" Laboratory, Royal Dutch Shell, Delft, Holland.

²⁰ See, "Viscosity at High Rates of Shear," by H. Blok, paper read before the 6th Congress of Applied Mechanics, Paris, September 22-29, 1946. Preprints of this paper may be obtained by applying to the "Delft" Laboratory (B.P.M.), 20 Broekmolenweg, Delft, Holland.

²¹ Cruft Laboratory, Harvard University, Cambridge, Mass.

²² "Sur l'Agitation Thermique des Liquides, Leurs Nouvelles Propriétés Thermomécaniques et leur Conductibilité Calorifique," by R. Lucas, *Journal de Physique*, vol. 8, 1937, pp. 410-428.

²³ Author's footnote.⁴

²⁴ See footnote¹⁴, p. 410.

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properties. The present method by means of the torsionally vibrating crystal presented is a new epic in viscosity and shear research.

AUTHOR'S CLOSURE

Mr. Blok has raised the question whether the rates of shear obtained by using the crystal are high enough to cause the viscosity to drop due to the shearing rate and Mr. Ramser has questioned whether the energy supplied by the crystal is enough to heat the liquid appreciably near the crystal and cause a lowering of viscosity over what would be measured by other methods. These questions have been considered for one liquid, the dimethyl phthalate and it has been shown that these effects are not noticeable for the amplitudes used.

The displacement of the crystal, which is maximum on the ends, can be calculated as follows. From Equation [48] we have that the angular velocity on the ends of the crystal is

$$\dot{\theta} = D_M E_0 \left[\frac{\text{Tanh } \frac{\Gamma l}{2} + \frac{Z_T}{Z_0}}{(Z_0 + Z_T^2/Z_0) + 2Z_T \coth \Gamma l} \right] \dots [48]$$

Inserting this expression in Equation [49] we find

$$i = i_C + i_R = E_0 \left(j\omega C_0 + \frac{2D_M}{E_0} \dot{\theta} \right) = E_0 j\omega C_0 + 2D_M \dot{\theta}$$

This equation says that the current through the crystal, when it is immersed in the liquid, is made up of two parts, i_C the part through the static capacity of the crystal, and the part, i_R , through the motional impedance of the crystal. If we balance out the capacitive part in a bridge circuit, the remaining part i_R is directly proportional to the angular velocity on the end of the crystal. If we measure the voltage across the crystal when the crystal is balanced at its resonance frequency, the current i_R is

$$i_R = E/R$$

where R is the shunt resistance in the balanced bridge. For the measurements made on dimethyl phthalate, given in Equation [10], the voltage E was 1 volt, and $R = 36,500$ ohms. Hence

$$i_R = \frac{1}{36,500} = 2.75 \times 10^{-5} \text{ amperes.}$$

The angular velocity on the end of the crystal is accordingly

$$\dot{\theta} = \frac{i_R}{2D_M} = \frac{2.75 \times 10^{-5}}{2D_M}$$

From Equation [54]

$$D_M = \frac{\pi f_R}{\sqrt{2}} \sqrt{\frac{IC_0}{r}}$$

after substituting the relation of Equation [50]. For this crystal $f_R = 13,948$; $l = 6.9$ cm; $I = \frac{\pi}{2} \rho(R^4 - R_0^4) = 0.159$; $C_0 = 140 \times 10^{-12}$ farads; $r = \text{ratio of capacities} = 46.5$. Hence

$$D_M = .0562$$

The angular velocity on the end of the crystal is therefore

$$\dot{\theta} = \frac{2.75 \times 10^{-5}}{2 \times .0562} = 2.44 \times 10^{-4} \text{ radians per sec.}$$

The linear velocity of any point on the end, being $R\dot{\theta}$, is

$$v_r = 2.44 \times 10^{-4} \times .465 = 1.13 \times 10^{-4} \text{ cm per sec.}$$

The maximum linear displacement d_0 is

$$d_0 = \frac{v_r}{2\pi f_R} = \frac{1.13 \times 10^{-4}}{6.28 \times 13948} = 1.29 \times 10^{-9} \text{ cm.}$$

This displacement sets up a shearing wave of the viscous type, which dies out according to the factor

$$d = d_0 e^{-\sqrt{\frac{\pi f \rho}{\eta}} z} = e^{-\alpha z} \text{ where } \alpha = \sqrt{\frac{\pi f \rho}{\eta}} = 560 \text{ nepers per cm for dimethyl phthalate}$$

The shearing strain is

$$\frac{d_0 - d(\Delta x)}{\Delta x} = \frac{d_0(1 - e^{-\alpha \Delta x})}{\Delta x} \doteq \frac{d_0(1 - 1 + \alpha \Delta x)}{\Delta x} = d_0 \alpha$$

For the value of d_0 and α found above the shearing strain is 7.2×10^{-7} which is still too small a strain to cause the effects observed by H. Blok.

The second problem of the temperature near the vibrating crystal is easily solved by using the equations of heat flow which take the form

$$C\rho \frac{\partial T}{\partial t} = -K\nabla^2 T + P$$

where C is the specific heat, ρ the density and K the heat conductivity of the liquid, and P the rate of production of heat per unit volume due to the converting of acoustic energy into heat energy. By referring to the equivalent circuit of a liquid (Fig. 8A), it is readily seen that the rate of energy production per unit volume in watts per cubic cm. is

$$P = (v_2 - v_1)^2 \frac{\eta}{(dx)^2}$$

where v_2 is the linear velocity at the distance x_2 and v_1 the linear velocity at the distance x_1 . Hence since $v_2 = v_r e^{-\alpha x_2}$, $v_1 = v_r e^{-\alpha x_1}$ we have

$$P dx = v_r^2 e^{-2\alpha x} (1 - e^{-\alpha dx})^2 \frac{\eta}{dx} = v_r^2 \alpha^2 \eta e^{-2\alpha x} dx$$

assuming that the surface is considered plane, since the viscous waves penetrate such a small distance from the crystal. If we integrate the total heat production from $x = 0$ to $x = \infty$ this gives

$$P_T = \int_0^\infty v_r^2 \alpha^2 \eta e^{-2\alpha x} dx = \frac{v_r^2 \alpha \eta}{2} = \frac{v_r^2}{2} \sqrt{\pi f \eta \rho}$$

and the total energy produced is equal to the total input energy $\frac{v_r^2}{2} R_M$ where R_M is the mechanical resistance of the viscous liquid. For $v_r = 1.13 \times 10^{-4}$, and $R_M = 98$ ohms per $\text{cm}^2 ds$ for dimethyl-phthalate, the total input energy is 6.28×10^{-7} watts per square centimeter. This checks quite closely with the input electrical energy $E^2/2R_E = 1/74,000 = 1.36 \times 10^{-5}$ watts, when this is divided over all the radiating surfaces.

Inserting the value of P in the heat equation, we have

$$C\rho \frac{\partial T}{\partial t} = -K\nabla^2 T + v_r^2 \alpha^2 \eta e^{-2\alpha x}$$

For steady state conditions $\frac{\partial T}{\partial t} = 0$ and for a plane heat wave

$$\nabla^2 T = \frac{\partial^2 T}{\partial x^2}. \text{ Hence}$$

$$K \frac{\partial^2 T}{\partial x^2} = v_r^2 \alpha^2 \eta e^{-2\alpha x}$$

Integrating these equations

$$T = T_0 + \frac{v_r^2 \eta}{4K} e^{-2\alpha x}$$

The value of heat conductivity for most liquids is around .001 cal per sq cm per sec per deg C per cm. Since 1 calorie per second is equal to 4.187 watts, the numerical value of the constant multiplying $e^{-2\alpha x}$ is

$$\frac{v_r^2 \eta}{4K} = \frac{(1.13 \times 10^{-4})^2 \times .178}{4 \times .0042} = 1.37 \times 10^{-7}$$

and hence the increase in temperature near the crystal surface is less than one millionth of a degree C. It has been checked experimentally that no change in the balancing resistance occurs over a 10 to 1 change in voltage from 1 to 10 volts, which again verifies that the rate of strain and the increase in temperature are entirely negligible for these types of measurements.