MEASUREMENT OF THE SHEAR ELASTICITY OF FLUIDS AND THEIR BOUNDARY LAYERS BY A RESONANCE METHOD

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A method is developed for measuring the shear moduli of liquids; for this purpose the change in the resonant frequency of a piezoelectric quartz crystal, induced by the presence of a liquid film on a crystal face under a quartz covering plate, is measured for very small vibrational amplitudes. For low-viscosity liquids (water and benzene) the shear modulus is of the order 10^4—10^5 dyne/cm^2. With increase of the crystal vibration amplitude the effective shear modulus decreases and the relative influence of dissipative forces increases. For nonpolar liquids the shear modulus remains unchanged at all distances from the quartz surface, whereas for polar liquids (water, alcohols, etc.) it increases sharply upon approaching to within 600—900 Å of the surface. The shear modulus data for thin water films are in qualitative agreement with those of an earlier article by one of the authors.[1]

INTRODUCTION

ONE of the present authors has shown[1] that thin films of water between two glass surfaces possess a measurable shear modulus. Proof that thin water films possess shear elasticity, together with a basis for measuring the corresponding shear modulus, was provided by a great increase (several orders of magnitude) in the vibrational frequency of a lens that was suspended, convex downwards, by a thin ribbon and lowered close to the bottom of a water-filled vessel. The original natural period of the suspended lens was of the order of minutes; in the presence of a 10^{-5}-cm water film the period dropped to a fraction of a second.

With the deformation of the thin water film between the vibrating lens and the bottom of the vessel the elastic component of resistance thus became highly dominant over the component depending on dissipative forces. The calculated effective shear modulus decreased rapidly with increasing thickness of the film and could not be detected at thicknesses exceeding 0.15 micron. It was reasonable to presume that the shear modulus existed for the water film bounded by glass surfaces because the boundary layer structure of the water then differed from that of water in bulk and resembled the structure of a solid.

Investigations of boundary-layer viscosity by the blower method[2-4] and by polymolecular adsorption of vapor[5] also furnished strong proof that polar-

liquid thin films on solid surfaces are influenced by the solids and acquire special properties different from the bulk properties of the liquids. On the basis of these experiments the authors of the articles referred to were able to postulate the existence of a special boundary-layer phase having properties that change abruptly from those of the bulk phase. One could thus speak of a phase transition between the boundary layer and the bulk of a liquid.

Recent original investigations of other polar-liquid boundary-layer properties have also confirmed that the influence of a solid wall penetrates far into a liquid. For example, it was shown in[6] that water in thin capillaries and pores having diameters smaller than 0.1 μ do not exhibit their maximum density at +4°C. In[7] it was shown that the thermal conductivity of water films on mica surfaces is anomalously increased (by more than one order of magnitude). Other very interesting work[8,9] has furnished convincing proof of changes in the thermodynamic properties of liquid boundary layers.

It can now be regarded as firmly established that the boundary layers of many polar liquids acted upon by the surface forces of solids acquire structures distinguished by a higher degree of ordering. It can therefore be assumed that the boundary layers of many liquid possess shape elasticity, i.e., a shear modulus. The special mechanical properties of films between two solid surfaces are also very interesting because they are associated with different aspects of the physics of surface and colloidal phenomena. These properties are especially important in accounting for the boundary-friction mechanism and for the mechanical properties of colloids.

It was therefore very important to continue the earlier work reported in[1] using a more suitable method that would permit shear modulus measurements at very small shear deformation amplitudes and at higher frequencies, when the relaxation of strains may possibly be less in evidence.

It was also interesting to attempt to detect and measure shear moduli in the interior of liquids. This kind of data was obtained by Mason[10] for a number of highly viscous liquids by reflecting transverse ultrasonic waves from the interface between fused quartz and a liquid. By measuring the amplitudes and phases of the reflected waves with and without the liquid on the quartz surface the shear elasticity and viscosity of the liquid can be determined. An example is polymerized castor oil, for which Mason obtained G = 1.2 × 10⁷ dyne/cm² and η = 18 poise. His negative results for low-viscosity liquids such as water, benzene etc. can

possibly be attributed to the damping out of shear waves at relatively short distances, and also to a reduced sensitivity of the method with decrease of the measurable shear modulus. It was therefore interesting to detect and measure the modulus for films considerably thicker than the boundary layers and yet thin enough so that negligible damping of the shear waves would occur within them.

EXPERIMENTAL PROCEDURE

We used a technique based on Mandel'shtam's idea[11] for determining the interaction forces between any body and a contacting quartz piezoelectric crystal from the frequency shift of the latter's natural vibrations. This idea has been used by Khaĭkin et al.[12] to investigate dry "static" friction forces manifested in "prior displacements" which resulted from the fact that objects lying on the surface of a vibrating quartz crystal are not entrained completely by the surface of the latter.

In the present work we have measured the shift of resonant frequency for quartz having one face vibrating in its own plane and separated from a quartz cover plate by a plane-parallel film of liquid. The observed increase of vibrational frequency compared with that of a crystal not bearing a liquid film and cover plate proved unambiguously that the liquid film possesses shear elasticity; if only dissipative (e.g., viscous) forces were operative here the resonant frequency could only have been reduced (even without taking account of the added mass).

It is easily seen, moreover, that if the positive shift of the resonant frequency is used to calculate the shear modulus while considering the liquid film to be ideally elastic and ignoring dissipative forces and relaxational processes within the latter, the derived effective shear modulus can only be smaller, not larger, than the true modulus. We shall show when analyzing the results that this error cannot reach 10% in most cases. Therefore, considering that the given investigation was the first to enable estimates of shear moduli for low-viscosity liquids, it is not expedient to introduce a correction for dissipative forces into the calculation of the shear moduli, especially since this correction can be accomplished unambiguously only with simultaneous measurement of change in the width of the resonance curve for the quartz crystal. The latter measurement was not obtained systematically in the present work.

We investigated a 5° X cut quartz crystal in the shape of a bar with a rectangular cross section (36 mm long, 12 mm wide, and 5 mm thick). The

working surface was a horizontal face perpendicular to the optic axis of the crystal; this face moved tangentially during longitudinal vibrations. The face was in contact with a liquid film under a solid cover plate (Fig. 1) having the dimensions 8 × 5 × 4.5 mm (the last dimension being the height). During vibrational motion of the crystal the cover plate is practically at rest because of the obviously small coupling through the film, which cannot transfer to the cover the huge accelerations involved in quartz natural vibrations (at 74.4 cps in our case).

In quartz of the given cut the Poisson ratio vanishes, although when possessing the aforementioned dimensions it interacts with low-frequency flexural vibrations.[10,13,14] Thus there existed a weak normal component, which in our case induced a negative frequency shift that was practically independent of the liquid film thickness or composition and could therefore be excluded easily.

The quartz crystal was mounted in a special holder that was clamped between two steel needles making contact on the nodal line through the middle of the crystal. The electrodes were separated from the crystal by air gaps not exceeding 0.5 mm. The electrodes were made of brass plates that were fastened in a Plexiglas frame by means of screws. The electrodes were applied with an air gap because the quartz crystal required continual special cleaning in the course of the experimental work and had to be removed from its holder on each occasion.

For the purpose of exciting the fundamental resonant frequency of the crystal we used a rf generator stabilized at 75 kc by a quartz resonator. This generator was modulated with ± 1 cps accuracy by an audio-frequency generator. As a result of balanced modulation the carrier frequency was compensated, and one of the side frequencies was partially tuned out by means of the circuit. The generator output voltage (variable from zero to a few tens of volts) was applied to the first pair of electrodes, which were placed on two lateral faces near one end of the crystal.

The applied alternating electric field induced oscillations of compression and dilatation in the crystal. The alternating emf induced by the direct piezoelectric effect was fed through a second pair of electrodes (placed similarly to the first pair but at the other end of the lateral faces) to an oscilloscope that was used to monitor the crystal vibrations and to measure its resonant frequency within ± 1 cps. By continuous variation of the modulating frequency one of the side frequencies can be made equal to the natural frequency of the crystal. The amplitude of the crystal vibrations then increases; this is accompanied by a corresponding rise of the

potential applied to the oscillograph, which measured this potential (usually not exceeding a few hundred millivolts) and thus recorded the resonance curve of the crystal. An oscillograph was required for rapid and accurate determination of the resonant frequency when investigating volatile low-viscosity liquids, since the film thickness could change during the measurements. Pointer-type instruments are very unsuitable because of their large time lag, as a result of which they can often "jump" through resonance without registering it, especially in the case of the small quartz vibrational amplitudes.

It can be seen from the theory of the foregoing method that determination of the shear modulus requires quite accurate determination of the liquid film thickness. We used the following interference method. The system represented in Fig. 1 is illuminated with monochromatic light impinging almost perpendicular to the surface of the cover prism and the reflected light is observed while the wavelength is varied continuously. If the liquid film possesses uniform thickness the field of view will be darkened periodically whenever the light-path difference in the film becomes equal to an odd number of half-waves. This path difference is given by

$$\Delta = 2Hn + \lambda/2,$$

where H is the film thickness and n is its refractive index.

Let the wavelengths λ_1 and λ_2 correspond to two successive dark bands as the wavelength is varied. The two path differences are

$$2Hn + \lambda_1/2 = (2k - 1)\lambda_1/2,$$

$$2Hn + \lambda_2/2 = [2(k + 1) - 1]\lambda_2/2. \tag{1}$$

Eliminating k, we obtain

$$H = \lambda_1\lambda_2/2n(\lambda_1 - \lambda_2). \tag{1'}$$

It is more convenient to use a nomogram equivalent to (1') than to compute the film thickness directly from the equation. The ordinate of this nomogram (Fig. 2) is the wavelength and the abscissa is the optical film thickness. The oblique straight lines correspond to the dark bands and were plotted

FIG. 1. Quartz piezoelectric crystal coupled to quartz plate. 1—quartz crystal, 2—liquid film, 3—cover plate.
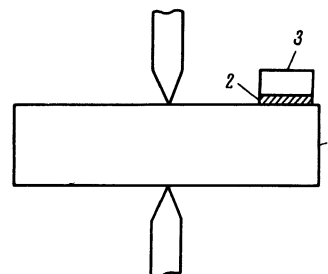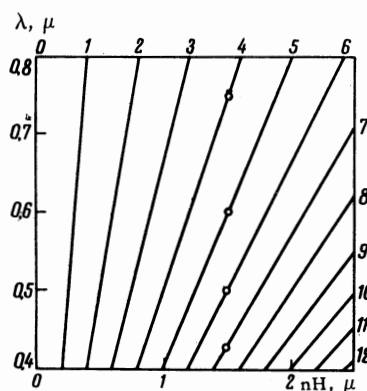
FIG. 2. Nomogram for determining film thickness.

from (1). The procedure for determining film thickness is as follows. The two wavelengths λ_1 and λ_2 previously defined are determined using a monochromator and are then plotted as horizontal straight lines on the nomogram. Among their intersections with the oblique lines we find two neighboring points lying exactly on a vertical line; the latter line determines the optical thickness of the film.

To produce relatively thick films of given thicknesses for investigating high-viscosity liquids we used the flow method described in[15,16].

We have thus far been considering films of uniform thickness, which are sometimes not easily produced. If a slightly wedge-shaped film is produced, one or two bands will be observed at smaller thicknesses and a somewhat larger band at greater thicknesses. Since the shift of the quartz frequency depends on the thickness, the nonuniformity of the film must be taken into account. This is done by determining an equivalent uniform thickness, for which purpose it is desirable to have the interference bands lying parallel to the direction of the quartz vibrations. It can then be shown by a relatively uncomplicated argument that the equivalent thickness relative to coupling rigidity is

$$H_e = \Delta H / \ln\left(1 - \frac{\Delta H}{H_1}\right) \approx H_m \left|\left(1 + \frac{1}{12}\left(\frac{\Delta H}{H_m}\right)^2 + \ldots\right)\right., \quad (2)$$

where H_1 is the film thickness at the thin edge; H_2 is the thickness at the thick edge; $H_m = (H_1 + H_2)/2$; ΔH is the difference between the thicknesses at the two edges. It can be seen that the error is negligible when the nonuniformity of the film is not excessive.

The experimental procedure was as follows. The experimental liquid was purified by known methods. All crystal surfaces and that of the covering prism after brief treatment in a chromate mixture were cleaned in a glow discharge using the technique

described in[17]. Immediately thereafter the crystal was placed in its holder, and the liquid film was applied to the crystal by a clean glass rod; the film was then carefully covered with the quartz prism. The shallow meniscus formed along the perimeter of the prism remained unchanged during the experimental work. Experiments with highly volatile liquids were performed in an atmosphere of the saturated vapor. To determine the film thickness it was first necessary, while observing the wedge interference pattern, to make the film uniformly thick by pressing lightly on the edge of the prism. The measured wavelengths for two dark bands were used to obtain the film thickness, after which the resonant frequency of the vibrating system was determined. The film thickness was varied by squeezing liquid out of the gap.

THEORY OF THE METHOD AND CALCULATIONS

It is easy to derive a general formula for the frequency shift Δf of a quartz piezoelectric crystal of mass M, caused by its interaction with the coverplate of mass m through a liquid film. However, it is possible to perform all calculations with a simpler approximate working formula, using the conditions

$$\Delta f / f_0 \ll 1, \quad (3)$$

$$m / M \ll 1, \quad (4)$$

$$H / \lambda \ll 1, \quad (5)$$

$$f_1 / f_0 \ll 1, \quad (6)$$

where λ is the length of the shear waves propagating in a film of thickness H as a consequence of the crystal vibrations; f_0 is the natural frequency of the crystal; f_1 is the natural frequency of the covering plate that results from its elastic coupling with the crystal surface through the liquid film. The fulfillment of condition (4) is associated with the fact that in our experiments M = 7.04 g and m ≈ 0.4 g.

The fulfillment of condition (5), which was verified a posteriori for all our experiments, resulted from the fact that the shear modulus (and therefore λ also) had a sufficiently high value (above 10^4 dyne/cm^2). The fulfillment of this condition permits neglect of the inertial forces acting on volume elements of the film, and it can also be assumed that the shear stress at all points of the film during the vibrations is a function of time only and is independent of distance from the crystal surface. In other words, we can make a quasistatic analysis of the deformation field in the film

produced by shear stresses despite the time dependence of the latter. As a result, the cover plate can be considered as having linearly elastic coupling with the crystal, and the rigidity k of the coupling for an assumed uniform film can be given by

$$k = SG / H, \qquad (7)$$

where H is the thickness of the film, G is its shear modulus, and S is the area of the bottom of the cover plate.

The fulfillment of condition (3) was also verified a posteriori for all our experiments by means of the relation

$$f_1{}^2 = \frac{k}{4\pi^2 m} = \frac{1}{4\pi^2} \frac{SG}{Hm}, \qquad (8)$$

where k is the rigidity of coupling between the covering plate and the crystal, and m is the mass of the plate.

The fulfillment of condition (6) would signify that when vibrations having the frequency f_0 are induced in the cover plate the amplitude of these vibrations is much smaller than the amplitude A of crystal surface vibrations, so that it is a good approximation to consider that the plate is motionless.

To calculate the frequency shift of the crystal when coupled with the plate we can use Rayleigh's method, which is based on determining the natural frequency by equating the maximum potential and kinetic energies, U and T, of the system. By equating the changes of U and T due to the presence of the cover plate, while assuming that the amplitude remains unchanged, we obtain

$$\Delta T = \pi^2 M A^2 \Delta (f_0)^2 = \Delta U = k A^2 / 2. \qquad (9)$$

It has here been assumed that the effect of the additional mass on T can be neglected in virtue of a motionless plate and thin liquid film. Hence, using (7), we obtain

$$k = 4\pi^2 M f_0 \Delta f, \qquad (10)$$

and therefore

$$G = 4\pi^2 M H f_0 \Delta f / S. \qquad (11)$$

When the conditions (4)—(6) are fulfilled Eq. (11) can also be applied unaltered to the case in which G acquires a complex value as a result of dissipative forces; Δf then is understood to be a complex frequency shift. If measurements of the real part of the frequency shift were combined with measurements of changes in the resonance curve width, thus enabling us to calculate the change in the imaginary part of the frequency shift (i.e., damping), we could determine simultaneously the absolute value |G| of the complex shear modulus and the loss angle.

However, since the shear elasticity of liquids is a relatively new phenomenon it seemed sufficiently interesting as well as expedient to restrict ourselves in the present work to measuring the effective shear modulus (which is equal to its real part), leaving complex measurements for some future time. This decision was all the more justified because there is reason to consider that the loss angle is small (see below), while its measurement would be interesting only over a broad frequency range with the associated experimental difficulties. Measurements at a single frequency cannot furnish a sound basis for any particular phenomenological treatment in which a liquid would be identified with an ideal body or model. Indeed, there are no natural solids or liquids that can be described by simple equations for all frequency intervals. We arrive only at the following qualitative conclusions.

If we identify a liquid with a "Kelvin body" and sum the elastic and viscous stresses (without real justification), the effective shear modulus obtained from (11) for the real part of the frequency shift coincides with the shear modulus of the Kelvin body. If we identify a liquid with a Maxwell body (with the relaxation time τ) and sum the deformations (which is also without justification), then the Maxwell shear modulus G will be related, as we know, to the effective shear modulus G_e by the expression

$$G_e = \frac{G}{1 + (1/\omega\tau)^2} = \frac{G}{1 + (G/\omega\eta)^2}, \qquad (12)$$

from which we see that $G > G_e$. However, there is no justification for considering the value of G obtained in this manner as truer than G_e, since the Maxwell modulus is not usually valid at low frequencies when $\omega\tau < 1$. Therefore, either (12) is unsuitable or there would be no sense in using it as the basis for a small correction. We note that for solids better results are obtained with Boltzmann's elastic lag equations, which are equivalent to a broad spectrum of relaxational frequencies.

We can expect that the investigated films of polar liquids will exhibit nonuniform properties in the transverse direction, i.e., the shear modulus of the film could be a function of the distance from a solid surface. Therefore the shear modulus derived from (11) will actually be a mean shear modulus $\overline{G(H)}$. To determine the true shear modulus as a function of distance from the crystal surface we shall divide our film into several layer elements that are parallel to the quartz surfaces and located at distances z from one of the surfaces. The displacement dx of each layer element will obviously be

$$dx = T\,dz\,/\,G(z)S, \qquad (13)$$

where T is the tangential shear stress. Integrating
(13), we obtain, for the purpose of determining the
coupling rigidity k,

$$\frac{X}{T} \equiv \frac{1}{k} = \frac{1}{S}\int_0^H \frac{dz}{G(z)}, \qquad (14)$$

where X is the displacement for the entire film.
Assuming that since the two surfaces are very
similar the film has symmetric properties, and
G(z) = G(H − z), we obtain, in place of (14),

$$\frac{1}{k} = \frac{2}{S}\int_0^h \frac{dz}{G(z)}, \qquad (15)$$

where h = H/2. Differentiating (15) and making use
of (10), we obtain

$$G(h) = \frac{8\pi^2 M f_0}{S}\left[\frac{d(\Delta f)^{-1}}{dh}\right]^{-1}, \qquad (16)$$

which gives us the shear modulus in the middle of
the film (at the distance h = H/2) from the quartz
surfaces.

The crystal resonant frequency shift Δf and the
film thickness H appear as a product in (11). This
indicates that if the liquid possesses a constant
shear modulus independent of the film thickness,
Δf should exhibit a hyperbolic dependence on H; in
other words, the shift of the resonant frequency
should be proportional to the reciprocal of the film
thickness. Any deviation from this relation will
indicate the presence of special boundary-layer
elasticity in the film. However, it follows from (16)
that in the presence of an anomaly it is more suit-
able to consider the dependence of the reciprocal
frequency shift on the half-thickness h of the film,
since this enables us to judge whether boundary-
layer elasticity exists and whether it is dependent
on distance from the solid surfaces. In analyzing
the experimental results we shall make use of both
dependences.

EXPERIMENTAL RESULTS

The investigated liquids were liquid petrolatum,
castor oil, oleic acid, water, acetone, alcohols,
acetic acid, benzene, and carbon tetrachloride.
When investigating viscous liquids it is necessary
to take into account the effect produced on the
vibrational system by dissipative frictional forces,
which can reduce the crystal resonant frequency,
and also the possibly nonlinear character of shear
elasticity in liquids. Therefore, in order to obtain
the "purest" values of the shear modulus, which
would be least distorted by damping, we plotted the
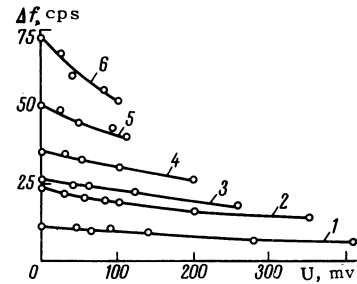dependence of the quartz frequency shift on the

FIG. 3. Δf versus amplitude for different thicknesses of a
film of liquid petrolatum. $1-7\mu$, $2-3.25\mu$, $3-2.8\mu$, $4-2.05\mu$,
$5-1.4\mu$, $6-1.04\mu$.

amplitude of the registered crystal voltage for
different constant film thicknesses; the curves
were extrapolated to zero amplitude. One series
of these dependences for different thicknesses is
shown in Fig. 3 pertaining to liquid petrolatum (the
abscissas are the registered crystal voltages and
the ordinates are the shifts of the crystal resonant
frequency). The curves can be extrapolated to zero
amplitude. The figure shows that the crystal fre-
quency shift is strongly dependent on the amplitude
of the vibrations. As the vibration amplitude de-
creases the positive frequency shift increases, and
the curve becomes steeper for the thinnest films.

Figure 4 shows the dependence of the resonant
frequency shift on the reciprocal of film thickness
for liquid petrolatum and castor oil as plotted from
extrapolated data. Practically perfect linearity is
observed; as already stated, this indicates that the
liquids possess a constant shear modulus (indepen-
dent of the film thickness).

Figure 5 shows the experimental results for
oleic acid for different amplitudes of the potential
applied to the crystal; the same coordinates are
used as in Fig. 4. Curve 1 corresponds to the
maximum amplitude of applied voltage; the other
curves correspond to fractions of this maximum:
Curve 2—one-half, curve 3—one-fourth, and
curve 4—one eighth. Curve 5 was plotted from the
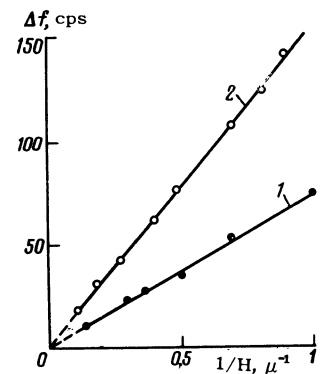extrapolation to zero amplitude, but the nearest

FIG. 4. Δf versus 1/H
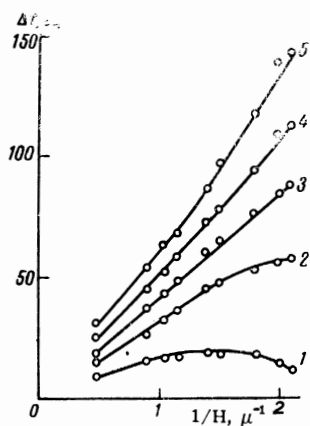for liquid petrolatum (curve
1) and castor oil (curve 2).

FIG. 5. Δf versus 1/H for oleic acid.

FIG. 6. Δf versus 1/H for liquid petrolatum at constant.

approach to linearity is found in curve 3.[1] This obviously indicates that the thinnest films of oleic acid possess the greatest boundary-layer elasticity. The curve corresponding to the maximum applied voltage amplitude is seen to have a clear maximum; therefore as the film thickness is reduced still further this curve should intersect the horizontal axis and enter the region of negative quartz resonant-frequency shifts. This obviously indicates that as the shearing deformations increase along with reduced film thickness the dissipative viscous forces increase more rapidly than the elastic forces, which are proportional to the shear deformation. Therefore the liquids are visco-elastico-plastic bodies with a low elastic limit. This conclusion is in agreement with the concepts and experiments of Nerpin and Bondarenko,[18] who measured the limiting shear stresses of polar liquids.

Figure 5 also shows that all curves converge toward the coordinate origin,[2] thus providing confirmation that the experimental film thicknesses were greatly exceeded by the wavelengths of shear vibrations in the liquid. If the film thickness were comparable with or much greater than the wavelength of shear vibrations the relation between the frequency shift, on the one hand, and the film thickness and shear modulus, on the other hand, would be much more complex and the foregoing theory would not have been applicable. In such instances one might use Smoluchowski's theory of vibrations in a two-layer system,[20] and (11) would represent the limiting case of this theory.

The data represented in Fig. 3 can be used to plot the dependence of the crystal frequency shift

on the reciprocal of film thickness at a constant shear angle. Figure 6 shows this dependence for three shear angles. Curve 1 pertains to the shear angle when the ratio of the registered crystal voltage to the film thickness was 100 mV/micron. For curve 2 the ratio was 50, while curve 3 pertains to an infinitely small shear angle (corresponding to extrapolation). We observe that all of the lines are straight and pass through the origin. This obviously signifies that the hysteresis loss angle resulting from dissipative forces depends on the size of the shear angle but not on film thickness and is identical throughout the latter. We can therefore assert that a film of liquid petrolatum is uniform with respect to both elastic and dissipative forces.

Figure 7 shows the dependence of the resonant frequency shift (extrapolated to infinitely small amplitudes) on the reciprocal of film thickness for water, acetone, and benzene. The polar liquids water and acetone exhibit a sharp deviation from proportionality for the thinnest films, whereas proportionality is maintained for benzene. This result indicates that all three liquids possess constant volume shear elasticity, while water and acetone also exhibit a considerable increase of mean shear elasticity in thinner films.

We have already stated that when special boundary-layer elasticity exists it is more advisable to consider the relation between the reciprocal of the resonant frequency shift and the half-thick-

FIG. 7. Δf versus 1/H for (1) water, (2) acetone, and (3) benzene.

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[1]Just the opposite result is obtained for liquid petrolatum.

[2]In[19], which was written by the present authors, the curves failed to converge towards the origin because of errors committed when determining film thicknesses.
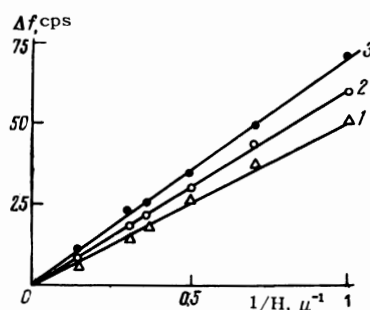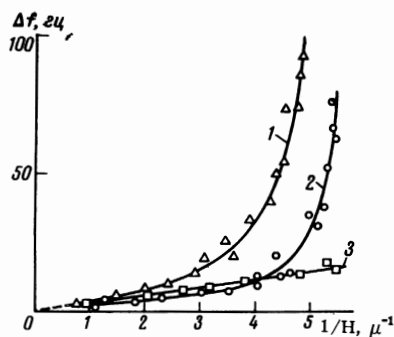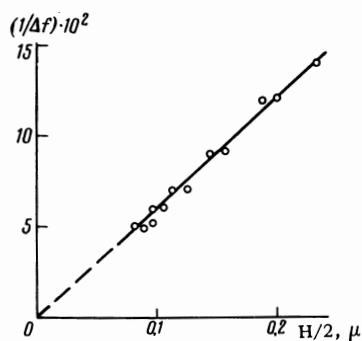
FIG. 8. $1/\Delta f$ versus $H/2$ for carbon tetrachloride.

FIG. 10. $1/\Delta f$ versus $H/2$ for butyl alcohol (1), hexyl alcohol (2) and acetic acid (3).

ness of the film. Figure 8 shows this relation for carbon tetrachloride; it is found to be linear and convergent towards the origin. Consequently we find that nonpolar carbon tetrachloride, like benzene, possesses constant volume shear elasticity that is independent of film thickness.

Figure 9 shows the same relations for the polar liquids acetone and for ethyl and octyl alcohol, while Fig. 10 shows the relation for butyl and hexyl alcohol and for acetic acid. The graphs are rectilinear in the investigated region of film thicknesses, thus indicating that for $h > 10^{-5}$ cm the shear elasticity is constant and equal to the bulk value, which can be determined from the slopes of the curves. However, since the graphs would pass through the origin as h approaches zero, but any intersection of the horizontal axis is impossible as representing a nonphysical passage of Δf through $\pm \infty$, for small $h = H/2$ the curve should exhibit a break or bending, as shown schematically by the dashed line in Fig. 9.

The minimum possible shear modulus in the region of boundary layer thicknesses is obviously derived by connecting the lower ends of the straight lines to the origin. The reciprocal slopes of these segments then yield the smallest possible boundary-layer elasticity, which exceeds the volume shear elasticity by more than one order of magnitude. Our experimental work is thus in fundamental
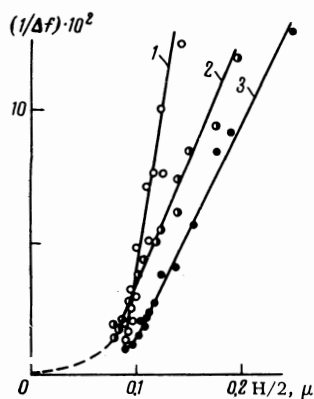

FIG. 9. $1/\Delta f$ versus $H/2$ for acetone (1), ethyl alcohol (2) and octyl alcohol (3).
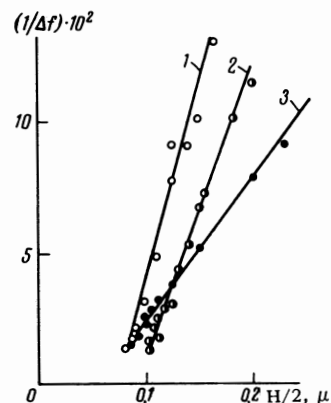
agreement with the existence of special boundary-layer phases.[2-5] An analysis of the graphs also yields the approximate thickness of the boundary layers. The upper limit is obviously the abscissa of the lowest experimental points on the curves, while the lower limit can be determined by extending our curves until they intersect with the horizontal axis. It is easily seen that these two limits lie close together in our experiments, the difference between them being under 0.01μ for acetone and a little above 0.01μ for ethyl alcohol. Therefore the average of the two limits can quite definitely be regarded as the thickness of the anomalous boundary layer. For example, in the cases of acetic acid and ethyl alcohol the lower limit of thickness is at least 0.06μ; the result for acetone and octyl alcohol is 0.08μ, and for water about 0.09μ.

The accompanying table gives the effective volume shear moduli calculated from experimental data using (11) and (16), and also the thicknesses of the boundary layers.

In contrast with the well-known method of Mason,[10] which is mainly suitable for investigating the shear elasticity of high-viscosity liquids, our present method is distinguished by its extreme simplicity and reliability as well as by the absence of any viscosity limit. Our method has also yielded positive results for low-viscosity liquids principally because of its high sensitivity and, possibly, because the spatial damping of vibrations is not significant in a thin liquid film. The method is equally successful in determining the shear modulus of such viscous liquids as castor oil and such low-viscosity liquids as acetone and benzene. Another advantage lies in the fact that the elastic properties of thin boundary layers can be investigated.

To sum up, our experimental work has proved that volume shear elasticity exists in all liquids and can be measured by the given method. Shear elasticity is thus one of the universal properties

Shear elasticity of liquids*

Liquid	Degree of purity	t, °C	$G_e \times 10^{-4}$ dyne, cm^2	Boundary-layer thickness, μ
Acetone	Distilled	25	0.42	0,08
Water	Triply distilled	23	1,1	0,09
Benzene	Dehydrated	14	1,3	0
Carbon tetrachloride	Distilled	16	2,3	0
Acetic acid	Distilled	17	1,9	0,06
Ethyl alcohol	Dehydrated	16	1,0	0,06
Butyl alcohol	Dehydrated	18	0,7	0,07
Hexyl alcohol	Dehydrated	26	0,9	0,08
Octyl alcohol	Dehydrated	25	1,2	0,08
Oleic acid	Dehydrated	16	0,30	—
Liquid petrolatum	Filtered	14	0,37	—
Castor oil	Filtered	17	0,80	—

*The bulk values of G_e are given.

of liquids. The thin boundary layers of polar liquids possess special mechanical properties that appear to result from a higher degree of molecular ordering than in the interior of the liquids.

It is appropriate here to recall Frenkel's ideas[21] that liquids, which resemble the crystalline state with respect to their structure and the character of their thermal motion, should also possess shear elasticity that would usually be masked by their fluidity. It can be presumed that our present results confirm these ideas qualitatively and demonstrate the existence of measurable shear elasticity in liquids at the frequencies that we have used. However, Frenkel believed that shear elasticity could be manifested only at considerably higher frequencies (of the order 10^{10} cps), so that in this respect our results were unexpected.

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114