PHYSICAL REVIEW A VOLUME 42, NUMBER 4 15 AUGUST 1990

Shear elasticity of low-viscosity liquids at low frequencies

B. V. Derjaguin, U. B. Bazaron, Kh. D. Lamazhapova, and B. D. Tsidypov
Institute of Physical Chemistry, Leninskii Pr. 31, 117915 Moscow, U.S.S.R.

(Received 11 January 1990)

The resonance method was applied to measure shear mechanical properties of liquids, and it has thus been established that such low-viscosity liquids as water, cyclohexane, hexadecane, and dibutyl phthalate possess a shear elasticity of about 10^6 dyn/cm^2 at a frequency of shear oscillations of about 73.5 kHz. Now, according to the existing concepts on the nature of liquids, their shear elasticity should be observed only at a frequency of about $10^{11}-10^{12}$ Hz. The present work maintains a comparison with the known works on measurements of the shear mechanical impedance of liquids. It has been shown that the results obtained here agree satisfactorily with measurements of the shear mechanical impedance of low-viscosity liquids at a frequency of 40 MHz.

At present, it is considered to have been firmly established that thin boundary layers of liquid acquire special properties under the effect of the surface forces of a solid, properties that differ from those of bulk liquid. In particular, the boundary layers of polar liquids possess an enhanced viscosity; also observed are a phenomenon of polymolecular adsorption of liquids on the surface of a solid and changes in their thermodynamic properties.[1]

In connection with the anomalous properties of the boundary layers of liquids, it has been shown that these may also possess special mechanical properties; in particular, a shear elasticity.[2] It is known that up to now no theory of boundary friction has been developed, which might be of major importance for enhancing the reliability and wear resistance of machines. To develop such a theory requires knowing the mechanical properties of boundary layers.

Our research work on the measurement of the shear elasticity of liquids had started with just the investigation of the shear mechanical properties of the boundary layers of liquids.[2] We actually detected a shear elasticity in thin layers of liquids at a frequency of shear oscillations of about 10 Hz. However, a detailed investigation of this property, depending on the thickness of a tested film, has shown that the shear elasticity is inherent to the bulk liquid. Moreover, it has been established that this property is possessed by all the liquids without exception, independently of their viscosity and polarity.[3-7] In accordance with the present notions, this property should have been observed at frequencies of $10^{11}-10^{12}$ Hz; that is, at 6–7 orders of magnitude higher frequencies than in the present experiments. This conclusion follows from the fact that the time of settled life of separate liquid molecules in a temporary equilibrium state is a relaxation time of the nonequilibrium state. The relaxation time is evaluated in accordance with the self-diffusion rate. Hence this time, when calculated with the Einstein formula, will be equal to

$$\tau = \frac{\delta^2}{6D} , \tag{1}$$

where δ is the average distance between liquid molecules; D is the self-diffusion coefficient. In the case of low-viscosity liquids, the calculations performed with that formula give for τ the values of the order of 10^{-11} sec. A similar result will be obtained, if the relaxation time of the nonequilibrium state is evaluated in accordance with the Maxwell rheological model, where the relaxation time is determined by a relationship

$$\tau = \frac{\eta}{G_\infty} . \tag{2}$$

Here η is the known tabular viscosity; G_∞ is the shear modulus at an infinitely high frequency or with instantaneous deformations. Generally, it is considered that the value of G_∞ is of the same order of magnitude as the value of the shear elasticity of a corresponding solid. In particular, it may be assumed for water that $G_\infty = 10^{10}$ dyn/cm^2, $\eta = 0.01$ P; then with formula (2) $\tau = 10^{-12}$ sec. Therefore it was considered that the shear elasticity of usually low-viscosity liquids must show up at the shear oscillation frequencies of about $10^{11}-10^{12}$ Hz; that is, at frequencies equal to or higher than the jump-over frequencies of separate liquid molecules.

The resonance method for measuring the shear elasticity of liquids, as developed by us, resides in the following. A piezoquartz crystal having the shape of a rectangular rod performs oscillations of compression and tension at a basic resonance frequency in the direction of its axis. A lateral horizontal surface performing oscillations in its proper plane is in contact with a liquid film covered by a quartz prism (Fig. 1). When the liquid tested possesses a shear elasticity, the resonance frequency of the oscillation system must increase, doing it inversely proportional to the thickness of a liquid interlayer, in accordance with the theory of the method adopted. Such a dependence was observed for all the liquids tested. In the absence of shear elasticity, the resonance frequency could have only decreased in accordance with the known Releigh theorem derived from the theory of oscillations.

The theory of the method gives the following expres-

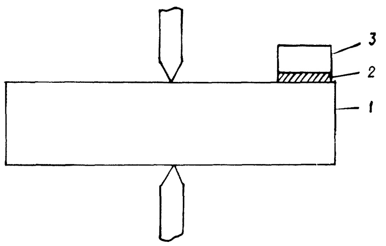

FIG. 1. Piezoquartz (1) with a liquid film (2) and a cover plate (3).

sion for a complex shift of the piezoquartz resonance frequency:[4]

$$\Delta f=\Delta f'+i\Delta f''=\frac{S\kappa G}{4\pi^2 M f_0}\,\frac{1+\cos(2\kappa H-\varphi)}{\sin(2\kappa H-\varphi)}\ , \tag{3}$$

where $G=G'+iG''$ is the liquid shear complex modulus, $\kappa=\beta i\alpha$ is its complex wave number, S is the cover-plate basis area (of the quartz prism), H is the thickness of the liquid interlayer, φ is the complex shift of phase when a shear wave is reflected from the "liquid-cover plate" interface, M is the piezoquartz mass, and f_0 is its resonance frequency.

Expression (3) is simplified to the utmost degree for the case when the thickness of a liquid interlayer $H \ll \lambda$, where λ is the length of a shear wave, and the cover plate is considered to be practically at rest. In this case $\varphi=0$, and expression (3) gives the following formula to calculate the shear elasticity:

$$G=\frac{4\pi^2 M f_0 \Delta f H}{S}\ . \tag{4}$$

From this formula, it becomes obvious that when liquids possess a shear elasticity, both the real and the imaginary frequency shifts must be inversely proportional to the thickness of a liquid interlayer. The mechanical-loss angle tangent is determined as follows:

$$\tan\theta=\frac{G''}{G'}=\frac{\Delta f''}{\Delta f'}\ . \tag{5}$$

where the imaginary shift of the resonance frequency $\Delta f''$ is equal to a half of the change in the width of the resonance curve of piezoquartz.

In our experiments, the mass of piezoquartz $M=6.7$ g, the cover-plate mass is equal to 0.2 g, and the cover-plate basis area $S=0.2$ cm^2. It is quite possible to ascertain that the cover plate may be considered to be practically at rest with the given dimensions of the cover plate and the measurable values of shear elasticity.

In Fig. 2 the experimental results obtained for four liquids are represented: dibutylphthalate, hexadecane, cyclohexane, and water. The abscissa plots the inverse values of the thickness of liquid interlayers, and the ordinate plots the positive shifts of the resonance frequency of piezoquartz, $\Delta f'$. The dependences are linear for all the four liquids. Hence, in accordance with formula (4), it follows that all the liquids possess a bulk shear elasticity. Similar linear dependences are obtained also for an imaginary shift of resonance frequency, $\Delta f''$, of piezoquartz. In Table I are presented the values of shear elasticity and the mechanical-loss angle tangent for the liquids tested, as calculated with formulas (4) and (5). It would be interesting to note that the nonpolar cyclohexane and hexadecane possess rather small values of the mechanical-loss angle tangent.

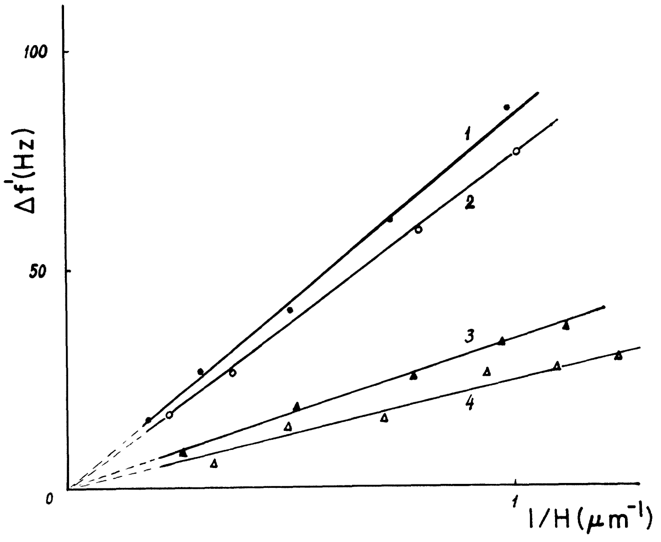

FIG. 2. Dependence of the real shift of the resonance frequency of piezoquartz for dibutylphthalate (1), hexadecane (2), water (3), and cyclohexane (4), on inverse thickness of a liquid interlayer.

Numerous investigations of the shear mechanical properties of liquids by other methods indicate that the liquids are Newtonian up to supersonic frequencies. This means that the shear elasticity must be absent also at the frequency of our experiment of 73.5 kHz. Below we shall prove that this contradiction is an apparent one. The shear mechanical properties are usually measured by two methods. The first method is based on a determination of mechanical impedance, when a rotating piezoquartz vibrator is immersed in the liquid under investigation.[7] In this method, the setup is calibrated by a standard liquid, which is considered to be explicitly Newtonian. Afterwards, on determining the constant of the setup, other liquids are investigated. In accordance to our data,[3-7] all the liquids possess a shear elasticity at the frequencies of shear oscillations of about 10^5 Hz; that is, in nature there is no explicitly Newtonian standard liquid. Therefore, it would be incorrect to measure the shear mechanical properties of liquids by the method of rotary or twisting oscillations.

TABLE I. Values of the shear elasticity and the tangent of the mechanical loss angle.

Liquids	T (°C)	G' (10^{-6} dyn cm^{-2})	$\tan\theta$
Water	23	0.31	0.3
Cyclohexane	22	0.22	0.09
Hexadecane	24	0.75	0.08
Dibutylphthalate	21	0.82	0.21

The second method to be used, at higher frequencies and having come to a wider application, is based on measuring the mechanical impedance of liquid when a shear wave is reflected from the "solid-liquid" interface. In the present method, the following formulas are valid:

$$G'=\frac{R_s^2-X_s^2}{\rho}\,,\quad G''=\frac{2R_sX_s}{\rho}\,, \tag{6}$$

where R_s is the active component and X_s is the reactive component of the characteristic resistance (impedance) of liquid. From this formula, it follows that, if a liquid possesses a shear elasticity, then $X_s<R_s$. Now, if the liquid is Newtonian; that is, if $G'=0$, then $X_s=R_s$. The effective viscosity which is experimentally determined, is calculated with the following formula:

$$\eta=\frac{2R_sX_s}{\omega\rho}\,, \tag{7}$$

where ω is the cyclic frequency of an experiment. The work by McSkimin and Andreatch[8] is of special interest for us: These authors had investigated the dynamic shear properties of low-viscosity liquids at a frequency of 40 mHz, including the liquids that were investigated by us in the present work. In Table II the results obtained by the authors for those liquids at an experimental temperature of 25 °C are presented. In the first column of the table are given the values of the density of the liquids tested; in the second column, the values of the active part; and in the third column, the values of the reactive part of the shear impedance of liquids. In the fourth column are presented the effective viscosity values calculated with formula (7), and in the last column the known values of tabular viscosity. It is readily visible that the calculated viscosity values η_e are close to the tabular values of η_t. Therefore, the authors have come to a conclusion that at the experimental frequency of 40 mHz these liquids are Newtonian; that is, they do not possess a shear elasticity.

Let us analyze the data presented in Table II. First of all, for water and cyclohexane $X_s>R_s$; though, in accordance with the theory of the method, if these liquids are Newtonian, then there should be $X_s=R_s$. Therefore, it is possible to suppose that in the determination of the reactive component X_s there exists a systematic error, which tends to make it greater (i.e., overrate the component). This error could have arisen owing to the existence of a normal component in the shear deformation at the solid-liquid interface.

In the case of more viscous hexadecane and dibutylphthalate, it is found that $R_s>X_s$. This means that these liquids actually possess a shear elasticity. For hexadecane, the shear elasticity calculated with formula (6) proves to be equal to 0.35×10^6 dyn cm^{-2}. In accordance with our data (see Table I), the shear elasticity of hexadecane is equal to 0.75×10^6 dyn cm^{-2}. These values are close to each other. Now, if the error of the determination of X_s is taken into account, then it will be possible to obtain a quantitative agreement with our results. If in the experiment of the aforesaid authors there did show up a shear elasticity equal to our result, then the reactive component X_s for hexadecane should have the value equal to about 1537 Ω cm^{-2}. In this case, the viscosity calculated with formula (7) proves to be equal to 2.73 cP, i.e., it is very close to the known tabular viscosity. From the aforesaid, it follows that the closeness of the experimental viscosity values to the tabular ones is not always a criterion of the absence of shear elasticity.

TABLE II. Viscosity values and other properties of the liquids under study.

Liquids	ρ (g cm^{-3})	R_s (Ω cm^{-2})	X_s (Ω cm^{-2})	η_e (cps)	η_t (cps)
Water	0.997	1011	1119	0.90	0.89
Cyclohexane	0.774	912	953	0.90	0.88
Hexadecane	0.770	1714	1630	2.89	3.10
Dibutylphthalate	1.041	4758	4604	16.66	16.37

Thus it may be concluded that between our results and the data set forth in Ref. 8 there is no essential contradiction. Moreover, if a systematic error committed in determination of the reactive component of the mechanical impedance could be taken into account, then the authors of Ref. 8 could be assumed to have corroborated our results.

The presence of shear elasticity at low frequencies proves that an earlier unknown, low-frequency, viscoelastic relaxation process takes place in liquids; the process may be attributed, probably, to collective interactions of molecules, because the relaxation time of nonequilibrium states of large groups of molecules may by many orders of magnitude exceed the time of settled existence of molecules of liquid.

There is no doubt that the existence of a low-frequency shear elasticity in liquids is of a great importance for the physics of the liquid state of matter and for cognate sciences, especially for the physical chemistry of surface phenomena, boundary layers, and disperse systems.

A unique series of works setting forth and experimentally substantiating the existence of shear elasticity of liquids is that written by Joseph and co-workers.[9] The basic method described in these works consists of measuring the time of propagation of a tangential shear wave pulse from one surface (the external cylinder) to another (the inner cylinder) through a liquid interlayer d, 0.25–3.0 mm thick. Knowing the propagation velocity of this pulse (in the case of its constancy when the interlayer thickness d is changing), the shear modulus could be calculated for a number of liquids, including pure glycerine and polydimethyl siloxanes of different molecular weights.

However, a quantitative comparison with the experimental results obtained by us in 20 years of investigations is difficult to make. This is due first of all to the fact that our measurements were effected at one frequency (about 70 kHz). That is why these measurements give an unambiguous value of the complex shear modulus of liquid, independently of any models of liquid dynamics (for instance, those of Maxwell or Boltzmann). Now, interpretation of the pulse propagation must be based on some empirical model of liquid dynamics, which would express the dependence of shear stress on frequency. Moreover, the comparison is limited to the fact that our research and that of Joseph and co-workers used but few cognate liquids. Nonetheless, some comparisons are feasible. Thus the value of shear modulus obtained for glycerine in Ref. 9 is smaller by one order of magnitude than ours. However, this might be attributed to the fact that the effective frequency of shear wave is different from our values (about 70 kHz).

I herewith express my gratitude to Professor D. D. Joseph for having sent me reprints of his papers.

---

[1] B. V. Derjaguin, *The Surface Forces and the Boundary Layers of Liquids* (Nauka, Moscow, 1983), pp. 3–12.

[2] B. V. Derjaguin, Z. Phys. **84**, 657 (1933); U. B. Bazaron, B. V. Derjaguin, and A. V. Bulgadaev, Zh. Eksp. Teor. Fiz. **51**, 969 (1966).

[3] U. B. Bazaron, B. V. Derjaguin, and O. R. Budaev, Dokl. Akad. Nauk SSSR **205**, 1326 (1972).

[4] K. T. Zandanova, B. V. Derjaguin, O. R. Budaev, and U. B. Bazaron, Dokl. Akad. Nauk SSSR **215**, 309 (1974).

[5] B. B. Badmaev, U. B. Bazaron, B. V. Derjaguin, and O. R. Budaev, Physica **122B**, 241 (1983).

[6] B. V. Derjaguin, U. B. Bazaron, K. T. Zandanova, and O. R. Budaev, Polymers **30**, 97 (1989).

[7] S. B. Grigor'ev, I. G. Mikhailov, and O. Sh. Khakimov, Akust. Z. **20** (1974).

[8] H. T. McSkimin and P. Andreatch, J. Acoust. Soc. Am. **42**, 248 (1967).

[9] D. D. Joseph, A. Narain, and O. Riccius, J. Fluid Mech. **171**, 289 (1986); D. D. Joseph, O. Riccius, and M. Arney, *ibid.* **171**, 309 (1986); O. Riccius, D. D. Joseph, and M. Arney, Rheol. Acta **26**, 96 (1987).