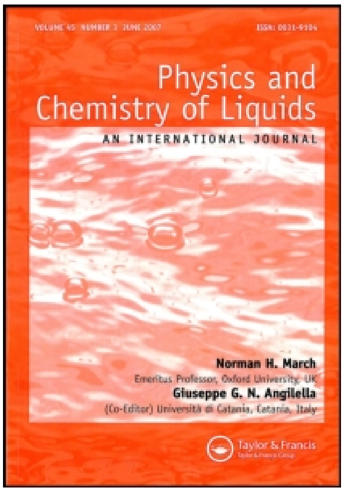


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# MEASUREMENT OF THE LOW-FREQUENCY SHEAR MODULUS OF POLYMERIC LIQUIDS

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The present work describes the resonance method for measurement of a low-frequency (about $10^5$ Hz) complex shear modulus of liquids by the use of a piezoquartz crystal. The problem of interaction of an oscillating system of the type piezoquartz–liquid interlayer–cover plate is analyzed. From the analysis of the problem there follow three methods for measuring the elasticity modulus of liquids. The investigation results of a homologous series of polymethyl siloxane liquids are presented. It has been shown that as the molecular weight of the series being investigated increases, the elasticity modulus value also increases, while the mechanical losses angle tangent passes through its maximum.

KEY WORDS: Relaxation, complex shear modulus.

## 1. INTRODUCTION

In the modern theories of liquids the relaxation period $\tau$, determining the time of conservation of nonequilibrium states, is estimated on the basis of self-diffusion rate, that period being equated to the time of stable existence of separate molecules. Such calculations give for the relaxation period of low-viscosity liquids the values of the order of $10^{-10}$ to $10^{-11}$ sec. This means that according to the existing notions on the nature of liquids their shear elasticity could have been detected only at the frequencies of shear oscillations higher than $10^{10}$ Hz. However, in works [1 – 3], [10, 11] it has been shown that all the liquids, independently of their viscosity, possess a shear elasticity at a frequency of shear oscillations of the order of $10^5$ Hz. The fact that liquids possess shear elasticity at such low frequencies proves that a previously unknown, low-frequency, visco-elastic relaxation process occurs in the liquids, the process probably being determined by collective interactions of large groups of molecules. The measured values of the elasticity moduli for low-viscosity liquids proved to be the order of $10^5$ to $10^6$ dyn/cm$^2$. The mechanical losses angle tangents are much smaller than

* Deceased.

unity. This suggests that the relaxation frequency of the given process is lower than the experimental frequency whose value was about 74 kHz.

A thorough investigation of the phenomenon detected is of a fundamental significance for a correct understanding of the nature of the liquid state.

The resonance method for measuring the shear elasticity of liquids, as used in works [1 – 3], is based on the use of a piezoquartz resonator. A major advantage of the given method for a measuring the viscoelastic properties of liquids resides in the absence of limitations for the liquids being investigated, which enables one to investigate a homologous series of polymethyl siloxane liquids, whose viscosity changes by four orders of magnitude.

## 2. THEORY OF THE EXPERIMENT

The resonance method for measuring shear elasticity consists of the following. A piezoquartz crystal (1) oscillates at a resonance frequency; its horizontal surface performing tangential shifts contacts a liquid interlayer (2) covered by a solid cover-plate (3). The cover-plate with a liquid film is put on one end of the piezoquartz (Fig. 1). When the piezoquartz oscillates, the liquid interlayer undergoes a shear deformation, and standing shear waves are likely to be established therein.

The parameters of the resonance piezoquartz curve change depending on the thickness of a liquid interlayer.

An expression for the complex shift of the piezoquartz resonance frequency due to its interaction with a liquid interlayer covered by a cover-plate is found by equating the impendances of liquid and piezoquartz [4], and has the following form:

$$\Delta f^* = \frac{S\varkappa G^*}{4\pi^2 M f_0} \cdot \frac{1 + \cos(2\varkappa^* H - \mathscr{S}^*)}{\sin(2\varkappa^* H - \mathscr{S}^*)}, \tag{1}$$

where $G^* = G^1 + iG''$ is the complex shear modulus of liquid, $\varkappa^* = \beta - i\alpha$ is its complex wave number, $H$ is the thickness of the liquid interlayer, and $\mathscr{S}^*$ is the complex phase shift when the wave is reflected from the liquid—cover-plate interface.

Taking into account that

$$G^* = \frac{\omega^2 \rho_e}{(\varkappa^*)^2} \tag{2}$$

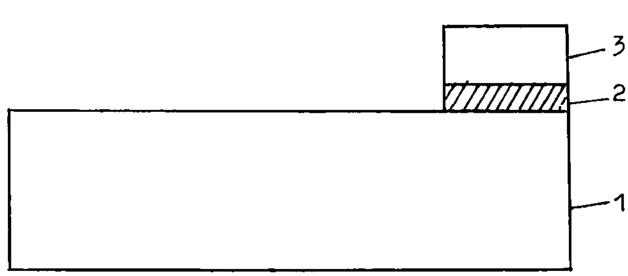


**Figure 1** Piezoquartz with an additional link. 1 is piezoquartz; 2 is liquid interlayer; 3 is a coverplate.

it is possible to separate expression (1) into a real and an imaginary part:

$$\Delta f' = \frac{S}{4\pi^2 M f_0} \cdot \frac{(G'\beta + G''\alpha)\sin 2\beta H + (G'\alpha - G''\beta) Sh 2\alpha H}{ch 2\alpha H - \cos 2\beta H}, \tag{3}$$

$$\Delta f'' = \frac{S}{4\pi^2 M f_0} \cdot \frac{(G''\beta - G'\alpha)\sin 2\beta H + (G''\alpha + G'\beta) Sh 2\alpha H}{ch 2\alpha H - \cos 2\beta H}, \tag{4}$$

The following expressions are derived for the components of the complex shift of phases:

$$\mathscr{S}' = \text{arctg} \frac{2\beta}{\frac{m(\varkappa^*)^2}{S\rho_e} - \frac{S\rho_e}{m}}, \tag{5}$$

$$\mathscr{S}'' = \text{arch} \frac{2\alpha}{\frac{m(\varkappa^*)^2}{S\rho_e} + \frac{S\rho_e}{m}}, \tag{6}$$

where $\rho_e$ is the density of liquid, $m$ is the mass of the cover-plate. The real part of the complex shift of phase (5) indicates a difference in phases between a direct and a reflected wave at the cover-plate surface, while the imaginary part (6) is characteristic of an additional decay caused by the inertial properties of the cover-plate. If we admit that the cover-plate mass is sufficiently large and it may be considered practically immovable, then the expressions (5) and (6) are greatly simplified, and $\varphi'' = 0$, which means total reflection of the wave. Now, in the case of the absence of a cover-plate, this is, when $m \to 0$, then the expressions (5) and (6) take the values of $\varphi' = 180^\circ$, $\varphi'' = 0$, respectively. This means when the shear wave is reflected from the free surface of liquid, the loss of a half-wave occurs.

From expressions (3) and (4), it is possible to obtain the maximum decay values in the following form:

$$H = \frac{\lambda}{4} \cdot n, \tag{7}$$

where the even values of $n$ relate to a system with the cover-plate, whereas the odd values to a system with the free surface. From Eq. (7), it is apparent that the first decay maximum in the system with the cover-plate is observed with the thickness of a liquid interlayer equal to $\lambda/2$, whereas that with the free surface at $\lambda/4$.

From formulas (3) and (4) there were computed dependences of $\Delta f'$ (curve 1) and $\Delta f''$ (curve 2) versus the thickness of the liquid interlayer for the case where $G' = 3.10^5$ dyn/cm$^2$ and tg$\theta = 0.3$ (Fig. 2).

It is possible to see that the dependences of the resonance frequency versus the thickness of the liquid interlayer give decaying oscillations, and when $H \to \infty$ the shear wave decays completely, and the frequency shifts tend to limit values.

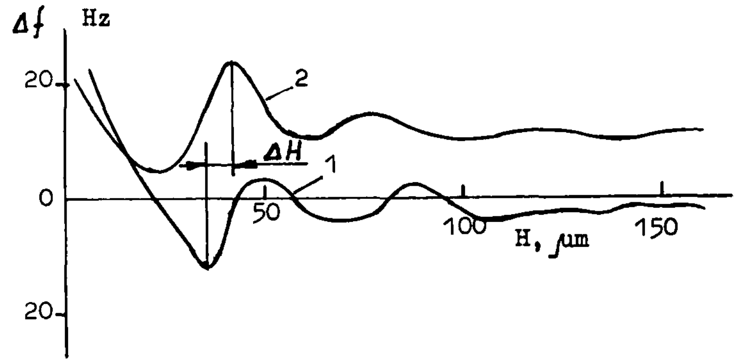


**Figure 2** Dependences of the real (1) and the imaginary (2) frequency shift on the thickness of the liquid interlayer.



Thus, from an analysis of expressions (3) and (4) follow three methods for measuring the shear modulus of liquids. The first method is realized with small thicknesses of the liquid interlayer, when $H \ll \lambda$. In this case, both the real and the imaginary shift of the resonance frequency are proportional to the inverse value of the thickness of the liquid interlayer. For the real shear modulus $G'$ and the mechanical losses angle tangent, tg$\theta$, the following formulas are obtained from expressions (3) and (4):

$$G' = \frac{4\pi^2 M f_0 \Delta f' H}{S}, \tag{8}$$

$$\mathrm{tg}\theta = \frac{\Delta f''}{\Delta f'}. \tag{9}$$

The second method for determining the value of $G'$ is based on measuring the length of the shear wave $\lambda$ according to decay maximum [5]. From the relationship (2), while using $\beta = 2\pi/\lambda$, it is possible to show that

$$G' = \lambda^2 f_0^2 \rho_e \cdot \cos\theta \cdot \cos^2\frac{\theta}{2} \tag{10}$$

The mechanical losses tangent angle is determined by the ratio of the distance between the positions of the first minimum of the real frequency shift and the first decay maximum $\Delta H$ to the wave length $\lambda$.

From Eq. (3), it is possible to show that the abscissa of the extremum points of the real frequency shift is determined by the expression:

$$\cos 2\beta H ch 2\alpha H - 1 = 0. \tag{11}$$

The minimum of $\Delta f''$ is situated to the left from the decay maximum (see Fig. 2). Therefore, the condition of that minimum may be represented as follows:

$$1-\cos\left[2\pi\left(1-\frac{2\Delta H}{\lambda}\right)\right]ch\left[2\pi\left(1-\frac{2\Delta H}{\pi}\right)tg\frac{\theta}{2}\right]=0, \quad (12)$$

where $\Delta H$ is the distance between the positions of minimum $\Delta f'$ and maximum $\Delta f''$. Hence, it follows that a certain value of $\theta$ corresponds to each value of $\Delta H/\lambda$. Thus, for determining the value of $G'$ it is sufficient to measure the value of $\theta$ according to the position of decay maxima and that of $\Delta H/\lambda$ for determination of the mechanical losses angle.

The third method is based on measuring the limit values of $\Delta f'_\infty$ and $\Delta f''_\infty$, to which they tend as the thickness of the liquid interlayer increases further, when the shear wave completely decays [6]. Expressions (2) and (3) as $H\to\infty$ take the following values:

$$\Delta f'_\infty = -\frac{SG'\beta}{2M\pi^2 f\cdot\cos\theta}\cdot\mathrm{tg}\frac{\theta}{2},\quad \Delta f''_\infty = \frac{S\bar{\bar{G}})/\beta}{2M\pi^2 f\cdot\cos\theta}. \quad (13)$$



Let us note that the liquid interlayer is located on the end of piezoquartz. As at $H\to\infty$ the shear wave completely decays, the need of a solid cover-plate becomes redundant, and the whole horizontal surface of piezoquartz can be coated by a thick layer of the liquid investigated. In this case, the following formulas for $G'$ and $\mathrm{tg}\theta$ can be derived from expressions (13):

$$G' = \frac{16\pi^2 M^2}{S^2\rho_e}\cdot[(\Delta f''_\infty)^2-(\Delta f')^2], \quad (14)$$

$$\mathrm{tg}\theta = -\frac{2\Delta f'_\infty\cdot\Delta f''_\infty}{(\Delta f''_\infty)^2-(\Delta f'_\infty)^2} \quad (15)$$

Here $S$ is the area of the whole horizontal surface of piezoquartz. From expression (14), it becomes apparent that $\Delta f''_\infty > \Delta f'_\infty$ when the liquid possesses bulk shear elasticity. Now, if the liquid is Newtonian at the experimental frequencies, then $\Delta f''_\infty = \Delta f'_\infty$. In the present measurement method an accurate determination of the real frequency shift is rather difficult because of the presence of a normal component of the working surface of piezoquartz, when the added mass of the film of the liquid being investigated makes its contribution to that shift. However, at $\mathrm{tg}\theta < 1$ when calculating the value of $G'$ with formula (14), the value of the real frequency shift might be neglected, because its contribution does not exceed 3%.

The present method for determination of the shear elasticity of liquid is analogous to the known impedance method [7]. The theory of impedance method gives the following formulas for determination of the real $G'$ and the imaginary $G''$ shear modulus of liquid:

$$G' = \frac{R_s^2 - X_s^2}{\rho}, \quad G'' = \frac{2R_s \cdot X_s}{\rho}, \tag{16}$$

where $R_s$ is the active component, $X_s$ is the reactive component of the characteristic impedance of liquid, and $\rho$ is its density. From expressions (16), it follows that $R_s > X_s$ if the liquid possesses the shear elasticity. Now, if the liquid is Newtonian, then $R_s = X_s$.

It is possible to see that there is complete analogy between expressions (14), (15), if we assume that

$$R = \frac{4\pi M}{S} \cdot \Delta f''_\infty \quad \text{and} \quad X = \frac{4\pi M}{S} \cdot \Delta f'_\infty$$

## 3. EXPERIMENTAL RESULTS AND THEIR DISCUSSION

In the present work there are presented experimental results of the investigation of a homologous series of polymethyl siloxane liquids, obtained by the aforesaid resonance method. All the three methods for measuring the shear modulus of liquids have been used.

An $X$ piezoquartz crystal at 18.5 °C was used in the work, the Poisson coefficient on the working surface of that crystal being equal to zero. The piezoquartz crystal dimensions are $37.4 \times 12 \times 5.5\,\text{mm}^3$; its mass was equal to 6.24 g, the resonance frequency 74 kHz.

In total, 9 liquids from the homologous series were investigated, whose viscosity varies from 25 to 520 Pa.

In Figure 3 are presented experimental dependences of the real (1, 2) and the imaginary (1′, 2′) frequency shifts for 900 grade polymethyl siloxane and 5300 grade

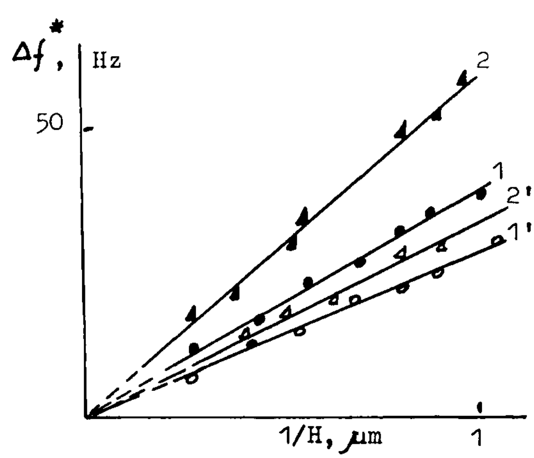


**Figure 3** Dependences of the real (1, 2) and the imaginary (1′, 2′] frequency shifts on the inverse thickness of the interlayer for the 900 grade polymethyl siloxane and the 5,300 grade polymethyl siloxane.

**Table 1**

| *Liquids* | $G' \cdot 10^{-6}$ dyn/cm$^2$ | tg$\theta$ | $\lambda$, μm | $G' \cdot 10^{-6}$ dyn/cm$^2$ | tg$\theta$ | $\Delta f''_x$ Hz | $G' \cdot 10^{-6}$ dyn/cm$^2$ |
|---|---|---|---|---|---|---|---|
| 25 grade PMS | 0.22 | 0.35 | — | — | — | 10 | 0.15 |
| 100 grade PMS | 0.6 | 0.5 | — | — | — | 16 | 0.43 |
| 200 grade PMS | 0.86 | 0.55 | — | — | — | 20 | 0.6 |
| 400 grade PMS | 1.24 | 0.75 | 160 | 1.0 | 0.7 | 23 | 0.88 |
| 900 grade PMS | 1.35 | 0.8 | 170 | 1.08 | 0.8 | 25 | 1.04 |
| 5,300 grade PMS | 2.12 | 0.6 | 200 | 1.8 | 0.6 | 29 | 1.4 |
| 20,000 grade PMS | 2.36 | 0.55 | 210 | 1.93 | 0.5 | 33 | 1.8 |
| 52,000 grade PMS | 2.6 | 0.5 | 220 | 2.4 | 0.45 | 37 | 2.2 |
| 50,900 grade PMS | 6.7 | 0.15 | 362 | 6.5 | 0.15 | 60 | 6.0 |



polymethyl siloxane on the inverse value of the thickness of the liquid interlayer, when $H \ll \lambda$. The linear dependences are obtained, which proves, in accordance with the aforesaid, that the liquids possess a complex shear modulus. Similar results are obtained also for other liquids from the homologous series being investigated. With formulas (8) and (9) corresponding to the given method, we obtain for the 900 grade polymethyl siloxane the value of $G' = 1.35 \cdot 10^6$ dyn/cm$^2$, and for the 5,300 grade polymethyl siloxane $G' = 2.12 \cdot 10^6$ dyn/cm$^2$. The mechanical losses angle tangents are equal to 0.8 and 0.6, respectively.

From the appended Figure, it is obvious that the shear elasticity increases by more than an order of magnitude as the viscosity or the molecular weight increases, too. The measurement results for $G'$ and tg$\theta$ are presented in Table 1 (see columns 1 and 2). From the Table, it is apparent that the mechanical losses angle tangents pass through a maximum; low-viscosity and high-viscosity polymethyl siloxane (PMS) possess smaller values of the mechanical losses angle tangent than those of the liquids possessing a medium viscosity.

It is also possible to note that the mechanical losses angle tangents of all the liquids of that series are small than unity. This proves that the relaxation frequency of the given process is lower than the experimental frequency which was equal to 74 kHz.

In the works by Barlow, Lamb *et al.* [8, 9] the shear properties of four polydimethyl siloxane liquids having a viscosity of 10 to 1,000 Ps were measured within a wide range of frequencies.

A corresponding calculation done for polydimethyl siloxane having a viscosity of about 1,000 Ps gives a value for $G' = 1.8 \cdot 10^6$ dyn/cm$^2$, while tg$\theta = 0.4$. As is obvious, these data are close to the results obtained in the present work.

Let us consider the results of determination of $G'$ and tg$\theta$ according to measurements of the shear wave length with regard to decay maxima. In Figure 4 are presented the experimental curves of dependences of frequency shifts upon the thickness of the liquid interlayer of the 5,300 grade PMS. Curve 1 relates to the real frequency shift, whereas

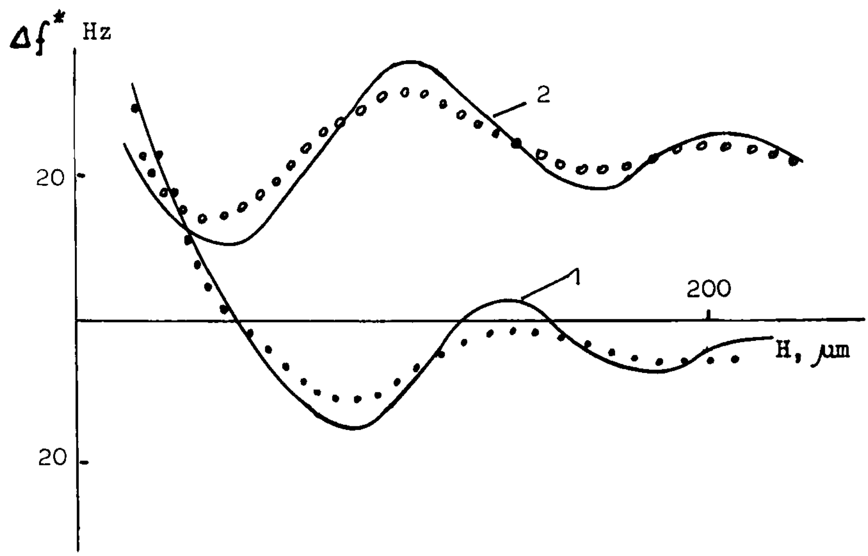


**Figure 4** Experimental points and theoretical curves (solid lines) of the dependences of frequency shifts versus the thickness of the 5,300 grade PMS liquid interlayer.



curve 2 to the imaginary frequency shift. According to decay maxima $\Delta f''_{\infty}$ the wave length for a given liquid $\lambda = 200\,\mu$m. With formula (10) we obtain for $G' = 2.12 \cdot 10^6$ dyn/cm$^2$. It is seen that the given result coincides with the result from Table 1 for that liquid, obtained by the first method, when $H \ll \lambda$. Calculating the mechanical losses angle tangent by the aforesaid method gives for that liquid the value of $\text{tg}\,\theta = 0.6$. For these values of the shear modulus and mechanical losses angle the dependences $\Delta f'$ and $\Delta f''$ versus the thickness of the liquid film (solid lines in Fig. 4) were computed with formulas (3), (4). It is seen that the experimental curves fairly well agree with the theoretical curves.

However, no oscillations of frequency shifts are observed for low-viscosity polymer liquids, such as 25 grade PMS and 200 grade PMS. Probably, because of the presence of a normal component on the working surface of piezoquartz the liquid film undergoes additional compression and tensile deformations, and the maxima of frequency shifts are levelled out. The results of measurement of $G'$ and calculation of $\text{tg}\,\theta$ are presented in Table 1 (see columns 3, 4).

When measuring the value of $G'$ by the third method, the whole horizontal surface of piezoquartz is coated by a thick layer of the liquid being investigated, in which the shear wave completely decays, and the limit values of $\Delta f'_{\infty}$ and $\Delta f''_{\infty}$ are measured. From Figure 2, it is apparent that at $G' = 3 \cdot 10^5$ dyn/cm$^2$ and $\text{tg}\,\theta = 0.3$ the shear wave completely decays at a distance $\lambda \approx 180\,\mu$m. Hence, when determining the shear elasticity by this method the thickness of the liquid layer for such a liquid must be at least equal to $180\,\mu$m. As has been indicated above, the value of $\Delta f'_{\infty}$ might be neglected.

For the investigated 5,300 grade PMS and 52,000 grade PMS the measured values of $G'$ are equal to $2.12 \cdot 10^6$ dyn/cm$^2$ and $2.6 \cdot 10^6$ dyn/cm$^2$ respectively. Calculation done with formula (14) gives for elasticity moduli the values of $G' = 1.4 \cdot 10^6$ dyn/cm$^2$ and $G' = 2.2 \cdot 10^6$ dyn/cm$^2$.

In Table 1 are also presented the results for other liquids. Comparing the values of shear moduli, obtained by three methods, it is possible to see that the maximum values of shear elasticity are obtained when measuring by the first method, with $H \ll \lambda$. In this case, the purity or cleanness of working surfaces and liquids is well conserved. A normal component does not exert its influence, because the cover-plate was chosen so as to be sufficiently small in mass. The minimum values of $G'$ are obtained by performing measurements by the third method. This is explained by the fact that the working surface of piezoquartz is utilized not to the full extent; for the thickness of the liquid layer is smaller on edges because of the meniscus than in the middle of the layer.

Thus, in the present work three methods were applied to determine the visco-elastic properties of the homologous series of polymethyl siloxane liquids. The experiments on propagation of shear waves in liquids well show that the low-frequency shear elasticity is an inalienable property of liquid in bulk, and prove the existence of visco-elastic relaxation in liquids. The existence of low-frequency (about $10^5$ Hz) shear elasticity in liquids is substantiated in the works by Joseph [12, 13], concerning the measurement of shear wave speeds and shear elasticity moduli of various liquids.

The co-authors dedicate this work to the memory of the prematurely died Ulzyto Batoevich Bazaron, prominent scientist and supervisor of these investigations at the Buryat Institute of Natural Sciences of the Siberian Division of Russian Academy of Sciences.



*References*

1. U. B. Bazaron, B. V. Derjaguin, and A. V. Bulgadaev. On the shear elasticity of the boundary layers of liquids. *Dokl. AN SSSR*, **160**, 799–803 (1965).
2. U. B. Bazaron, B. V. Derjaguin and A. V. Bulgadaev. Investigation of the shear elasticity and their boundary layers by the dynamic method. *Dokl. AN SSSR*, **166**, 639–643 (1966).
3. U. B. Bazaron, B. V. Derjaguin and A. V. Bulgadaev. Measurements of the shear elasticity of liquids and their boundary layers by the resonance method. *Zhurn. eksper. teoret. fisiki*, **51**, 969–981 (1966).
4. K. T. Zandanova, B. V. Derjaguin, O. R. Budaev and U. B. Bazaron. The complex shear modulus of liquids and its dependence on the shear deformation angle. *Dokl. An SSSR*, **215**, 309–312 (1974).
5. U. B. Bazaron, B. V. Derjaguin, O. R. Budaev and B. B. Badmaev. Determination of the low-frequency complex shear modulus of liquids according to measurements of shear waves. *Dokl. AN SSSR*, **238**, 50–53 (1978).
6. B. B. Badmaev, K. T. Zandanova, O. R. Budaev and U. B. Bazaron. Low-frequency complex shear modulus of water, ethylene-glycol, and triethylene-glycol. *Dokl. AN SSSR*, **254**, 381–385 (1980).
7. H. I. McSkimin and P. Andreatch. Measurement of dynamic shear impedance of low-viscosity liquids at ultrasonic frequencies, *J. Acoust. Soc. Am.*, **42**, 248–252 (1967).
8. A. J. Barlow, G. Harrison and I. Lamb. Viscoelastic relaxation of polydimethyl siloxane liquids, *Proc. Roy. Soc.*, **282**, **1389**, 228–251 (1964).
9. I. Lamb, P. Lindon and Andio. Frequency measurements of the viscoelastic properties of polydimethyl siloxane liquids, *J. Acoust. Soc. AM.*, **41** (4), 1032–1042 (1967).
10. B. V. Derjaguin, U. B. Bazaron, K. I. Zandanova, A. R. Budaev. The complex shear modulus of polymeric and small-molecule liquids. *Polymer*, **30**, 97–103 (1989).
11. B. V. Derjaguin, U. B. Bazaron, Kh. D. Lamazhapova and B. D. Tsidypov. Shear elasticity of low-viscosity liquids at low frequencies. *Physical Review*, **42** (4), 2255–2258 (1990).
12. D. D. Joseph, A. Narain and O. Riccius. Shear wave speeds and elastic moduli for different liquids. *Part I. Theory. J. Fluid Mech.*, **171**, 289–308 (1986).
13. D. D. Joseph, O. Riccius and M. Arney. Shear wave speeds and elastic moduli for different liquids. Part II, Experiments. *J. Fluid Mech.*, **171**, 309–338 (1986).