Low-frequency (10⁵ Hz) shear modulus of nanosuspension

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Abstract. The low-frequency shear wave propagation in a suspension of silica nanoparticles in a polyethylsiloxane liquid was studied. The shear wave length was measured on ultrasonic interferometer, and it is equal to 55 μm. The value of the tangent of the mechanical losses angle is determined to be 0.18. These parameters were used to calculate the shear modulus of the investigated colloidal suspension; its value is 0.15×10⁵ Pa. The results obtained are in quite agreement with the data obtained by another way of the acoustic resonance method.

1. Introduction
Nanosuspension is a dispersed two-phase system consisting of a dispersion medium and a dispersed phase. Nanosuspension has special structural and mechanical properties, such as elasticity, viscosity, strength and ductility, which are manifested during shear deformation. The structure and rheological properties of the nanosuspension are mainly determined by the interaction of the particles of the dispersed phase with the molecules of the dispersed medium and with each other.

Studies of the rheological properties of nanosuspensions have been actively pursued over the past two decades. It was found that these properties depend on the size, shape, kind and concentration of nanoparticles [1]. However, there are still no unambiguous conclusions regarding the nature of these parameters of nanoparticles influence on the rheological properties of nanosuspensions [2, 3]. Therefore, experimental studies of the rheological properties of nanosuspensions by different methods are relevant. It is also of great practical importance in connection with the numerous areas of practical application.

In [4-6], the shear elasticity of SiO₂ nanosuspension in PES-2 at small thicknesses of the liquid layer was measured by the acoustic resonance method. However, the result obtained can be attributed to the special properties of the boundary layers of nanosuspensions. Therefore, a study of the possibility of a low-frequency shear wave propagation in a thick layer of nanosuspension would confirm that shear elasticity is its bulk property.

2. Method
In this work, the propagation of a low-frequency (10⁵ Hz) shear wave in a colloidal suspension of nanoparticles of silica SiO₂ in a polyethylsiloxane liquid PES-2 is studied using an acoustic resonance method on an ultrasonic interferometer. The value of the shear modulus of the investigated nanosuspension from the measured values of the shear wave length and the tangent of the mechanical losses angle was calculated.
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**Figure 1.** Piezoquartz with an additional bond: 1 – piezoquartz, 2 – liquid film, 3 – cover plate.

The essence of the acoustic resonance method is as follows. The horizontal surface of the piezoquartz crystal X-18.5° cut in the form of a rectangular bar with dimensions of 34.9 x 12x6 mm, weighing 6.82 g, contacts the liquid layer covered with a solid cover plate [7-9]. The cover plate is located at one end of the piezoelectric quartz, figure 1. When the piezoelectric quartz oscillates at a resonant frequency of 73.2 kHz, the liquid layer experiences dynamic shear deformations and a standing shear wave must be established in it. Depending on the thickness of the liquid layer, the resonance frequency of the piezoquartz and the width of the resonance curve change. This is the expression of the complex shift of the resonant frequency \( \Delta f^* \) [7-9]:

\[
\Delta f^* = \frac{SG^* k^*}{4\pi^2 Mf_0} \cdot \frac{1 + \cos(2k^* H - \phi^*)}{\sin(2k^* H - \phi^*)},
\]

(1)

where \( G^* = G' + iG'' \) is the complex shear modulus of the liquid, \( S \) is the area of the base of the cover plate, \( k^* = \beta - i\alpha \) is its complex wave number, \( H \) is the thickness of the liquid layer between the piezoquartz and the cover plate, \( \phi^* \) is the complex phase shift that occurs when a viscoelastic wave is reflected from the liquid – cover plate interface, \( M \) is the mass of the piezoquartz, and \( f_0 \) is its resonant frequency.

Given that \( \phi^* = 0 \) the following expressions are obtained by dividing \( \Delta f^* \) into real \( \Delta f' \) and imaginary \( \Delta f'' \) frequency shifts [7-9]:

\[
\Delta f' = \frac{S}{4\pi^2 Mf_0} \cdot \frac{(G' \beta + G'' \alpha) \sin 2\beta H + (G' \alpha - G'' \beta) \sinh 2\alpha H}{\cosh 2\beta H},
\]

(2)

\[
\Delta f'' = \frac{S}{4\pi^2 Mf_0} \cdot \frac{(G'' \alpha - G' \beta) \sin 2\beta H + (G' \alpha + G'' \beta) \sinh 2\alpha H}{\cosh 2\alpha H - \cos 2\beta H}.
\]

(3)

Using the ratio \( (k^*)^2 = \frac{\omega^2 \rho}{G} \) it can be seen from these expressions, that the frequency shifts give damped oscillations with an increase in the thickness of the liquid layer. The maximum attenuation, which is observed in the opposite phase of the forward and reverse waves, can be used to determine the length of the shear wave \( \lambda \). The first maximum attenuation will be observed when the thickness of the liquid layer is \( \lambda/2 \). We can obtain a calculated formula for the real shear modulus in the form by using the expression (3) [7-9]:

\[
G' = \frac{\lambda^2 f_0^2 \rho \cos \theta \cos^2 \frac{\theta}{2}}{2}.
\]

(4)
where $\theta$ is the angle of mechanical losses, $\rho$ is the density of the liquid under study. The value of $\tan \theta$ is determined by the ratio of the distance $\Delta f$ between the first minimum and maximum of the real frequency shift to the length of the shear wave $\lambda$ [7-9].

Thus $G'$ and $\tan \theta$ can be determined by measuring the shear wave length in a thick liquid layer.

A polyethilsiloxane liquid PES-2, which is a mixture of polymers of linear (C$_2$H$_5$)$_3$Si-O-[Si(C$_2$H$_5$)$_3$O]-Si(C$_2$H$_5$)$_3$ and cyclic [(C$_2$H$_5$)$_3$SiO]$_3$ structures, was used as a base liquid to obtain a nanosuspension. Table 1 shows the main properties of the polyethilsiloxane liquid PES-2 [10]. And a silicon dioxide nanosize powder SiO$_2$ with a size of 50 nm, trade mark Tarkosil T-0.5 were used as a dispersed phase.

**Table 1.** The main properties of the polyethilsiloxane liquid PES-2.

| Molecular weight | Density at 20ºC, kg/m$^3$ | Viscosity, mm$^2$/s | Boiling point, ºC (at 133 – 400 Pa) | Pour point, ºC |
|------------------|-----------------------------|----------------------|-------------------------------------|----------------|
|                  | 940                         | at -60 °C 20 °C 60 °C| 110 – 150                           | -110           |
| 341              | 312                         | 9                    | 4                                   |                |

3. Results and discussion

Another way of defining $G^*$ follows from the analysis of expressions (2) and (3). If the thickness of the liquid layer $H$ is much less than the shear wave length $\lambda$, i.e. $H \ll \lambda$, the expressions (2) and (3) are extremely simplified. For the real $G'$ and imaginary $G''$ shear moduli, as well as for $\tan \theta$, the following formulas are obtained [7-9]:

$$G' = \frac{4\pi^2 M f_0 \Delta f' H}{S}, \quad G'' = \frac{4\pi^2 M f_0 \Delta f'' H}{S}, \quad \tan \theta = \frac{G''}{G'} = \frac{\Delta f''}{\Delta f'}. \quad (5)$$

It can be seen from these formulas, that the complex shift of the resonant frequency is proportional to the inverse of the thickness of the liquid layer. Thus, in this method of measuring $G^*$, it is sufficient to measure the thickness of the liquid layer $H$, and the real shift of the resonant frequency $\Delta f'$ and the imaginary shift $\Delta f''$ by the broadening of the resonant curve. In [7-9], this method was used to measure the complex shear modulus of a colloidal suspension of silica SiO$_2$ nanoparticles in a polyethilsiloxane liquid PES-2 at small thicknesses of the liquid layer. Linear dependences of the frequency shifts on the inverse thickness of the liquid layer were obtained. The values of the shear modulus and the tangent of the mechanical loss angle were calculated using formulas (5). The dependences of these parameters on the size of nano-inclusions and their concentration were investigated. Thus, for 0.5 wt.% with particles dimensions of 50 nm, the values of the shear modulus $G = 0.17 \cdot 10^5$ Pa and the tangent of the mechanical losses angle $\tan \theta = 0.18$ were obtained [4].

A stable SiO$_2$/PES-2 nanosuspension was obtained as follows. After the introduction of silicon dioxide nanoparticles into the base liquid, the resulting dispersed system was thoroughly dispersed by ultrasound. This made it possible to destroy the agglomerates of nanoparticles as much as possible and to obtain their uniform distribution in the bulk of the dispersed medium [4-6]. The cover plate with the liquid layer was freely located at one end of the piezoelectric quartz when measuring the complex shear modulus of the nanosuspension at small thicknesses of the liquid layer, when $H \ll \lambda$. The thickness of the liquid layer was changed by displacing the liquid from under the cover plate. But when measuring $G'$ by the propagation of a shear wave, the cover plate was fixed rigidly and moved vertically by mechanical devices, which made it possible to regulate the thickness of the liquid layer over a wide range. Thus, an ultrasonic interferometer was implemented for low-frequency shear waves, described in detail in [7-9].

Figure 2 shows the experimental and theoretical dependences of the real $\Delta f'$ and imaginary $\Delta f''$ frequency shifts as a function of the thickness of the SiO$_2$/PES-2 liquid layer. Curve 1 refers to the real frequency shift, and curve 2 – to the imaginary one. As can be seen from the figure, there is a damped oscillation of frequency shifts. The shear wave length in a given nanosuspension can be determined...
from the attenuation maxima (curve 2), and it is equal to 55 μm. With respect to the \( \Delta H/\lambda \) ratio, the value of the tangent of the mechanical losses angle is determined to be \( \tan \theta = 0.18 \). The value of the shear modulus is calculated according to the formula (4), and it is equal to \( G' = 0.15 \times 10^5 \) Pa. The results of the \( G' \) measurement obtained by the two methods of the acoustic resonance method are quite consistent with each other.

**Figure 2.** Theoretical (solid lines) and experimental (points) dependences frequency shifts on the thickness of the liquid layer for SiO\(_2\)/PES-2: 1 – real, 2 – imaginary frequency shifts.

4. Conclusion

Thus, the propagation of a low-frequency (10\(^5\) Hz) shear wave in a colloidal suspension of SiO\(_2\)/PES-2 was studied for the first time using an ultrasonic interferometer for shear waves. The shear wave length and the tangent of the mechanical losses angle were used from extreme values of the real and imaginary frequency shifts to calculate the value of the shear modulus of the investigated nanosuspension. The agreement of the experimental results obtained by the two ways of the acoustic resonance method confirms that the shear elasticity of the investigated nanosuspension is a property of the nanosuspension in the bulk.

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