Nonlinear viscoelastic properties of nanosuspensions

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Abstract. This paper studies the dependence of the shear elasticity modulus and the coefficient of dynamic viscosity of the suspensions on the magnitude of the shear strain of nanoparticle suspensions in a polymer liquid. As the dispersion medium, polyethylsiloxane liquid PES-2 was used, the solid dispersed phase - silica nanoparticles and fullerenes. We used the acoustic resonance method for determining the complex shear modulus of liquids using a piezoquartz resonator. Studies have shown nonlinear behavior of viscoelastic parameters of suspension samples depending on shear stress.

1. Introduction
There are many methods for studying the viscoelastic properties of liquids and multiphase media. Resonance methods for measuring the complex shear modulus of liquids are based on measuring the resonance characteristics of an oscillatory system. The elastic forces arising from the shear deformation of the liquid increase the resonant frequency of the vibrator, and the viscous ones increase the attenuation of the oscillatory system. It is well known that linear viscoelasticity is observed only at small deformations. With increasing strain, the resonance curve of the oscillatory system deforms. This paper presents a study of viscoelastic properties of colloidal suspensions of silica dioxide nanoparticles and fullerenes using a resonance method in dependence on the amplitude of shear vibrations. Polyethylsiloxane liquid was used as a base fluid. The wide range of working temperatures (from -60 to +150 °C) allows to widely using them in modern technology. Silica dioxide nanopowder SiO2 obtained by gas-phase synthesis [1], and fullerenes C60, purchased from Company “NeoTechProduct”, were used for suspensions.

2. Method
The viscoelastic properties of nanoparticle suspensions are studied by the acoustic resonance method using a piezoelectric crystal [2-4]. A piezoelectric crystal in the shape of a rectangular bar performs compression and tension oscillations at the fundamental resonant frequency. The liquid is applied to one end of the horizontal surface of the piezoelectric quartz and covered with a solid fused silica cover-plate. A certain crystal cut (X-18.5 °), having a zero Poisson's ratio on the working face, allows one to obtain purely shear deformations in the studied liquid layer. In this case, standing shear waves are established in it. Depending on the thickness of the liquid layer, the parameters of the resonance curve of the system change. Under the assumption that the cover-plate is loosely bonded to the piezoquartz through the liquid layer and, therefore, is at rest and the thickness of the interlayer is much less than the shear wavelength in the liquid, the complex shear modulus $G^*$ and the tangent of the mechanical loss angle tanθ of the investigated liquid will be determined by the following expressions:
\[ G^* = \frac{4\pi^2 M f_0 \Delta f^* H}{S}, \quad \tan \theta = \frac{G''}{G'} = \frac{\Delta f''}{\Delta f'}, \] (1)

where \( G^* = G' + iG'' \) is the complex shear modulus of the fluid; \( \Delta f^* = \Delta f' + i\Delta f'' \) is the complex shift of the resonant frequency; \( M \) is the mass of the piezoelectric quartz; \( S \) is the area of the cover-plate base; \( f_0 \) is the resonant frequency of the piezoelectric quartz; \( H \) is the thickness of the liquid layer. The resonant frequency of the piezoelectric crystal was 73.2 kHz, the mass was 6.82 g, and the area of the base of the cover-plate was 0.2 cm².

The imaginary shift of the resonant frequency is equal to the change in the attenuation of the oscillatory system:
\[ \alpha' \Delta = \Delta f, \] where \( \Delta \alpha \) is the change in the width of the resonance curve of the piezoelectric quartz. Knowing the change in the resonance frequency and the width of the resonance curve, it is possible to determine the complex modulus of shear of the liquid.

3. Results and discussion
According to theory of a nonlinear oscillatory system it is known that its properties are determined through the parameters of the resonance curves. In the case of nonlinearity of the shear elasticity of liquids, the resonance curve of the oscillatory system of the piezoelectric quartz — the interlayer of the liquid — the cover-plate will deform with an increase in the amplitude of the oscillation of the piezoelectric quartz becoming more asymmetric, and the properties of the oscillatory system will be determined through the parameters of the resonance curves. The vibration amplitude of a piezoelectric crystal can be determined using a method based on the principle of the Fabry-Perot interferometer, where the optically polished end face of a piezoelectric crystal is used as one of the mirrors [5]. The obtained dependence of the amplitude of the oscillation of piezoelectric crystal \( A \) on the voltage removed from it makes it possible to measure the amplitude with sufficiently high accuracy. The \( A/H \) ratio can serve as a measure of angular deformation.

Figure 1 shows the change in the shape of the resonance curves with increasing values of the driving force oscillating the piezoelectric quartz for the hexadecane layer studied in [6] by the acoustic resonance method. Curve 1, taken at low vibration amplitudes, is symmetric and corresponds to the region of linear elasticity. As the driving force increases, the resonance curve becomes steeper from the low frequency side and further exhibits instability. The middle line of the resonance curve 3 actually depicts the dependence of shear elasticity on the angle of deformation.

**Figure 1.** Resonance curves for various driving forces with a maximum amplitude of oscillation: 1 – 10 Å; 2 – 100 Å; 3 – 300 Å [6].
Figure 2 shows the dependences of the real and imaginary components of the shear modulus calculated by formula (1) on the shear angle for samples of silica suspensions with a nanoparticle size of 100 nm with a concentration of 1.25 wt.% and fullerenes with a concentration of 1.5 wt.% in a polymer liquid PES-2. Suspensions are obtained by ultrasonic method. For ease of analysis, the results are presented depending on the value \((A/H)^{1/2}\). At small deformation angles, the components of the complex shear modulus are constant, then, with an increase in the shear angle, \(G'\) decreases, and \(G''\) passes through a maximum. Similar curves for pure liquids were obtained in \([5,7]\). It can be assumed that the liquid has an equilibrium supramolecular structure and, at small angles of shear deformation, a region of linear elasticity is detected. At a certain critical shear stress \(P_c\), the equilibrium structure begins to collapse and its viscoelastic properties change. The critical shear stress corresponds to a certain critical shear angle \(\varphi_c\), which can be determined from the data in Fig. 2.

In the region of linear elasticity, \(G'\) and \(\tan\theta\) for the suspensions studied are \(G' = 2.5 \times 10^4\) Pa and \(\tan\theta = 0.35\) and \(G' = 1.2 \times 10^4\) Pa, \(\tan\theta = 0.55\), respectively.

Figure 3 shows the graphs of effective viscosity versus shear strain angle for these suspensions. Viscosities are calculated using Maxwell's rheological model by the formula:

\[
\eta_{\text{eff}} = \frac{G'(1 + \tan^2\theta)}{2\pi\eta_0 \tan\theta}.
\]

**Figure 2.** Experimental dependences of real (1) and imaginary (2) parts of shear modulus on the shear deformation angle for suspensions: (a) SiO\(_2\)/PES-2, 1.25 wt.%; (b) C\(_{60}\)/PES-2, 1.5 wt.%.  

**Figure 3.** Dependence of effective viscosity on the shear deformation angle for suspensions: (a) SiO\(_2\)/PES-2, 1.25 wt.%; (b) C\(_{60}\)/PES-2, 1.5 wt.%.
The suspensions are characterized by a constant increased viscosity when shear angles smaller than the critical value $\varphi_c$. At these region effective viscosities of suspensions are higher than the value of viscosity for base liquid, which have been determined by a rotation method using a rheometer Physica Anton Paar MCR302. It equals to 0.01 Pa·s. With a further increase in the shear angle, the structure is destroyed and the viscosity decreases to the smallest value.

Figure 4 shows the dependence of the shear stress in the suspension layer on the magnitude of the shear strain, the dashed line shows the linear dependence of the shear stress. Critical shear stress when the linearity of the dependence is violated, for the suspension $\text{SiO}_2/\text{PES-2}$ is $P_c = 0.45 \times 10^3$ Pa and for the $\text{C}_{60}/\text{PES-2}$ is $P_c = 1.04 \times 10^3$ Pa. The nonlinearity of the shear elasticity of the samples with an increase in the angle of deformation is clearly visible in the figure; moreover, for a silicon dioxide suspension having a lower value of the tangent of the angle of mechanical losses, the nonlinearity is more pronounced.

![Figure 4. Dependence of shear stress on the shear strain for suspensions: (a) $\text{SiO}_2/\text{PES-2}$, 1.25 wt.%; (b) $\text{C}_{60}/\text{PES-2}$, 1.5 wt.%. The dashed line corresponds to a linear dependence.](image)

4. Conclusion

Thus, the shift of the resonance frequency of the vibrational system of piezoelectric quartz — the suspension layer — the overlay depends on the amplitude of the shear strain, which indicates the nonlinearity of the viscoelastic properties of the suspensions under study.

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