Influence of the structure of the boundary layer of an adsorbed viscoelastic fluid on the dielectric properties of a metamaterial

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Abstract. We study the change in the shear elasticity of a viscous fluid near a solid surface of a metamaterial. The interest in studying the shear mechanical properties of these fluids is caused by their wide use in engineering. Surface forces in boundary layers or thin films of classic molecular systems should be considered when describing different phenomena in near-surface layers. We obtained the solution for two-particle distribution function at low densities. It is shown that the solution describes the transition from axial to spherical symmetry while each particle goes to infinity.

1. Introduction

Rheological measurements are a powerful method for studying the physical properties of liquids. Many methods for studying the mechanical properties of viscoelastic materials have been developed. Most of them are associated with acoustic measurements of various parameters of liquids.

To study very viscous (glassy) substances, melts of polymers, low-frequency vibrators are usually used, whereas for low-viscosity liquids and solutions, sound and ultrasonic vibrators are used. The frequency range of these methods extends from $10^{-4}$ to $10^9$ Hz, and the measured modules reach $10^9$ Pa. In recent years, much attention was given to viscoelastic liquids with a non-Newtonian behavior [1-3]. According to the existing concept of the nature of liquids, the shear elasticity of liquids should be observed under shear oscillations with the periods comparable with the time intervals of the particle jumps between the temporary equilibrium states. These intervals being identified with the relaxation time of the nonequilibrium state estimated as about $10^{-10}$–$10^{-12}$ s from the self-diffusion rate, and the calculations for low-viscosity. Hence, the shear elasticity of such liquids should be observed at the frequencies of shear oscillations of $10^{10}$–$10^{12}$ Hz.

However, as follows from experiments [4, 5] all liquids without exception demonstrate shear elasticity near frequency of $10^5$ Hz. Thus an unknown yet low-frequency viscoelastic relaxation process takes place in liquids. Presumably, it is caused by collective excitations of large groups of interacting molecules having a relaxation time which by many orders of magnitude exceeds the time of temporal stability of individual molecules. The characteristic feature of the shear mechanical properties of regular liquids is the small value of the mechanical loss tangent ($<1$). According to the Maxwell rheological model, this means that a relaxation frequency of an investigated process is lower than the frequency used in the experiment.
2. Acoustical method

Our experiments were performed at the frequencies 40 and 74 kHz. The presence of the low-frequency shear elasticity was revealed by the acoustic resonance method [4, 5] described as follows. A piezoelectric quartz resonator made of 18.5° X-cut quartz crystal with zero Poisson’s ratio oscillates at its fundamental resonance frequency. The horizontal surface of the crystal contacts with a liquid layer covered with a solid strap. Shear standing waves are excited in the layer experiencing shear strains. The parameters of the resonance curve of the system can vary in dependence on the film thickness.

Equating the impedances of the piezoelectric quartz and the liquid, one can derive the complex shift of the resonance frequency of the oscillatory system [6]. These frequency shifts perform damped oscillations, and with the increase in the liquid layer thickness, they tend to some limiting values.

When the liquid layer thickness is much less than the shear wavelength and the strap is practically at rest, we obtain the following expressions for the real shear modulus and the mechanical loss tangent:

\[
G' = \frac{4\pi^2 M f_0 \Delta f H}{S} \tag{1}
\]

\[
\tan \theta = \frac{G''}{G'} = \frac{\Delta f'}{\Delta f''} \tag{2}
\]

where \(G^* = G' + iG''\) – complex shear modulus of liquid, \(\Delta f^* = \Delta f + \Delta f''\) – complex frequency shift, \(M\) – the piezoquartz mass, \(H\) – the liquid layer thickness, \(S\) – the cover-plate square, \(f_0\) – the resonance frequency of the piezoquartz. The imaginary frequency shift is equal to the shift of the resonance half-width. When the liquid possesses a measurable shear modulus, according to (1) the real frequency shift must be inversely proportional to the liquid layer thickness. The latter was determined by the interference method. A positive shift of the resonance frequency indicates presence of the shear elasticity.

Several liquids presented in Table 1 were studied. The choice of these liquids is caused, first, by their wide use in engineering (studying the shear mechanical properties). Second, study of the homologous series of different liquids is of special interest, because a change in number of the chain links is accompanied by changes in the shape and size of molecules as well as in character of their interaction. All this affects the viscoelastic properties of liquids (i.e. structure) of the homologous series. For all studied liquids we obtained linear dependence of the resonance frequency shift on the inverse thickness of the liquid layer. According to (1), such a linearity indicates the presence of the bulk shear elasticity. Using (1) and (2), we calculated the values of \(G\) and \(\tan \theta\). The results obtained [6] at the frequencies 40 kHz and 74 kHz are presented in the Table 1.

| Liquid           | 40 kHz  | 74 kHz  |
|------------------|---------|---------|
|                  | \(G', 10^5 \text{ Pa}\) | \(\tan \theta\) | \(G', 10^5 \text{ Pa}\) | \(\tan \theta\) |
| Vaseline oil     | 1.13    | 0.60    | 1.36    | 0.50    |
| Ethylene glycol  | 0.39    | 0.72    | 0.91    | 0.24    |
| Diethylene glycol| 0.51    | 0.44    | 1.22    | 0.31    |
| Triethylene glycol| 0.74  | 0.65    | 1.28    | 0.27    |
| PES-1            | 1.26    | 0.18    | 9.63    | 0.11    |
| PES-2            | 0.97    | 0.19    | 4.81    | 0.63    |
| PES-3            | 0.85    | 0.21    | 3.45    | 0.87    |
| Dibutyl phthalate| 0.65    | 0.29    | 0.97    | 0.11    |
| Oleic acid       | 0.76    | 0.23    | 1.63    | 0.91    |

As seen in Table, for all liquids the obtained values of the elastic modulus are smaller and the mechanical loss tangents are greater for 40 kHz than for 74 kHz. For example, for ethylene glycol, the
real shear modulus is $0.39 \times 10^4$ Pa at the frequency 40 kHz and $0.91 \times 10^5$ Pa at 74 kHz. The mechanical loss tangent is 0.72 at 40 kHz and 0.24 at 74 kHz. In the simple Maxwell rheological model with a single relaxation time the mechanical loss tangent is equal to 1 at the relaxation frequency. Hence, the relaxation frequencies of all studied liquids are less than 40 kHz. Therefore, it is of interest to study the shear elasticity at lower frequencies. Thus, all liquids studied in the experiment possess measurable shear moduli at the given frequencies of shear oscillations. The presence of the low-frequency shear elasticity in regular and low-viscosity liquids means that the values of the shear stress relaxation time estimated on the basis of the time within which single liquid molecules remain in the temporal equilibrium states are wrong and confirms the hypothesis that the dominant role is played by the collective interactions of clusters.

We assume that any liquid represents a micro heterogeneous media which consisting of two dynamical components – arranged fields (clusters) disposed in nonarranged loose-packed matrix [7]. Clusters are rearranged by outer influence, which is expressed by diffusion change of fluctuation holes between those components. Getting off the atom from a cluster means formation of fluctuation hole, while its addition to cluster means hole shutting. Using data on temperature dependence of mechanical loss angle tangent of Vaseline oil at 40 and 74 kHz the activation energy of cluster disintegration process was evaluated. The obtained value, which is of the order of hydrogen bond energy (~5 kcal/mol), gives evidence that the low-frequency relaxation process in liquid is related to some low-energy process.

As a next step, we intend to cover the surface of the piezoquartz resonator with a hyperbolic metamaterial consisting of alternating dielectric and metal films and to measure the dependence of the dielectric constant of the nanocomposite on known fluid shear moduli [8]. In addition, the characteristics of the fluid are determined from the model of the liquid bordering with solid.

3. Structure and permittivity of metamaterial
In previously described experiments we studied boundary layers of liquids which thickness exceeds surface forces radius and, at the same time, is less than macroscopic scale (30–40 Å). In this case, the microstructure of boundary layer changes due to particle reordering near hard surface.

Structure properties define permittivity of liquid [9-11]. In particular, for bulk liquids static permittivity is evaluated via pair correlation function near hard surface. In the same way permittivity is evaluated for boundary layers.

Structure of hard surface defines potential field affecting boundary layers of liquids. For hyperbolic metamaterial which was studied in our experiments [8] it is necessary at first to calculate the potential field, produced by surface. Also we need to take into account real intermolecular potentials (like Lennard-Jones etc.)

However, we may quantitatively describe such system by model near the hard surface as already suggested in our papers [12-14]. In this work we obtained one- and two-particle distribution function for molecular system at low density. The results allow to obtain permittivity properties for molecular system near hyperbolic metamaterial.

4. Common equations
Statistics of the considered molecular system is based on Born-Green-Yvon-equations system (also known as BGY hierarchy) for I-particle functions and on $g_{i...j}(r_1,...,r_j)$ for ensemble of identical particles. These particles interact with each other through potential $\Phi_i(r)$, where $r = |r_i - r_j|$ is the distance between centers of particles $i$ and $j$. The diameter of each particle is $\sigma$.

The BGY-equations system may be transformed to equations for one- and two-particle distribution functions, which may be written as Ornstein-Zernike [11]:

$$\omega = n \int G_2 c_{12}^{(0)} d(2) + \ln a; \quad h_2 = c_{12}^{(2)} + n \int c_{13}^{(2)} h_{23} d(3)$$

(3)
Here we integrating on coordinates of $i$-particle: $d(i) = dr$, $n$ – density, $G_i = \exp(-\Phi_i(kT)^{-1} + \omega_i)$ one-particle distribution function, which describes particle position; $\Phi_i$ - potential energy in external field; $\omega_i$ - one-particle thermal potential; $a$ – activity coefficient, which is defined by condition of passing to isotropic system. $h_y = [\exp(-\Phi_y(kT)^{-1} + \omega_y) - 1]$ is the pair correlation function connected with two particle distribution function by expression: $G_{ij} = G_jG_i(1 + h_y)$; $\omega_y$ is two-particle thermal potential, which takes into account indirect interaction of two particles; $C^{(k)}_{ij}$ – direct correlation functions:

$$C_{ij}^{(1)} = h_y - \omega_y - \frac{1}{2} h_y (\omega_y + M_{ij}^{(1)})$$
$$C_{ij}^{(2)} = h_y - \omega_y + M_{ij}^{(2)}$$

Functions $G_i(r_i)$ and $G_{12}(r_1,r_2)$ are critical ones while they describe internal structure and let us obtain thermodynamic parameters of the system. Equations (3) and (4) are difficult to solve because $M_{ij}^{(1)}$ and $M_{ij}^{(2)}$ contains infinite series of distribution functions. To use the following equations in practice one should approximate these series by simple expressions (closures). Thus we can obtain approximated equations for high density systems. We use Martynov-Sarkisov approximation [15].

Space-heterogeneous systems (liquid near a hard surface) are described by one- and two-particle distribution functions: $G_i(r_i)$ and $G_{12}(r_1,r_2)$. Boundary condition for these equations is a transition from a hard surface to a liquid.

**Figure 1.** Axial symmetry of two-particle distribution function near hard surface

5. **Molecular system of liquid near hard surface**

Let’s form the equations for molecular system near hard surface. When solving equation (3), the origin is located in the center of the particle contacting with hard surface. The $Z$ axis is perpendicular to the surface, so the liquid is placed in the upper half-space ($z \geq 0$). The bottom half-space ($z < 0$) is unavailable for the particles (Fig. 1). Such a system has axial symmetry, $G_i(r_i) = G_i(z_i) = \exp(\omega_i(z_i))$ $G_{12}(r_1,r_2) = G_{12}(z_1,z_2,r_{12})$ (5)

where $r_{12}$ is measured in particle diameter units, $z_j \geq 0$ – particle distance from the surface. Boundary conditions for $G_i(r_i)$ and $G_{12}(r_1,r_2)$ are defined as follows
\[
\omega_1(z_1) \rightarrow 0, \quad G_1(z_1) \rightarrow 1
\]
\[
G_{12}^{(0)}(r_{12}) = \lim_{z_1 \to \infty, z_2 \to \infty, r_{12} \to \text{const}} G_{12}(z_1, z_2, r_{12}) \tag{6}
\]

6. Molecular system changes at low densities

Close order in a molecular system changes even at low densities. Let’s take, for example, rarefied gas. Thermal potential is obtained through series expansion by density powers. At the first order we get:

\[
\omega_1(z_1) = n\omega_1^{(1)}(z_1), \quad \omega_{12} = n\omega_{12}^{(1)}, \quad G_{12} = G_{12}^{(0)} + nG_{12}^{(1)} \tag{7}
\]

Substituting (9) into (7, 8) we obtain expression for factoring coefficients

\[
\omega_{12}^{(10)}(R_{12}) = \frac{2\pi}{3} \left( R_{12}^3 - 3R_{12} + 2 \right) \theta(1 - R_{12}) \tag{10}
\]

The solution (12) describes transition from axial to spherical symmetry while each particle goes to infinity. For all other values of \( z_1, z_2 \) equation (12) describes close order change near surface. We should note that (12) is right only for low density molecular systems, but might be extrapolated for higher density field and get dielectric properties of liquid near surface of hyperbolic metamaterial.
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