

## Research of Viscoelastic Properties of Liquids

B. B. Badmaev<sup>1</sup>, T. S. Dembelova<sup>1</sup> and B. B. Damdinov<sup>1,2</sup>

<sup>1</sup>Institute of Physical Materials Science, Siberian Branch of RAS, Ulan-Ude, 670047 Russia

<sup>2</sup>Buryat State University, Ulan-Ude, 670000 Russia, E-mail: dababa@mail.ru

**Abstract:** The shear elasticity of different liquids has been studied experimentally at relatively low frequencies  $10^5$  Hz. The real and imaginary shear moduli of different liquids have been measured using the acoustic resonance method. A low-frequency viscoelastic relaxation process is assumed to occur in a liquid with a period of relaxation much longer than the lifetime of the individual liquid particles.

**Keywords:** liquids, shear and loss modulus, viscosity, resonance method, cluster

### Introduction

We should take into account surface forces boundary layers and thin films of classic molecular systems when describing phenomena (adsorption, wetting) in near-surface layers. In such cases a molecular system has axial symmetry, so we may apply a model of a liquid near a solid surface. Other cases for such a model are phases contact for liquid-steam, liquid-crystal, where there is big difference between concentration of contacting phases. The behavior of viscoelastic fluids near boundaries is very close to that of colloidal particles or granulated materials. This work continues our study of the viscoelastic shear properties of different fluids. Experimental setups were designed for using the acoustic resonance method at frequencies of 40 and 74 kHz. The viscoelastic shear properties (real and imaginary shear moduli and mechanical loss tangents) of some liquids were measured at shear vibration frequencies lower than  $10^5$  Hz.

### 2. Resonance method

According to classical ideas liquid form does not have the elasticity. However, in several studies [1-3] shear elasticity of liquids was discovered at relatively low frequencies of  $10^5$  Hz. We have continued the study of the complex shear modulus of liquids using the unusual resonance method with quartz crystal [4,5]. The sample liquid is placed in the gap between the oscillating piezoelectric quartz and solid quartz cover-plate. It has been shown that for small angles shear deformation region of linear elasticity observed when stress in the film of liquid is proportional to the deformation [2]. The shear modulus of liquids decreases with deformation angle increasing. Maxwell proposed the simplest rheological model of a viscoelastic fluid, which consists of a spring and damper/plunger connected in series in a viscous medium [3]. In this model, the elastic properties are determined by the spring; viscous friction is determined by the damper and is characterized by the viscosity. In such a model, total strain  $\gamma$  is the sum of the strain of the elastic component, which obeys Hook's law, and a viscous component, which obeys Newton's law. Immediately after force is applied, the spring is elastically deformed, and a viscous flow develops during the action of the force; it produces part of the strain that does not disappear after the action ceases. If harmonically varying voltage is applied to a Maxwell body  $\sigma = \sigma_0 \cos \omega t$ , where  $t$  is the time,  $\omega = 2\pi f$  is the cycle frequency, and  $\sigma_0$  is amplitude, the strain also varies harmonically:  $\gamma = \gamma_0 \cos(\omega t - \theta)$ , where  $\gamma_0$  is the strain amplitude and  $\theta$  is the phase shift between the voltage and strain. Complex shear modulus  $G^* = G' + iG''$  must be taken into account.  $G'(\omega)$  is the dynamic modulus of elasticity (for frequency  $\omega$ ) and  $G''/\omega = \eta(\omega)$  is the dynamic viscosity; it plays the part of viscosity in acoustic equations. A Maxwell medium behaves like an ordinary viscous fluid at low frequencies ( $\omega\tau < 1$ ); the real shear modulus increases with the frequency and behaves like an elastic solid at very high frequencies ( $\omega\tau > 1$ ). According to the Maxwell relaxation theory and the thermal motion of fluid particles, fluids can display shear elasticity only at frequencies higher than those of molecule jumps from one point in time to another. The lifetime of individual molecules of ordinary low-viscosity fluids can be estimated at  $10^{-11}$  to  $10^{-12}$  s.

### 3. Experimental results

Different fluids were selected for our study: glycols, alcohols, polymer fluids, and impregnating solutions.

Figure 1 shows the dependence of  $G'$  and  $G''$  on the angle of shear deformation for ethylene glycol. It is visible that liquid structure remains constant and the shear modulus decreases with increasing of deformation angle.

It has been suggested the existence of a liquid structure in conditions close to rest, especially near the solid surface. It can be supposed that liquid has some structure at small amplitude of shear deformation. This structure, probably, concerned with clusters is broken with increasing of deformation. Linear dependences of

the real and imaginary frequency shifts on the reciprocal layer thickness were found for all of the fluids studied at a frequency of 40 kHz. The calculated values of the modulus of shear elasticity  $G'$ , mechanical loss tangent  $\tan\theta$ , and the viscosity for the liquids studies are given in Table 1.

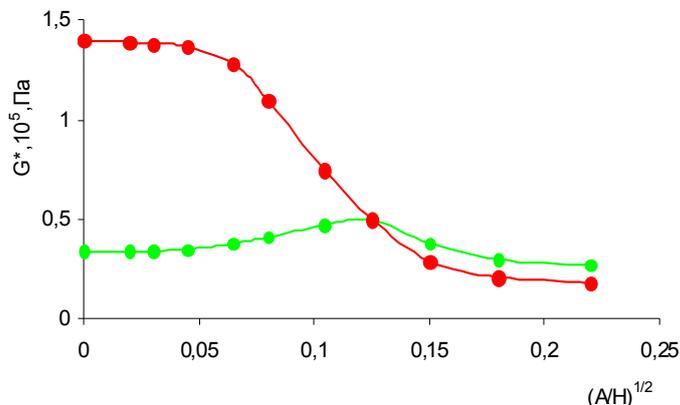


Figure 1. Dependencies of real (red) and imaginary (green) shear modulus on shear deformation angle for ethylene glycol

Table 1. Viscoelastic properties of different fluids at a frequency of 40 kHz

Fluid	$t, ^\circ\text{C}$	$G' \times 10^{-5}, \text{Pa}$	$\text{Tan}\theta$	$\eta_M, \text{Pa s}$	$\eta_T, \text{Pa s}$
Ethylene glycol	22	0.40	0.76	0.324	0.019
Diethylene glycol	24	0.51	0.65	0.546	0.032
Triethylene glycol	23	0.74	0.44	0.639	0.034
Dibutyl phthalate	24	0.65	0.29	0.958	0.002
Butyl alcohol	22	0.94	0.22	1.770	0.003
Oleinic acid	19	0.76	0.23	1.380	0.030
Butyl acetic acid	24	0.64	0.43	0.695	0.003

Table 2. Viscoelastic properties of different fluids at a frequency of 74 kHz

Fluid	$t, ^\circ\text{C}$	$G' \times 10^{-5}, \text{Pa}$	$\text{Tan}\theta$	$\eta_M, \text{Pa s}$	$\eta_T, \text{Pa s}$
Ethylene glycol	22	0.91	0.24	0.861	0.019
Diethylene glycol	24	1.22	0.31	0.933	0.032
Triethylene glycol	23	1.28	0.27	1.100	0.034
Dibutyl phthalate	24	0.85	0.21	0.900	0.002
Butyl alcohol	22	1.03	0.10	2.250	0.003
Oleinic acid	19	1.60	0.21	0.697	0.030
Butyl acetic acid	24	0.76	0.32	0.567	0.003

The results from studying the viscoelastic properties of these fluids at a frequency of 74 kHz are given in Table 2 for comparison. We can see that the real values of the shear modulus decline with frequency, while the mechanical loss tangent increases, remaining lower than unity [5].

#### 4. Results and discussion

Relaxation spectrometry is based on the discreteness of fluids and solid structures, and therefore the discreteness of relaxation processes. The latter are associated with different forms of the thermal motion of structural elements in subsystems, i.e., with the discrete spectrum of molecular mobility. Characteristic relaxation time  $\tau_i$  in the discrete spectrum of each relaxation process depends on the temperature, according to the familiar Boltzmann–Arrhenius equation [3]. Coefficient  $B_i$  for kinetic units of complex nature depends on features of their internal structure. Activation energy  $U_i$  characterizes cohesive forces between the kinetic units and their interactions. For simple kinetic units (atom and molecule), coefficient  $B_i$  is considered the time of one attempt of a particle to overcome the potential barrier during thermal oscillations. The time of one attempt is equal to period of oscillation  $\tau_0$  of a kinetic unit; hence,  $B_i \approx \tau_0 \approx 10^{-12}$  s. Spectra can be measured using both quasi static (stress relaxation) and dynamic (mechanical and dielectric loss) methods. A discrete spectrum and the contributions from individual relaxation transitions to the general process are either calculated from stress relaxation isotherms or determined from the positions of maxima on a continuous spectrum of relaxation times. In polymer physics,  $\alpha$ -relaxation process is considered a transition

from high-elasticity to glassy elastic-solid state under an external mechanical action at different frequencies. Shear elasticity and the transition of ordinary fluids to the elastic state, i.e., mechanical glass-transition, are observed at transition frequencies  $\nu = 10^9\text{--}10^{11}$  Hz, since water and other fluids are characterized by relaxation time  $\tau = 10^{-10}\text{--}10^{-12}$  s. This high-frequency relaxation process in fluids can be considered an  $\alpha$ -relaxation process by analogy with polymers. Along with the  $\alpha$  relaxation process, which proceeds during glass formation, a so called  $\lambda$ -transition or a group of  $\lambda$ -transitions is observed in amorphous polymers above the temperatures of glass formation. This relaxation process is not accompanied by variations in chemical structure (without the breaking of C–C and other chemical bonds). The nature of the  $\lambda$ -relaxation process is associated with the breakdown and recovery of a microvolume physical unit ( $\lambda$  unit) of a molecular network. We hypothesize that dynamic structural microinhomogeneity is a feature of both polymers and fluids, and not only highly viscous but also ordinary, less viscous fluids [5]. In our opinion, there is no fundamental difference between highly viscous and ordinary liquids. There is only a quantitative difference; i.e., the lifetime of clusters in ordinary low viscous fluids is much shorter than in highly viscous fluids. Within the cluster model, the low-frequency viscoelastic relaxation of fluids is due to the breakdown of relatively long-lived clusters (temporal ordered microregions of the structure). The nature of these clusters varies: they form and break down over time. Their lifetimes are short, not because of large particles but by the large number of linked molecules  $z$  in a cluster. The cluster breaks down via a linked molecule–free molecule transition that is similar to a water droplet breaking down as a result of the evaporation of individual molecules. This multistage process is characterized by short relaxation time  $\tau$ . Let us consider the activation energy of a low-frequency viscoelastic relaxation process as temperature-independent by analogy with the  $\lambda$ -relaxation process in amorphous polymers, which characterizes the cohesive force between a cluster and the kinetic unit responsible for this process.

## 5. Conclusion

So, tested liquids possess the constant shear modulus at small angles of shear deformation. The low-frequency relaxation process in liquids concerns to low energy processes and explained by interactions of large molecule groups (clusters). The presented acoustical resonance method is proposed as the most convenient and precise method for determination the shear elasticity modulus for liquids of any viscosities.

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## Дифференциация наночастиц диоксида кремния по размерам акустическим методом

Калашников С. В.<sup>1</sup>, Номоев А. В.<sup>2</sup>, Дзидзигури Э. Л.<sup>3</sup>

<sup>1</sup>Лаборатория физики наносистем Бурятского государственного университета, г. Улан-Удэ, ул. Смолина 24а, e-mail: betch\_kail@mail.ru

<sup>2</sup>Лаборатория физики наносистем Бурятского государственного университета, г. Улан-Удэ, ул. Смолина 24а, e-mail: NomoevAV@mail.ru

<sup>3</sup>Национальный исследовательский технологический университет «МИСиС», Москва, Ленинский пр., 4, e-mail: avrore@gmail.com

**Ключевые слова:** электронный ускоритель, наночастицы, распределение по размерам, фигуры Хладни, фракционирование, ультразвук, сепарация.