ULTRASONIC PROPERTIES OF LIQUIDS, LIQUID CRYSTALS, SUSPENSIONS AND EMULSIONS
The Absorption of Sound in Suspensions Due to the Acoustic Wake Effect

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The absorption of sound in suspensions with particles much smaller than the acoustic wavelength is mainly due to the viscous drag between the fluid and the particles. In addition, viscous asymmetries generated in the flow field by the particles, partially entrained by the acoustic field, contribute to it. Such asymmetries, known as acoustic wakes, are considered in this work to derive the absorption coefficient based on the modification of the slip flow velocity. An experimental study is also presented where the value of the absorption coefficient is determined.

DERIVATION OF THE ABSORPTION COEFFICIENT INCLUDING THE ACOUSTIC WAKE EFFECT

The absorption coefficient in suspensions of rigid particles when \( kR_i \ll 1 \) (being \( k \) the wavenumber and \( R_i \) the particle radius) can be derived from the equation of motion of the particles. The force acting on a spherical particle of radius \( R_i \) in a viscous fluid is described as

\[
F = 6\pi \eta R_i V_i = m_i \frac{du_i}{dt}
\]

where \( u_i \) is the instantaneous velocity of the sphere of mass \( m_i \), \( \eta \) is the dynamic viscosity of the fluid and \( V_i \) the slip flow velocity, defined as the velocity difference between the particle and the fluid at its location \( V_i = u_i - u_f \).

Including this expression in Eq. (1)

\[
\frac{dV_i}{dt} = \frac{V_i}{\tau_i} \frac{du_i}{dt}
\]

Let’s consider an incident wave with a velocity amplitude \( U_0 e^{i\omega t} \) and angular frequency \( \omega \). If we take into account the acoustic viscous wakes generated by suspended particles, the velocity of the fluid at the location of the \( i \)-th particle is described as

\[
u_{ik} = -\frac{3R_k V_k}{2r^2} \left( 1 + \frac{3R_k |V_k|}{8\nu} \right)
\]

with

\[
\nu_{ik} = \frac{3R_k V_k}{2r} \left( 1 + \frac{3R_k |V_k|}{8\nu} \right)
\]

at \( \theta=0^\circ \) (head of the wake) and as

\[
u_{ik} = \frac{3R_k V_k}{2r} \left( 1 + \frac{3R_k |V_k|}{8\nu} \right)
\]

at \( \theta=\pi \) (tail of the wake) on a reference system that oscillates with the acoustic field. In both equations \( \nu \) is defined as the kinematic viscosity of the fluid and \( r \) the distance between the \( i \) and \( k \)-th particle locations. Eqs. (4) and (5) are expanded in the Fourier Series and become

\[
u_{ik} = A_i e^{i(\omega t - \phi_i)}
\]

at \( \theta=0^\circ \) and

\[
u_{ik} = A_i e^{i(\omega t - \phi_i)} + b_i e^{i(2\omega t - \phi_i)} + c_i e^{i(3\omega t - \phi_i)}
\]

at \( \theta=\pi \) with

\[
a_i = -\frac{3R_k U_0 l_k}{2r_0} \left( 1 + \frac{R_k U_0 l_k}{\pi \nu} \right)
\]

\[
b_i = (-1)^i \frac{3R_k U_0 l_k^2}{4\omega \omega_i} q_i
\]

\[
c_i = (-1)^{i+1} \frac{3R_k U_0 l_k^2}{4\omega \omega_i} \left( q_i e^{i(\omega t - \phi_i)} - q_i \right)
\]

where \( q_i \) and \( l_i \) are the particle entrainment and the slip flow coefficients respectively referred to \( i \) and \( k \)-th
particles and $\varphi_1$ and $\varphi_0$, the particle shifts. Then, Eq. (2) becomes a system of two differential equations of motion. Solving this system we obtain an expression for the slip flow velocity

$$V_i(\theta)=V_i(0)\left[1+\frac{i\omega}{(1/\tau_i - i\omega)}\right]e^{i\omega T}$$  \hspace{1cm} (8)

at $\theta=0^\circ$, being $\tau_i$ the particle relaxation time, and

$$V_i(\pi)=V_i(0)\left[1+\frac{i\omega}{(1/\tau_i - i\omega)}\right]e^{i\omega T}$$

(9)

at $\theta=\pi$. From Eqs. (8) and (9) the absorption coefficient is derived from the average rate of the instantaneous energy loss. At $\theta=0^\circ$ (head of the wake) it acquires the expression:

$$2\alpha_0=\frac{6\pi\omega}{(1/\tau_i - i\omega)^2R^2}\left[\left(U_0 + \frac{Ae^{-i\varphi_0}}{-\varphi_0}\right)\right]^2$$ \hspace{1cm} (11)

and at $\theta=\pi$ (tail of the wake):

$$2\alpha_\pi=\frac{6\pi\omega}{(1/\tau_i - i\omega)^2R^2}\left[\left(U_0 + \frac{Ae^{i\varphi_0}}{-\varphi_0}\right)\right]^2 - \frac{48\pi\omega R}{(1/\tau_i - i\omega)^2R^2}\left(M\right)^2$$ \hspace{1cm} (12)

with $M = b'_1 e^{-2(\varphi_1-\varphi_0)} + b''_1 e^{-i(\varphi_1+\varphi_0)}$.

The absorption coefficient takes different values at $\theta=\pi$ and $\theta=0^\circ$. This coefficient is compared to that obtained by Urick [2] for particles satisfying $kR<<1$, as shown in Figure 1 for a spherical glass particle with radius $R=4\mu m$ immersed in air. Urick’s results fully coincide with those ones obtained first by Epstein and Temkin [3].

**EXPERIMENTAL DETERMINATION OF THE ABSORPTION COEFFICIENT DUE TO THE ACOUSTIC WAKE EFFECT**

An experimental study carried out previously by the authors to determine the absorption coefficient in a range of acoustic frequencies between 20Hz and 3kHz [5] is used in this work to determine the absorption coefficient. Spherical glass particles with diameters of $7.9\mu m \pm 0.8\mu m$ and a density $\rho_g=2.4g/cm^3$, immersed in air, were used in the experiment. Acoustic fields with velocity amplitudes varying between 0.1m/s and 1m/s were applied.

From the particle displacements measured directly on the filmed particle trajectories their entrainment was determined. Some experimental values of this coefficient are shown in Table I.

<table>
<thead>
<tr>
<th>Frequency (Hz)</th>
<th>$U_0$ (m/s)</th>
<th>$q_0$</th>
<th>Absorption coefficient at $\theta=0^\circ$</th>
<th>Absorption coefficient at $\theta=\pi$</th>
</tr>
</thead>
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<tr>
<td>100</td>
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<td>0.90</td>
<td>7.89 $10^{-14}$</td>
<td>3.54 $10^{-16}$</td>
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<td>0.10</td>
<td>1.75 $10^{-13}$</td>
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<td>0.95</td>
<td>0.08</td>
<td>1.82 $10^{-13}$</td>
<td>7.46 $10^{-14}$</td>
</tr>
</tbody>
</table>

**REFERENCES**


Research Project supported by CAM "Mecanismos de interacción presentes en la aglomeración acústica de nanopartículas en..."
Cluster Model of Low-frequency Visco-elastic Relaxation in Liquids

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The hypothesis about a micro inhomogeneous structure of liquids has been suggested. It is assumed that in liquids there are fluctuation clusters – dynamic ordered micro volumes. The mechanism of low-frequency visco-elastic relaxation in liquids is probably connected to breaking of the cluster. The energy of activation of this relaxation has been estimated.

INTRODUCTION

Shear elasticity of liquids at high frequencies of the order $10^{10}$ Hz is known for a long time and is explained by the mobility of separate particles (the frequency of the transition from liquid to elastic - solid condition is comparable to the frequency of molecule fluctuation). An astonishing fact established for last years, is the presence of shear elasticity of liquids at low frequencies $10^4$-$10^5$ Hz [1,2]. The detailed systematic research, confirming the existence of low-frequency shear elasticity for all liquids was carried out [3]. Bazaron [3] suggest this transition to be low-frequency visco-elastic relaxation, caused by the collective interactions of large groups of molecules. At the same time, the nature of cooperative movements of the large groups of molecules is not discussed.

In work [4] there was developed an idea that low-frequency relaxation in liquids is similar to the slow $\lambda$ - relaxation process in amorphous polymers, which is observed above their glass temperature and is explained by the break-up of physical micro-volume associated groups of molecular network. It was proposed that, relaxation time of the low-frequency relaxation process in liquids is determined by the lifetime of similar fluctuation of physical units. Any other attempts of interpretation of this phenomenon have not yet been undertaken by now.

This work presents an approximate cluster model of low-frequency transition from liquid state to visco-elastic condition.

Model

On the base of similarity of acoustical behaviour of high-viscous liquids and micro-inhomogeneous media, Isakovitch and Chaban [5] suggested the relaxation theory, according to which high-viscous liquid is micro-inhomogeneous binary medium, consisting of ordered and disordered areas. This theory lay in accordance with the experimental data and successfully explains anomalous absorption and sound velocity dispersion in high-viscous liquids.

Within the framework of the analogous two-level cluster model the physical-mechanical properties of glasses and their melts are described quite satisfactorily [4,5]. Proceeding from these models, we suggest a hypothesis for dynamic structural micro-inhomogeneity to be characteristic not only for high-viscous liquids and glasses, but also for simple liquids with low viscosity, i.e. it is a distinctive feature of all liquids. There is only a quantitative difference between high-viscous and low-viscous liquids; namely, the lifetime of micro inhomogeneties in ordinary low-viscous liquids (such as water and acetone) is significantly less than that in high-viscous liquids (like glycerin).

According to our cluster model, any liquid present micro-inhomogeneous medium, consisting of two dynamic components - of ordered areas (clusters), located in the inhomogeneous disorder matrix. When influenced externally, the clusters subject to reorganization that is expressed in diffusion exchange by fluctuation holes - exited kinetic units between these components. The free fluctuation volume is concentrated in the disorder matrix as holes. A break-off of the kinetic unit (atom or group of atoms) from the cluster indicates the formation of a fluctuation hole, and its addition to the cluster means the hole slamming. The low-frequency visco-elastic relaxation of liquids is caused by dissociation of relatively long-living clusters, which nature is fluctuation: they form and break up with time. The lifetime is great not because of the large size of particles, but owing to a large number $z$ of the connected molecules, included in cluster. The cluster dissociation occurs by transition ”the bonded molecule - free molecule”, reminding the liquid drop dissociation on account of evaporation of separate molecules. Such a multi-stage process is characterized by the large relaxation time $\tau$.

Let us suppose that, as in a case of $\lambda$ - relaxation process in amorphous polymers, the activation energy
of low-frequency relaxation process \( U \) does not depend on temperature. It characterizes the cohesion energy between the cluster and kinetic unit, responsible for this relaxation transition. Relaxation time of process of the cluster dissociation depends on free activation energy: \( F=U-TS \), where \( S \) - entropy of activation [4]. Let cluster consist of \( z \) kinetic units. The lifetime is determined by the equation

\[
\tau = B \exp[(U - TS)/kT]
\]

(1)

Thermodynamic probability of cluster existence \( W \) in the known Boltzman’s equation as a first approximation is natural to assume that

\[
S = k \ln W
\]

(2)

The more number of units in cluster the more probability

\[
W = c^z
\]

(3)

Hence from formulas (1) - (3), we have:

\[
\tau = c^z B \exp(U/kT)
\]

(4)

Factor of proportionality \( c \) is equal to unit, for \( z = 1 \), when "cluster" consists of one kinetic unit, the size \( \tau \) is determined under the formula:

\[
\tau = B \exp(U/kT)
\]

(5)

Where preexponent \( B \) is the time of one attempt of a particle to pass through a potential barrier \( U_i \), or otherwise, period of its fluctuations near equilibrium state \( \tau_0 \) [4].

\[
B \approx \tau_0 \approx 10^{12} \text{ sec.}
\]

Therefore equation of relaxation time (4) gives

\[
\tau = B_i \exp(U/kT)
\]

(6)

Where preexponent \( B_i \) for low-frequency relaxation process appears in \( z \) times more, than in case of high-frequency relaxation process, connected with mobility of a separate particle:

\[
B_i = zB
\]

(7)

By substituting (6) in a condition of a maximum of mechanical losses [4]

\[
\omega \tau_j = 2\pi \nu \tau_j = \epsilon_j
\]

(8)

We receive the following connection between frequency and temperature (in our case \( i=\lambda \)):

\[
v = v_\lambda \exp(U/kT)
\]

(9)

\[
v_\lambda = \epsilon_\lambda / 2\pi B_i
\]

(10)

Accordingly to a known Debye’s ratio for dielectric relaxation in liquids \( c_i \approx 1 \) is condition of a maximum mechanical and dielectric losses (8) for small-scale transitions. For relaxation transitions in amorphous polymers connected to mobility of macromolecule segments (in particular, at \( \lambda \) - relaxation process), the \( c_i \approx 10 \) [4].

**Discussion of results**

Two maxims are found out at 303K and 323K on temperature dependence of tangent mechanical loss angle for vaseline oil at frequency \( v_1 \approx 40 \) kHz [6]. By analogy to polymers it is possible to assume, that two \( \lambda \) - relaxation process (\( \lambda_1 \) and \( \lambda_2 \)) there are in vaseline oil in an interval of temperatures 300-340K, appropriate to two different types of physical units - clusters. It is known that in amorphous polymers observe one or whole group of the \( \lambda \) - transitions with identical activation energies, but with different factors \( B_i \) [4].

The maximum at 283K is found out on temperature dependence of tangent mechanical loss angle for vaseline oil at frequency \( v_2 \approx 74 \) kHz [7].

We receive the following approached estimation of activation energy of the low-frequency visco-elastic relaxation process for vaseline oil, by formula (9)

\[
U = k \ln \left( \frac{v_1}{v_2} \right) \left[ \frac{1/T_1 - 1/T_2}{kT_1/kT_2} \right] \approx 22 \text{kcal/mol}
\]

Thus, the preliminary result of estimation is in the following – the low-frequency relaxation process in liquids concerns to low energy processes (\( U \approx 5 \text{ kcal/mole} \)).

Knowing \( U \), it is possible to estimate the preexponent \( B_i \) for vaseline oil. For this purpose it is necessary to calculate \( v_\lambda = v_1 \exp(U/RT_1) = 7 \times 10^4 \text{ Hz} \)

And to substitute in equation (11)

\[
B_i = \frac{\epsilon_\lambda}{2\pi v_\lambda} \approx 2 \times 10^{-9} \text{ sec}.
\]

According to (6) for one particle \( B \approx 10^{12} \text{ sec} \). The number of units in vaseline oil cluster is \( z = B_i / B = 10^5 \) at \( c_i = 10 \) and \( z = 10^7 \) at \( c_i = 1 \).

**REFERENCES**

Molecular mechanisms of acoustic relaxation processes in propyl alcohols and their water solutions

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The experimental results of n-PrOH and i-PrOH by mean of acoustic spectroscopy are presented. The analysis of observed molecular mechanism is performed.

INTRODUCTION

Many properties of alcohol-water mixtures have been studied extensively [1, 2]. The relay light scattering experiments have been carried out on ethyl, isopropyl, propyl and tr.-butyl alcohols. In these solutions the additional maximums of intensity of light scattering were observed at the following concentrations: \( x_2 = 0.09, 0.06, 0.05, 0.03 \) (\( x_2 \) - moll fractions of alcohol) accordingly. It was found that in isopropyl alcohol-water system with heavy water such a concentration maximum does not exist. It and disappearance of additional maximum is not caused by fluctuations of concentration. The analysis of the data reported in the literature has shown, that the complex mechanism of concentration fluctuations suggests the occurrence of molecular structures such as clusters. However up to the present there is no uniform view on all the complexities of the phenomena observed in these systems.

The aim of this work was to obtain kinetic data for i-PrOH and n-PrOH alcohol-water binary liquid system in a wide range of frequencies.

Methods

In this work deals was we determine the density \( \rho \), the coefficient of shear viscosity \( \eta_s \), sound attenuation \( \alpha \cdot f^{-2} \), and the velocity of sound propagation \( c \) in aqueous solutions of n-PrOH alcohol-water of the following concentration: 0; 0.03; 0.058; 0.135; 0.18; 0.25; 0.5; 1 and in aqueous solutions of i-PrOH alcohol-water of the following concentration: 0; 0.03; 0.058; 0.1; 0.13; 0.15; 0.18; 0.25; 0.5; 1 (moll fractions of alcohol). Sound attenuation was determined by using pulse method technique in the frequency range of 5-2500 MHZ, with the error of (2+5)%. The velocity of sound was measured by using pulse-phase technique with the error of (0.1+0.5)% in the temperature range 293+343K and the frequency range mentioned above.

The methods of these measurements are fully described in [3].

The n-PrOH and i-PrOH alcohols with purity 99.5% were taken from the Chemistry Faculty of Kyiv Taras Shevchenko National University. The water used for preparing the samples was distilled twice.

Result and discussion

The measurements of density and shear viscosity of solutions at temperature 293 K have shown that the density of solutions decrease with increasing of concentration. Besides in concentration range 0 - 0.25 (moll. frac.) the dependence of density on concentration is linear and in the range 0.25-1 (moll. frac.) the essential deviation from linear law was observed.

The dependence of shear viscosity on concentration have shown presence of width maximum at concentration of alcohol near 0.25 (moll. frac.).

The analysis of experimental data obtained from the measurements of sound velocity has demonstrated that it depends on concentration and temperature. At the concentrations of alcohol smaller than 0.058 (moll. frac.) the temperature dependence of sound propagation velocity goes through a maximum. But if the concentration of alcohol is more than 0.058, the maximum disappears and with increasing the temperature the velocity decreases according to linear law. Such behavior of c(T) dependence is caused by structural changes in the solution due to the change of alcohol concentration.

The dependence of sound velocity on concentration goes through a maximum at the concentration \( x_2 = 0.06 \) (moll. frac.). The dependence of velocity value is not symmetrical in relation to this maximum (fig. 1).

The analysis of experimental data has shown, that in the solutions under study the absorption of sound depends on its frequency. This relaxation can be described in [4] by the following expression:
\[ \frac{\alpha}{f^2} = \frac{2\pi^2 c}{c_0^2} \sum \frac{b_i \tau_i}{1 + (\omega \tau_i)^2} + B \]

where \( c \) is the velocity of sound at frequency \( \omega = 2\pi f \); \( c_0 \) is the velocity of sound at \( \omega \tau_{ps} \ll 1 \); \( b_i \) and \( \tau_i \) are relaxation forces and times of \( i \)-th simple relaxation region accordingly; \( B \) is high frequency \( (\omega \tau_{ps} \gg 1) \) limit of quantity \( \alpha/f^2 \).

\[ \frac{\alpha_{M}}{f^2} = 26.3 \frac{\eta}{\rho c^3} \]

The relaxation force \( (b_i) \) for the two regions was calculated by using the expression

\[ b_i = \frac{A_i c_0 f}{\pi}, \quad i=1,2 \]

is presented in table.

<table>
<thead>
<tr>
<th>( T ) (K)</th>
<th>( A_1 ) (10^{-15} m^{-1} c^2)</th>
<th>( A_2 ) (MHz)</th>
<th>( \alpha_{M} f^{-2} ) (MHz)</th>
<th>( f_1 )</th>
<th>( f_2 )</th>
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<th>( b_2 ) (10^3)</th>
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Thus, we can conclude, that the value of \( A \) and \( b \) monotonously decreases with increasing the temperature. Such behavior of this quantity is typical for solutions, where acoustical relaxation is caused by the processes of reorganization of structure or conformational transformations of molecules [5].

REFERENCES

Acoustic relaxation of polymers studied by Brillouin light scattering

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Brillouin light scattering is used for studying the spectrum of density fluctuations of glass forming polymers in the frequency range 0.3-30 GHz. The systems investigated, i.e. polycrylates, polybutadiene and epoxy resins, show two distinct relaxation processes. The one is the structural relaxation related to cooperative molecular motions, and the second is a thermally activated process related to intra-molecular motions. This scenario is confirmed by the results of dielectric and inelastic x-ray scattering investigations performed in the same samples. The temperature behavior of the structural relaxation is compared with the predictions of the mode-coupling theory of supercooled systems.

Brillouin light scattering (BLS) is a powerful non-destructive technique for investigating the viscoelastic properties of polymers in the hydrodynamic (low $q$) limit. It does not need the use of transducers for generating and detecting acoustic waves since it consists of inelastic scattering of light by thermally excited acoustic modes. Moreover it operates in the hypersonic frequency region ($\sim$ 0.3 - 30 GHz), difficult to be accessed by more traditional ultrasonic techniques. This frequency region has been recently shown to be relevant for polymers and, more in general, for glass forming systems since it is the scenario of a dynamic transition occurring in the supercooled state of matter, described by the mode coupling theory (MCT) [1]. In this region, the divergence of the structural relaxation time starts to occur for decreasing temperature, connected with a singularity in the nonergodicity parameter (Debye-Waller factor), responsible for the structural arrest, i.e. for the glass transition of the system. In real systems, this scenario is complicated by the existence of different molecular motions corresponding to different characteristic relaxation times, whose nature is still not completely understood. Polymers exhibit a number of such relaxation phenomena which, in some cases, can be related to the local rearrangement of side groups. In the high $q$ limit of neutron scattering investigations, it has been possible to single out the contribution of the structural relaxation and show that it is consistent with the predictions of MCT [1]. In this paper we try to extend this result to the hydrodynamic limit of BLS.

The systems investigated are polymethylacrylate (PMA, $T_g$=283K) [2], polyethylacrylate (PEA, $T_g$=250K) [2], polybutylacrylate (PBA, $T_g$=203K) [3], polybutadiene (PB, $T_g$=178K) [4-6], diglycidyl-ether of bisphenol A (DGEBA $T_g$=258K) [7].

Brillouin spectra were collected starting from the liquid down to the glassy state using a Sandercock type (3+3)-pass tandem Fabry - Perot interferometer. Polarized ($I_{//}$) and depolarized ($I_{\perp}$) spectra were recorded in the back-scattering geometry in order to obtain the isotropic spectrum ($I_{\rho\rho}$) by a simple subtraction procedure [7]. This procedure is illustrated in Fig.1 for the case of polybutadiene at $T = 270$ K. The spectrum of density fluctuations can be written as:

$$I_{\rho\rho} (\omega) = \frac{I_{//}}{\omega} \text{Im} \left\{ \frac{1}{\omega^2 \rho / q^2 - M' (\omega)} \right\}$$  \hspace{1cm} (1)

where $\rho$ is the average mass density, $q$ is linked to the wavenumber of the incident light $k_i$ and to the refractive index of the medium $n$ by the relationship $q=2n k_i$, and $M(\omega)=M' (\omega)-iM'' (\omega)$ is the longitudinal acoustic modulus. The information on the dynamics of the system is now included in the frequency behavior of the longitudinal modulus. If a single channel exists for the exchange of energy between acoustic phonons
and molecular motions, a single dispersion of the modulus can be found, which can be described by a Cole-Davidson relaxation function:

\[ M(\omega) - M_\infty = \frac{M_0 - M_\infty}{(1 + i\omega\tau)^\beta} + i\omega\eta L \]  

(2)

where \(M_0\) and \(M_\infty\) are the low and high frequency limits for the modulus, respectively, \(\tau\) is the relaxation time, \(\beta\) the stretching parameter and \(\eta_L\) the unrelaxed longitudinal viscosity. In previous investigations BLS spectra have been fitted by Eq.1 and 2, assuming a single relaxation process. This was supposed to be the structural relaxation, which is responsible for the glass transition. As a result of this analysis, the nonergodicity parameter of our systems (Fig.2) show a flat behavior, with no evidence of a critical temperature in the supercooled phase.

**FIGURE 2.** Temperature dependence of the nonergodicity parameter of different polymers obtained from fitting Brillouin spectra with a single relaxation function.

More recently, evidence has been given of the coupling of density fluctuations with fast relaxations of intramolecular nature. A bimodal relaxation function has been thus introduced for taking into account both processes:

\[ M(\omega) - M_\infty = \frac{M_\alpha - M_\infty}{(1 + i\omega\tau_\alpha)^\beta_\alpha} + \frac{M_0 - M_\infty}{(1 + i\omega\tau_\beta)^\beta_\beta} + i\omega\eta L \]

where the label \(\alpha\) is used for the structural relaxation and \(f\) for the fast relaxation of intramolecular nature. Due to the large number of free parameters, a fit of BLS spectra by use of the bimodal relaxation function requires some parameter to be independently determined through different techniques. In the case of DGEBA we used the shape parameters obtained from dielectric spectra [7]. The nonergodicity parameter obtained by this procedure is shown in Fig.3. A decrease with temperature can be seen, resembling the square root behavior predicted by the MCT.

**FIGURE 3.** Nonergodicity parameter of PB and DGEBA obtained by fitting Brillouin spectra with a bimodal relaxation function.

Unfortunately, in the high frequency region the quality of the data is not sufficient to reveal the possible presence of a singularity. More favorable was the case of PB where we took advantage of inelastic x ray spectra (IXS) [4-7] extending the spectrum of density fluctuations up to about 2THz. The joint analysis of BLS and IXS give the nonergodicity parameter reported in Fig.3, where a square root singularity is well evidenced, with a critical temperature of 224±5K, close to 216K previously obtained in the high \(q\) limit by neutron scattering experiments.

In conclusion, the temperature behavior of the nonergodicity parameter determined from BLS spectra in the hydrodynamic limit are consistent with the predictions of MCT. This result highlights that the MCT is able to describe also the dynamics of complex systems, such as supercooled polymers, provided that the effect of fast secondary relaxations is properly taken into account.

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Observation of Pseudocapillary and Rayleigh Waves Propagating on Gels

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Surface-wave propagation was studied around sol to gel transition temperature in agarose and kappa-carrageenan solutions. The existence of two surface modes on gels, pseudocapillary and Rayleigh waves, was theoretically predicted, and experimentally demonstrated by the measurements of surface-wave velocity at the frequency of 400 Hz. The restoring force of pseudocapillary wave was surface tension coupled with shear elasticity, and the velocity of the pseudocapillary wave was almost two times that of the Rayleigh wave which emerged when shear-elasticity force exceeded surface-tension force. The theory predicts that the pseudocapillary wave radiate shear wave into the bulk of gel. This shear wave was directly observed by visualizing the propagation using a stroboscopic photoelasticity technique.

1. Introduction

Surface wave propagation on gelling materials has received much interest concerning the nature of restoring force. Onodera and Choi predicted that two surface modes, pseudocapillary and Rayleigh waves, can propagate on gel by analyzing a dispersion relation with taking both shear elasticity and surface tension into consideration. We have shown the direct experimental evidence of the two surface modes on agarose and kappa-carrageenan gels by measuring the phase velocity of both modes in accordance with the theoretical prediction. The velocity of the pseudocapillary mode was smoothly connected to that of the pure capillary mode when the measurement was carried out during the sol to gel transition. The Rayleigh mode emerged when shear-elasticity force exceeded surface-tension force. The Rayleigh mode grew to be dominant and the pseudocapillary mode disappeared as the gelation proceeded. We have also demonstrated the radiation of shear waves radiated from the pseudocapillary mode using a stroboscopic photoelasticity imaging.

2. Experiment

Pulsed surface waves excited with a piezo-bimorph transducer were measured using a laser beam deflection from a sample surface. A one-cycle signal of 500 Hz was applied to the transducer so as to gain a high resolution in time. A position sensitive photodiode detects a deflection angle which gives a waveform proportional to the surface gradient. The phase shift of the waveform as a function of propagation distance gives the velocity of the surface waves. The experiment was performed with decreasing temperature from 42°C to 18°C at a constant rate.

A still image and slow-motion pictures of shear waves propagation were realized using a stroboscopic photoelasticity technique in agarose gels. Shear waves in the gel induces a birefringent effect, which rotates the polarization angle of an incident light pulse. A still image was obtained by synchronizing the timing of the light pulse and surface waves with a constant delay time.

3. Results and discussion

Typical oscilloscope tracings observed at a distance of 8 mm from the transducer in 0.5 % agarose are shown in Figs. 1 (a) to (c), indicating the transition of the mode types. Figure 1 (a) represents pseudocapillary waves observed at 35.0°C at which temperature gelation process has already started but surface tension rather than elasticity dominates the restoring force of the surface waves. In Fig. 1(b), Rayleigh waves emerge behind the pseudocapillary wave in the time axis at 27.5°C. The Rayleigh waves are dominant below 25°C and increase in amplitude as decreasing temperature. Figure 1(c) denotes typical Rayleigh waves observed at 18.2°C which showed no dispersive behavior.

The phase velocities measured are shown in Fig.2. The solid and open circles denote the velocities of the pseudocapillary and Rayleigh waves, respectively. The velocity above 38°C, the sol-gel transition temperature, is almost constant, indicating the surface mode in this range has a pure capillary wave.
nature. The velocity increases with decreasing temperature below 38°C, which results from the emergence of shear elasticity due to gelation. The velocity of another branch, the Rayleigh waves, also increases with decreasing temperature, though the degree of the increase is smaller. According to the theory of Onodera and Choi, the velocities of the pseudocapillary mode and the Rayleigh mode are approximately given by

\[ v_c = \sqrt{\frac{\gamma k + 4G}{\rho}} \]  
\[ v_R = 0.955 \sqrt{\frac{G}{\rho}} \]  

Here \( \gamma \) is surface tension, \( k \) is wavenumber, \( G \) is shear elasticity and \( \rho \) is density. The Rayleigh mode emerges when shear elasticity develops and exceeds the critical value of \( (\gamma \omega)^{1/3} \), where \( \omega \) is angular frequency. We have fitted the eq.(2) to the experimental values of Rayleigh wave velocity, and obtained the values of shear elasticity as \( G=1.1 \times 10^4 (T-T_0) \) Pa where \( T_0=38^\circ C \). Using these values we calculated the velocity of pseudocapillary mode with eq.(1) and the calculated curve is represented in Fig.2. The agreement with the experimental data is fairly good.

The theory predicts that pseudocapillary mode radiates shear waves into the bulk of a gel. Figure 3 shows a photoelastic image of shear waves in agarose gel at 31.7°C. The inclined straight wavefronts are ascribed to the leaked shear waves, and the circular wavefronts to the shear waves excited by the transducer.

In conclusion, the existence of two surface-wave modes has been demonstrated in accordance with the theory.

REFERENCES
Acoustical Investigation of Rheological Properties of Polymer Liquids

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Results of low-frequency shear elasticity investigations of homological range of polymethylsiloxane (PMS) and polyethylsiloxane (PES) liquids are presented. The resonance acoustical method with piezoquartz resonator has been used. It was shown that the value of PMS modulus of shear elasticity is increased with molecular weight rising, and tangent of mechanical-loss angle passes the maximum value being smaller than unity. In accordance with Maxwell’s rheological model it means, that a relaxation frequency of these liquids is lower than the experiment one (74 kHz). As for PES, with increasing of chain number the shear elasticity modulus is decreased and after the minimum value risen. The tangent of mechanical-loss angle is smaller than unity for liquids with small chain number. However as the latter is risen the former is increased and became more than unity. Consequently the relaxation frequency of PES-liquids passing experiment frequency goes towards a range of high frequencies.

INTRODUCTION

Investigation of shear mechanical properties of liquids is one of the direct approaches to the study of the basic problem of physics of liquids – the nature and character of the processes of rearrangement of intermolecular structure. In the studies of the problem of structural relaxation of liquids, the deviation from Newtonian behavior is of prime interest. Earlier it was shown that all liquids, regardless of their viscosity and polarity, exhibit complex shear elasticity at the frequencies of shear oscillations about 10^5 Hz [1-3]. According to the existing concept of the nature of liquids, this effect must be observed only at the frequencies of 10^10 – 10^12 Hz evaluated by the frequency of liquid particle jumps from the temporary equilibrium states [4]. It is also assumed that the shear elasticity of liquid should be of magnitude of the order of the shear elasticity of a corresponding solid. Investigations of low-frequency shear elasticity of liquids by the resonance method using of a piezoelectric quartz device showed that this phenomenon is unrelated to the properties of the boundary layers of liquid, since there is no dependence of the shear modulus on the thickness of the liquid interlayer [3]. The fact that the revealed phenomenon is a bulk property of liquid confirms the possibility of the shear wave propagation in liquid.

METHOD

If a uniform layer of viscoelastic liquid is spread upon a horizontal surface of piezoelectric quartz plate executing tangential oscillations, standing shear waves should arise in this layer. Parameters of the resonance curve of the piezoelectric plate will depend on the thickness of the liquid layer. However, in the experiment it is difficult to achieve the uniformity in thickness of the liquid layer because of the edge effects and to take into account their influence on the measurements. Therefore, in our experiment the liquid was confined between the piezoelectric plate and a strap.

It is assumed that the coupling through the liquid interlayer is low, then under tangential displacements of the upper face of piezoquartz, the liquid interlayer is subjected to shear deformations, but the strap is at rest practically. Under these conditions, for the real and imaginary components of the complex shift of the frequency, the following relations are obtained [3]:

\[
\Delta f' = \frac{SG\beta}{4\pi^2 Mf_o \cos \theta} \cdot \frac{\sin 2\beta H - \tan \frac{\theta}{2} \sin 2\beta H \cdot \tan \frac{\theta}{2}}{\sin 2\beta H \cdot \tan \frac{\theta}{2} - \cos 2\beta H}
\]

\[
\Delta f'' = \frac{SG'\beta}{4\pi^2 Mf_o \cos \theta} \cdot \frac{\sin 2\beta H \cdot \tan \frac{\theta}{2} + \sin 2\beta H \cdot \tan \frac{\theta}{2}}{\sin 2\beta H \cdot \tan \frac{\theta}{2} - \cos 2\beta H}
\]

where \( G' \) and \( G'' \) are the real and imaginary shear moduli of liquid, \( S \) is the area of the strap, \( H \) is the thickness of the interlayer, \( M \) is the mass of the piezoquartz, \( f_o \) is its resonance frequency, \( \tan \theta = G''/G' \) is the tangent of mechanical loss angle, and \( \beta \) is the attenuation coefficient. Figure 1 shows the theoretical dependences of \( \Delta f' \) and \( \Delta f'' \) on the thickness.
of the liquid interlayer for $G' = 10^6 \text{ dyn/cm}^2$ and $\tan \theta = 0.3$. The analysis of these expressions gives three methods of determination of the $G'$ and $\tan \theta$. The first method is connected with the wave propagation with the length of wave

$$\lambda = \frac{1}{f_0 \cos (\theta / 2)} \sqrt{\frac{G'}{\rho \cos \theta}}.$$  

The second method is based on the determination of the limit shift of frequencies $\Delta f'_{\infty}$ and $\Delta f''_{\infty}$ at $H \gg \lambda$:

$$\Delta f'_{\infty} = \frac{SG'}{2\pi Mf_0 \lambda \cos \theta}, \quad \Delta f''_{\infty} = -\Delta f'_{\infty} \cdot \tan(\theta / 2).$$

The third method is realized at $H \ll \lambda$, and equations for $\Delta f'$ and $\Delta f''$ become simplified:

$$\Delta f' = \frac{SG'}{4\pi^2 Mf_H}, \quad \Delta f'' = \frac{SG'}{4\pi^2 Mf_H} \tan \theta = \Delta f' \tan \theta.$$  

All these methods give satisfactory agreement of results. Comparison the values of shear moduli obtained by the third methods [5,6] is shown that the third method is more precise in determination of shear modulus.

**RESULTS**

Investigation of shear elastic modulus and the tangent of the mechanical loss angle of homological range of polymethylsilsloxane and polyethilsloxane polymer liquids was carried out using the third method when the thicknesses of the liquid interlayer being much less than the shear wavelengths ($H \ll \lambda$). The piezoelctric crystal was of X-18.5° cut with the mass $M = 6.28 \text{ g}$. Poisson’s ratio at its working surface is equal to zero. The resonance frequency of the quartz is 74 kHz, and its size is 34.7x12x5.5 mm$.^3$. The strip area is $S = 0.2 \text{ cm}^2$. The temperature of experiments $T$, values of the real shear modulus $G'$, tangents of the mechanical loss angle $\tan \theta$ and liquid viscosity $\eta$ are presented in Table 1.

**Table 1.** Low-frequency shear elasticity modulus, tangent of mechanical loss angle and viscosity of PES and PMS liquids

<table>
<thead>
<tr>
<th>$t \degree C$</th>
<th>$G' 10^6$ \text{ dyn/cm}^2</th>
<th>$\tan \theta$</th>
<th>$\eta$, P</th>
</tr>
</thead>
<tbody>
<tr>
<td>PMS-25</td>
<td>24</td>
<td>0.22</td>
<td>0.35</td>
</tr>
<tr>
<td>PMS-100</td>
<td>23</td>
<td>0.6</td>
<td>0.5</td>
</tr>
<tr>
<td>PMS-200</td>
<td>22</td>
<td>0.86</td>
<td>0.55</td>
</tr>
<tr>
<td>PMS-400</td>
<td>23</td>
<td>1.24</td>
<td>0.75</td>
</tr>
<tr>
<td>PMS-900</td>
<td>22</td>
<td>1.35</td>
<td>0.8</td>
</tr>
<tr>
<td>PMS-5384</td>
<td>22</td>
<td>2.12</td>
<td>0.6</td>
</tr>
<tr>
<td>PMS-20000</td>
<td>23</td>
<td>2.36</td>
<td>0.55</td>
</tr>
<tr>
<td>PMS-52000</td>
<td>24</td>
<td>2.6</td>
<td>0.5</td>
</tr>
<tr>
<td>PMS-509000</td>
<td>23</td>
<td>6.7</td>
<td>0.15</td>
</tr>
<tr>
<td>PES-1</td>
<td>23</td>
<td>9.83</td>
<td>0.11</td>
</tr>
<tr>
<td>PES-2</td>
<td>24</td>
<td>4.81</td>
<td>0.63</td>
</tr>
<tr>
<td>PES-3</td>
<td>24</td>
<td>3.45</td>
<td>0.87</td>
</tr>
<tr>
<td>PES-4</td>
<td>23</td>
<td>2.96</td>
<td>2</td>
</tr>
<tr>
<td>PES-5</td>
<td>24</td>
<td>5.9</td>
<td>6.6</td>
</tr>
</tbody>
</table>

Table 1 shows that the value of shear elasticity modulus of PMS liquids increase with viscosity or molecular weight rising, and the tangent of mechanical-loss angle passes the maximum value being smaller than unity. In accordance with Maxwell’s rheological model relaxation frequency of liquid is $f_{rel} = f_0 \tan \theta$. So it means, that the relaxation frequency of these liquids is lower than the experiment one. Table 1 also shows that for PES the shear elastic modulus decreases with viscosity increasing and after the minimum value rises. The tangent of mechanical-loss angle is smaller than unity for low-viscosity liquids. However as the latter is risen the former is increased and became more than unity. Consequently the relaxation frequency of PES-liquids passing experiment frequency goes towards a range of high frequencies. Such behavior of shear elasticity shows the influence of molecular chain length on viscoelastic parameters of polymer liquids.

**REFERENCES**

Optical Excitation and Detection of Picosecond Acoustic Pulses in Liquid Mercury

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Laser picosecond acoustics is a pulse-echo technique for the excitation and detection of ultrashort acoustic pulses in the 1 GHz-1 THz range, and has been applied to a wide variety of thin solid films. However, the optical generation of picosecond acoustic pulses in liquids has not been studied. Here we describe experiments on thin films of liquid Hg and demonstrate the excitation and detection of picosecond acoustic pulses. This type of study should lead to an understanding of the acoustic generation mechanisms in liquid metals on ultrashort time scales.

Laser picosecond acoustics has proved very successful for investigating the properties of thin solid films and multilayers\cite{1,2}. It has also been applied to solid-liquid interfaces with transparent liquids\cite{3}. However, the optical generation of picosecond acoustic pulses in opaque liquids, in which the sound generation occurs in the liquid itself, has not been studied. In this work we have chosen the liquid metal mercury as a sample. The experiment relies on the use of a tightly focused sub-picosecond pump laser beam to excite electrons in the near-surface region of the Hg film (~10 nm in depth). These hot electrons are expected to diffuse and transfer their energy to the lattice typically within 1 ps. Thermal expansion occurs as the thermal stress propagates out of the laser-heated region within a time governed by the longitudinal sound propagation time across this region. The size of this heated region depends on both electron and thermal diffusion\cite{4}.

The Hg is clamped to a thickness of \( \sim 1.5 \ \mu \)m between two sapphire plates (Z cut). Longitudinal acoustic pulses are excited with sub-picosecond pump optical pulses in the infrared (750 nm). Delayed optical probe pulses of the same wavelength measure the transient changes in reflectance and phase on reflection from the same side of the sample in a Mach-Zehnder interferometer arrangement\cite{5}, as shown in Fig. 1. Optical pulses of duration \( \sim 200 \) fs are derived from a Ti:sapphire mode-locked laser with an 82 MHz repetition rate. Both pump and probe beams were focused to the same \( \sim 35 \) \( \mu \)m diameter spot at low \( \sim 10^6 \) angles of incidence. The pump and probe pulse fluences were 0.44 mJcm\(^{-2}\) and 0.03 mJcm\(^{-2}\), respectively. We estimate that the pump pulses induce a maximum transient temperature change of \( \sim 70 \) K in the Hg film. Variations in reflectance and phase of the probe beam are measured by monitoring the quantities \( \rho = \delta R / 2 R \) and optical phase \( \delta \phi \), where \( R \) is the reflectivity. The optical phase is obtained from the difference between the signals from the photodiodes in Fig. 1\cite{5,6}. The relative amplitude change \( \rho \) and phase change \( \delta \phi \) are related to the complex reflectance \( r \) by the equation \( \delta r / r = \rho + i \delta \phi \).

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure1.png}
\caption{Mach-Zehnder interferometer set-up.}
\end{figure}

The results for the variations of \( \rho \) and \( \delta \phi \) are shown in Fig. 2. The acoustic echoes in reflectance \( (\rho) \), \( \sim 100 \) ps in duration, have an approximately Gaussian shape, whereas the echo in phase has a step-like shape. These shapes are characteristic of the expected unipolar strain pulse shape that arises because of the greater
acoustic impedance of the sapphire. Also evident in both plots is a signal at \( t = 0 \) corresponding to a sudden temperature rise and subsequent decay owing to thermal diffusion. From the known longitudinal sound velocity for liquid Hg[7], 1450 m/s, we can determine the thickness of the Hg as 1.45 \( \mu \text{m} \) from the echo time. Measurements were also made at the time corresponding to the second echo, and the two echoes for \( \rho \) are shown in the inset of Fig. 2, with the background variation subtracted. From the ratio of the Fourier transforms of these echoes, we can derive the acoustic attenuation as a function of frequency[1]. The data (obtained up to \( \sim 7 \) GHz) can be fitted by the equation \( \alpha = A + B f^2 \). We find \( B = 9000 \text{ m}^{-1}\text{GHz}^{-2} \), a value in reasonable agreement with lower frequency determinations (<1 GHz) in the literature[7]. The non-zero value found for \( A = 102000 \text{ m}^{-1} \) might be an artifact of the choice of acoustic reflection coefficient (0.387) from the Hg/sapphire boundary. The value of \( A \) only affects the echo height, not the echo shape.

**FIGURE 2.** Experimental \( \rho \) and \( \delta \Phi \) variations for Hg. Inset: 1st and 2nd echoes in \( \rho \) (solid lines) and a theoretical fit (dotted line) to the 1st echo.

Armed with the value of the constant \( B \) we can proceed to try to model the echo shapes by assuming some form for the initial stress pulse shape and propagating the pulses according to the measured attenuation. This has been done for \( \rho \) in the inset of Fig. 2 assuming that the generation mechanism is the simple thermoelastic one in the absence of any diffusion. The theory for detection was based on that described elsewhere[1,6]. We can account reasonably well for the observed pulse width, but the slight asymmetry and appearance of a trailing edge is not explained by the theory. A similar discrepancy is found for the phase data. In fact it is easy to show for the present experimental geometry that the phase signals are approximately equal to the integral of the reflectance signals, and therefore the phase data here do not provide any significant new information about the strain pulse shape. The phase signals are dominated by the interface displacement variation, and the reflectance signals are in fact proportional to the strain pulse shape itself (owing to the constrained elastic boundary condition and to the fact that the acoustic wavelength is much greater than the optical penetration depth). The fit in Fig. 2 is therefore not sensitive to the choice of photoelastic constants for Hg, which to our knowledge have not been measured.

In order to verify that the asymmetry was not a nonlinear effect, we repeated the measurements for different values of the pump fluence, down to 10 times smaller than that used above. We could not detect any significant change in the acoustic pulse shape. The slight asymmetry may be related to the heat conducted to the sapphire substrate from the Hg during the acoustic pulse generation process, and to the resulting strain generation in the sapphire. We are at present in the process of modelling the effect of both thermal and electron diffusion to determine their effect on the acoustic pulse shape. Experiments on thinner films would also help elucidate further the picosecond acoustic generation mechanisms in liquid Hg.

**REFERENCES**

The propagation of ultrasonic waves in magnetic liquids: A comparison with theory

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The investigation of ultrasonic waves propagation in water-based magnetic liquid EMG-605 are presented. The measurements of velocity and attenuation of ultrasound were carried out as a function of magnetic field strength and the angle between the wave and the direction of magnetic field. The experimental results were compared with the predictions of existing theoretical models.

INTRODUCTION

Magnetic liquids are homogeneous colloidal suspensions of ferromagnetic particles in a carrier liquid. Typically, the diameter of the magnetic particles in the suspension ranges from 50 to 100 Å. To avoid coagulation they are coated with a surface-active dispersive medium. However, microscopic observations of magnetic liquids in DC magnetic field show that a certain amount of colloidal particles forms aggregates (clusters) which — especially in water based ferrofluids — tend to join into a chain-like structure as long as hundreds nanometers. This internal microstructure enhances stiffness of the liquid, induces anisotropy of its mechanical properties, and contributes to the dissipation of energy due to interaction of clusters with the surrounding liquid.

THEORETICAL BACKGROUND

Hydrodynamic equations for ferrofluids have been given in terms of local magnetization \( m(r,t) \) as an extra hydrodynamical variable independent of the usual variables such as pressure, density, temperature and velocity. Parsons [1] has interpreted the direction of \( m \) as a nematic-like degree of freedom with \( m = mn \) where \( n \) is a unit vector (the director) which lies along the average orientation of the magnetic easy axis of the grains. He showed that the sound velocity and attenuation are anisotropic and have \( \sin^2 2\theta \) dependence either in the velocity or attenuation. Assuming the anisotropy of viscosity tensor the anisotropy of attenuation of the ultrasound has the form \( c_1 + c_2 \cos^2 \theta + c_3 \cos^4 \theta \) [2]. If the external magnetic field is strong enough, the ferrofluid particles tend to form stable chains parallel the direction of magnetic field \( H \). The vibrations of such chains under the influence of ultrasonic wave give rise to additional damping of sound [2] and change the observed anisotropy in ultrasound velocity [3].

In order to describe the dependence of the ultrasound propagation on the magnetic field strength we have developed two-phase model of magnetic liquid. The model takes into account mutual interaction of clusters with free liquid producing attenuation and dispersion of waves for transversally isotropic system [4].

RESULTS AND ANALYSIS

Measurements of absorption and velocity were carried out using the Matec Pulse Echo-Overlap technique. In order to measure the effect of the magnetic field on the velocity and attenuation of ultrasonic wave the measuring cell was placed between pole pieces of electromagnet which yielded a maximum field of 1 T. A description of experimental setup can be found elsewhere [5].

The measurements were carried out in a magnetic liquid denoted as EMG-605 (produced by Ferrofluidics Inc.) consisting of magnetite particles \( \text{Fe}_3\text{O}_4 \) suspended in water. The particle distribution was a normal distribution with a maximum at 100 Å.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{ultrasonic_velocity_attenuation.png}
\caption{Ultrasonic velocity (open circles) and attenuation (closed circles) as a function of magnetic field strength. The solid and dash lines show predictions of two-phase model [4] for velocity and attenuation, respectively.}
\end{figure}
Fig. 1 shows the results of measurements of the velocity and attenuation as a function of the magnetic field strength carried out in 50 °C at 1.18 MHz. It can be seen that the velocity increases monotonically but attenuation approaches maximum value and then drops to the level observed for the case of no magnetic field. Solid and dash lines represent predictions of our two-phase model of ferrofluid. A good quantitative agreement has been obtained for the velocity results. For attenuation two-phase model leads to the values significantly lower then those obtained from experiment but correctly predicts the shape of the attenuation curve.

The angular dependence of ultrasonic velocity and attenuation for two values of magnetic field strength are shown in Fig. 2. The measurements were carried out for $T = 20$ °C and $f = 4.37$ MHz. The theoretical predictions for the velocity results (solid lines on graphs on the left) were calculated as the sum of $\sin^2 \theta$ behavior due to $\delta n$ dynamics [1] and $\cos^4 \theta$ behavior due to chain vibrations [3]. The attenuation results were analyzed in terms of Taketomi’s theory [2]. The solid lines (graphs on the right) represents the sum of attenuation due to rotational motions of the clusters and translational motions of the cluster chains. Both contributions are also shown separately as the dash and dotted lines, respectively. It should be noted that for weak magnetic field the rotational component is much bigger then translational while for the strong magnetic field both components have comparable order of magnitude. It confirms the fact that cluster chains start to form in rather strong magnetic fields.

ACKNOWLEDGMENTS

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Ultrasonic Investigations of Aqueous Solutions of α- and β-Cyclodextrin with Some Surfactants

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Measurements of velocity and absorption of ultrasonic waves in aqueous solutions of α- and β-cyclodextrin (chemical compounds which are able to form inclusion complexes) with some surfactants were carried out at different temperatures and concentrations. The frequency range from 1 MHz to 150 MHz was covered by resonator and pulse methods. On the ground of these measurements, according to the principles of ultrasonic spectroscopy, the occurrence of one or two ultrasonic relaxation processes has been established. Explanation of the molecular origins of the relaxation processes has been proposed.

Keywords: cyclodextrins, surfactants, ultrasonic spectroscopy, relaxation processes

INTRODUCTION

Cyclodextrins (CDs) are known to form so-called inclusion complexes by capturing a number of compounds into their cavities without covalent bonds, e.g. \cite{1}.

It has been demonstrated, e.g. \cite{2-4}, that the addition of the CD to an aqueous solution of a surfactant affects dramatically the physicochemical properties of the solution because of the screening the hydrophobic moieties of the surfactant molecules from contact with the surrounding aqueous media by CD molecules.

The ultrasonic spectroscopy technique is an important tool for elucidation of basic solution processes and reaction mechanisms occurring in the microsecond to nanosecond range \cite{5}. One such area still not well understood is the inclusion of guest molecules by CDs in their cavities.

EXPERIMENTAL PART

Measurements of the absorption coefficient, \( \alpha / f^2 \), in aqueous solutions of α-CD (Aldrich) and β-CD (Aldrich) with sodium alkyl sulfates \( \text{C}_n\text{H}_{2n+1}\text{OSO}_3\text{Na} \) (n=6, 8, 10, 12, 14) (Aldrich) were performed in the frequency range 1 MHz to 150 MHz at 15, 25, 35 and 45°C and at the concentration of 0.04 M and 0.01 M of each of the components for α-CD and β-CD, respectively. At 25°C the measurements were also made for 0.01, 0.02 and 0.03 M equimolar aqueous solutions of α-CD with sodium alkyl sulfates.

The measurements were made by means of the resonator and pulse methods in the frequency range 1-10 MHz and 10-150 MHz, respectively.

The parameters of the theoretical equations

\[
\frac{\alpha}{f^2} = B + \sum_{i=1}^{l} \frac{A_i}{1 + (f/f_i)^2},
\]

\[
\mu = 2 \sum_{i=1}^{l} \mu_{\text{ex}} \frac{f/f_i}{1 + (f/f_i)^2},
\]

were adjusted to the measured values of absorption by means of nonlinear regression. The adjusted parameters are: the relaxation frequency, \( f_i \), the relaxation amplitude, \( A_i \), the contribution to the sound absorption from any other processes that may occur at higher frequencies beyond the frequency range measured, \( B \), and the maximum of the excess absorption per wavelength, \( \mu_{\text{ex}} \). \textit{f} is the measured frequency, \( \alpha \) is the ultrasonic absorption, \( \mu = (\alpha/B) \lambda^2 \) is the excess absorption per wavelength \( \lambda \) (\( \lambda = c/f \), \( c \) is the speed of sound), \( l \) is the number of relaxation processes (\( l=1 \) or 2 in our case). The relation between \( A_i \) and \( \mu_{\text{ex}} \) is as follows: \( \mu_{\text{ex}} = f_i A_i (c/2) \).

RESULTS AND DISCUSSION

Representative plots of the dependence of the excess sound absorption per wavelength, \( \mu \), on frequency, \( f \), for α-CD systems are shown in Figs. 1 and 2 (for β-CD systems these plots are similar).

For α-CD the occurrence of two relaxation processes for the surfactants with the decyl, dodecyl and tetradecyl hydrocarbon chains of the sodium alkyl sulfates can be noticed, while only one relaxation process has been found for the hexyl and octyl chains. In the case of β-CD a border between one and two relaxation processes is shifted towards the shorter chains and lies between hexyl and octyl chains.

A linear dependence of \( \mu_{\text{ex}} \) on concentration \( C \) as well as an independence of \( f_i \) with the concentration indicate that the origin of the relaxation is a first-order or a pseudo-first-order process.
\[ \frac{k_{12}}{k_{21}} \]

where \( A_1 \) and \( A_2 \) denote two stages of the inclusion complex, \( k_{12} \) and \( k_{21} \) are the rate constants of the direct and opposite reactions, respectively.

The rate constant \( k_{12} \). This means less steric hindrance of the longer (and more hydrophobic) hydrocarbon chain into the hydrophobic cavity of \( \alpha \)-CD and \( \beta \)-CD. For the short hexyl or octyl chains in the case of \( \alpha \)-CD and the hexyl chain in the case of \( \beta \)-CD (these chains have rather weak hydrophobicity), this kind of penetration does not take place, thus there is no low-frequency relaxation process in the aqueous solutions of \( \alpha \)-CD and \( \beta \)-CD with sodium hexyl sulfate, and of \( \alpha \)-CD with sodium octyl sulfate. This different behaviour of the \( \alpha \)-CD and \( \beta \)-CD solutions should be joined with the dimensions of the cavity, which are greater for \( \beta \)-CD than for \( \alpha \)-CD. This means less steric hindrances when the alkyl chain penetrates the \( \beta \)-CD’s cavity than the \( \alpha \)-CD’s one. It seems that the stability of the inclusion complexes depends mainly on a geometric factor i.e. similarity between the cavity dimensions and the penetrating moiety.

**REFERENCES**


**Table 1.** Some kinetic parameters of the low-frequency relaxation processes for aqueous solutions of \( \alpha \)- and \( \beta \)-CD with sodium alkyl sulfates \( \text{C}_n\text{H}_{2n+1}\text{OSO}_3\text{Na} \) at 25°C.

<table>
<thead>
<tr>
<th>( n )</th>
<th>( K )</th>
<th>( k_{12} \times 10^{-3} \text{[s}^{-1}] )</th>
<th>( K )</th>
<th>( k_{12} \times 10^{-3} \text{[s}^{-1}] )</th>
</tr>
</thead>
<tbody>
<tr>
<td>8</td>
<td>( \cdot )</td>
<td>( \cdot )</td>
<td>32.1</td>
<td>4.33</td>
</tr>
<tr>
<td>10</td>
<td>30.2</td>
<td>3.83</td>
<td>40.5</td>
<td>4.72</td>
</tr>
<tr>
<td>12</td>
<td>56.9</td>
<td>4.94</td>
<td>71.0</td>
<td>5.33</td>
</tr>
<tr>
<td>14</td>
<td>99.4</td>
<td>5.54</td>
<td>112</td>
<td>5.85</td>
</tr>
</tbody>
</table>

The obtained results suggest that the origin of the low-frequency relaxation process is the penetration of the hydrophobic alkyl chain of the surfactant into the cavity of \( \alpha \)-CD and \( \beta \)-CD. The rate constant \( k_{12} \) and the equilibrium constant for reaction (3), \( K = k_{12}/k_{21} \), increase when the alkyl chain becomes longer (Table 1). These facts reflect a deeper penetration of the longer (and more hydrophobic) hydrocarbon chain into the hydrophobic cavity of \( \alpha \)-CD and \( \beta \)-CD. For the short hexyl or octyl chains in the case of \( \alpha \)-CD and the hexyl chain in the case of \( \beta \)-CD (these chains have rather weak hydrophobicity), this kind of penetration does not take place, thus there is no low-frequency relaxation process in the aqueous solutions of \( \alpha \)-CD and \( \beta \)-CD with sodium hexyl sulfate, and of \( \alpha \)-CD with sodium octyl sulfate. This different behaviour of the \( \alpha \)-CD and \( \beta \)-CD solutions should be joined with the dimensions of the cavity, which are greater for \( \beta \)-CD than for \( \alpha \)-CD. This means less steric hindrances when the alkyl chain penetrates the \( \beta \)-CD’s cavity than the \( \alpha \)-CD’s one. It seems that the stability of the inclusion complexes depends mainly on a geometric factor i.e. similarity between the cavity dimensions and the penetrating moiety.
The subject of this paper is the experimental investigation of scattering, of attenuation and velocity of ultrasonic waves at 3 MHz in suspensions of glass globes. Average radius of the particles was 12 micrometers. Volume concentration of particles was varied from 0 up to 55%. Researched energy balance of concentration dependence of attenuation and velocity of ultrasonic waves.

This paper is devoted to the experimental researches of scattering, velocity and attenuation of ultrasonic waves in water suspensions of glass particles. The sondage of suspensions was realized by impact ultrasonic waves with frequency \( \omega R/2 \pi = 3 \text{MHz} \). Precision of measurements is about 1-5%. For all sizes of particles the requirement \( kR < 1 \), where \( k \) - wave number, \( R \) - radius of a particle was maintained.

In the range of small concentrations all kinds of losses ultrasonic energy are additive and additional attenuation coefficient \( \Delta \alpha \) is represented as: \( \Delta \alpha = \alpha_\delta + \alpha_\tau + \alpha_\eta + \alpha_\delta \), where \( \alpha_\delta \), \( \alpha_\tau \), \( \alpha_\eta \), \( \alpha_\delta \) are loss coefficients of ultrasonic energy caused by mechanisms of a scattering, heat exchange, viscous drag and internal process in particles. When the sizes of particles are less than the lengths of thermal and viscous waves excited on a surface of particles at irradiation by ultrasonic waves, these coefficients can be calculated by the formulas [1-3]:

\[
\Delta \alpha = n T 0 c_0^3 \left( \frac{\rho_2 - \rho_1}{\rho_1} \right)^2 \left( \frac{1}{2} \frac{1}{\beta_1} - \frac{1}{\beta_2} \right)
\]

\[
\alpha_\tau = \frac{1}{6} \chi_2 \left( n T c_\parallel < \rho \right) \left( \frac{\rho_2}{\rho_2 - \rho_1} \right)^2 \left( \frac{\rho_2 - \rho_1}{\rho_1} \right)
\]

\[
\alpha_\eta = \frac{12}{\sqrt{2}} m R \omega \eta \left( \frac{\rho_2}{\rho_1} \right)^{1/2} \left( \frac{1}{\rho_1} \right)^{1/2} \left( \frac{1}{2 + (\rho_1 / \rho_2)} \right)
\]

Velocity of ultrasonic waves \( c \) is calculated according to the following expressions:

\[
c = c_{cT} \Delta c_T \Delta c_\eta, \quad c_{cT} = \left( \frac{\rho}{\beta_0} \right)^{1/2}.
\]

\[
\Delta c_T = \frac{1}{2} T c_0^3 \left( \frac{\rho_2}{\rho_1} \right)^2 \left( \frac{\beta_2}{\beta_1} \right)^2 \left( \frac{1}{2} \frac{1}{\beta_1} - \frac{1}{\beta_2} \right)^2
\]

\[
\Delta c_\eta = \frac{1}{2} T c_0^3 \left( \frac{\rho_2}{\rho_1} \right)^2 \left( \frac{1}{2} \frac{1}{\beta_1} - \frac{1}{\beta_2} \right)^2
\]

where \( \rho \), \( \chi \), \( \delta \), \( \beta \), \( \eta \) are the density, isothermal compressibility and viscosity accordingly. Here index 1 designates fluid medium; index 2, solid.

The contribution of the mechanism of scattering to attenuation of ultrasonic waves in suspensions was determined experimentally with the help of the methods designed in the St.-Petersburg University, due to which it was possible for the first time in the world to detect and to measure scattered ultrasonic waves from phantoms [4,5].

\[
\xi = \omega \rho \eta R^2, \quad a = \frac{1}{2} \left( \frac{\rho_2 - \rho_1}{\rho_1} \right)^2, \quad b = \frac{2}{9} \left( \frac{\rho_2 - \rho_1}{\rho_1} \right)^2
\]

\[
\Delta c_T = \frac{1}{2} T c_0^3 \left( \frac{\rho_2}{\rho_1} \right)^2 \left( \frac{1}{2} \frac{1}{\beta_1} - \frac{1}{\beta_2} \right)^2
\]

\[
\Delta c_\eta = \frac{1}{2} T c_0^3 \left( \frac{\rho_2}{\rho_1} \right)^2 \left( \frac{1}{2} \frac{1}{\beta_1} - \frac{1}{\beta_2} \right)^2
\]
The sample was positioned in centre of the cuvette. The axis of radiating and receiving quartzes passed through centre of symmetry of the sample. Pressure amplitude of scattered wave was measured at scattering angle change from 0 up to 140°. After 140° started the field of an overlap of quartzes.

Fig. 1 represents ultrasonic background (1) and directional diagram of scattered waves of a suspension of glass particles (2) at n=0.4 %. The obtained experimental data \( P / P_0 \) allowed to define an indicatrix of scattered ultrasonic wave amplitudes \( J / J_0 \) (3) and to calculate energy balance at distribution of ultrasonic waves in suspensions. For explored suspensions the relation of scattered energy to total losses \( J / \Delta J = 10^{-2} \), consequently the main cause of attenuation of ultrasonic waves in suspensions of glass particles at \( kR < 1 \) are the dissipative losses. The observed data of additional attenuation \( \Delta \alpha \) and of ultrasonic waves velocity \( c \) in suspensions in all range of variation of concentration of particles are represented by the diagrams in Fig.2 and Fig.3. As it is shown on the diagram of Fig.2 it is possible to see three reference fields in the dependence \( \Delta \alpha = f(\% ) \). In the range of small concentrations \( n_0 \in 0.01-10\% \), where practically there are no contacts between particles, \( \partial \Delta \alpha / \partial n \) has linear dependence on the concentration. In this range theoretical straight line A, calculated according to the formula (1), satisfactorily agrees with experimental data. In the range of formation of discrete clusters \( n \in 10-20\% \) concentration coefficient of additional attenuation is \( \partial \Delta \alpha / \partial n \ll \partial \Delta \alpha / \partial n_1 \), and in the range of \( n_1 \gg 20\% \) where infinite clusters appear having fractal structure [6] with Hausdorff dimensionality \( < 3 \), \( \partial \Delta \alpha / \partial n \gg \partial \Delta \alpha / \partial n_1 \).

It is from the graph 1 of Fig.3 that in the range of small concentrations \( n \in 0.1-10\% \) the velocity of ultrasonic waves decreases with growth of concentration of particles: \( \partial c / \partial n \ll 0 \). In the range of concentrations \( n \in 10-20\% \) its value becomes minimum: \( \partial c / \partial n \sim 0 \). At further growth of concentration the velocity of ultrasound starts to increase. Negative concentration coefficient of velocity of ultrasound in the range of small concentrations is most probably explained by a dominant role of additive density of suspension. In this concentration range theoretical values of velocity (curve 2 Fig. 3) satisfactorily agree with experimental data. Calculations and direct observations under microscope have shown that the change of ultrasonic attenuation and velocity is correlated with structural modifications in suspensions.

REFERENCES

Pulse-echo Technique for Speed of Sound Measurements in high-pressure Liquids

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Measurements of the speed of sound in liquids at high pressures provide a simple and accurate method for obtaining fundamental thermodynamic information on the fluid under study. This work describes the design and construction of an ultrasonic cell intended to operate between 230 K and 400 K and up to 70 MPa. Owing to the high sensibility of speed of sound to temperature fluctuations, the apparatus is thermostated with a stability of \( \pm 3 \) mK over the working temperature range. The experimental technique is based on a pulse-echo method, adopted in reason of its high accuracy in time delays measurements, the overall accuracy being limited by the independent determination of the cell length. The experimental setup is currently under development. Preliminary results indicate an achievable accuracy in the speed of sound measurement in the order of \( \pm 0.05\% \).

INTRODUCTION

An accurate measurement of the velocity of sound \( u \) as a function of pressure and temperature can provide useful information about thermodynamic properties of fluids, as density \( \rho \), specific heats at high pressures \( C_p \), and once \( u, \rho \) and \( C_p \) are known for temperatures and pressures of interest, it’s possible to calculate other properties as isothermal and isobaric compressibilities \( (k_t \) and \( k_s))\) and the cubic expansion coefficient \( (\alpha_p)\), where direct measurements are extremely difficult [1].

EXPERIMENTAL APPARATUS AND OBSERVATIONS

An experimental apparatus for the determination of the phase velocity of ultrasonic waves in liquids is under construction in our laboratory.

The core of the system is a small ultrasonic cell (82 mm of length and 43 mm of diameter, see figure 1) provided with two reflectors placed at unequal distances from a single transmitting-receiving piezoceramic transducer (13 mm of diameter and 2 mm thickness) held by clamping rings.

The cell is made of stainless steel, because this material is chemically resistant, has a high reflection coefficient (high acoustic impedance) and a high acoustic attenuation (echo trains from the reflector’s external surface must vanish prior to the generation of the next pulse). To minimize the signal distortions due to reflections in intermediate layers, the transducer and the reflectors are assembled in a rigid structure, and the liquid is directly in contact with the electrodes of the transducer.

Ultrasonic bursts in the 1-10 MHz frequency range are produced by a function generator connected to the transducer.

The complete system will include a circuit designed to create high pressure in the liquid under test, a stainless steel vessel in which the ultrasonic cell will be placed, and a liquid state P.I.D. (Proportional-Integral-Derivative) controlled thermostat with a temperature stability of \( \pm 3 \times 10^{-3} \) K.

FIGURE 1. The ultrasonic cell

At the moment this apparatus operates in deionized water and exploits a simple pulse-echo technique. The transducer is excited with a single five-cycle tone burst with amplitude of 10 V peak-peak and generates two acoustic waves that spread in opposite directions; each wave hits one reflector inducing two sets of echoes. Both the main electrical signal delivered to the transducer and the echoes coming from reflectors are recorded by a digital oscilloscope. The burst period is chosen low enough to obtain
complete decay of the echoes and jet high enough to have the best performances of the storage system. The complete waveform, that correspond to a duration of 100 µs, is digitized at a sampling rate of 500 MS/s. Data, in the form of signal amplitude vs. time vectors, are collected by a computer and echoes signals are extracted. The transit time reference is the time corresponding to the maximum echo amplitude. The computer program cuts ten acoustic cycles around this transit time reference. Each echo is so represented by 238 samples,

\[ V_j(t_i), \quad j = 1, 2; \quad i = 1, \ldots, 238 \]  

where \( V_j(t_i) \) is the voltage associated to echo 1 at time \( t_i \) (see figure 2).

FIGURE 2. The echoes of the first and the second reflector arriving at the transducer.

Signal data vectors are then submitted to a two parameters fit program that minimize the following expression:

\[ F(A, \tau) = [V_j(t_i) - A \cdot V_2(t_i + \tau)]^2 \]  

where \( A \) is an amplitude factor which is required to compensate the greater attenuation suffered by the second reflection and \( \tau \) is the delay existing between the first and the second echo (or \( t_2 - t_1 \)). The aim consists in finding \( A \) and \( \tau \) that cause the best overlapping of the two echoes. Given a calculated delay time \( \tau \), the corresponding value of \( A \) is given from the following expression:

\[ A = \frac{\sum_i V_1(t_i) \cdot V_2(t_i + \tau)}{\sum_i V_2^2(t_i + \tau)} \]  

Obtained a reliable value of \( \tau \) from the fit procedure, the sound speed in the liquid under study is assumed to be:

\[ u_{\text{op}} = \frac{2\Delta L}{\tau} \]  

where \( \Delta L \) is the difference between the acoustic paths traveled by the two echoes (if diffraction effects are neglected, the acoustic path is equivalent to the geometrical distance between transducer and reflector) [2].

To further improve the accuracy in time delay measurements, this apparatus will adopt the phase comparison pulse-echo method. This technique is based on the generation of two consecutive burst signals delayed by an appropriate time \( \tau \) such that the echo of the first pulse traveling the longer path and the echo of the second pulse traveling the shorter path coincide at their arrival at the transducer. The phase difference between the two overlapping echoes is equal to

\[ \Delta \phi = \omega \tau \]  

where \( \omega \) is the angular frequency of the burst. By adjusting this frequency, it is possible to find the so called null frequencies, which cause the two echoes to cancel each other. The null frequencies satisfy the following relation

\[ f_n \tau = n + \frac{1}{2} \]  

where \( n \) is a integer number. The measurement of two successive null frequencies gives the transit time \( \tau \) the overall accuracy being limited by an independent determination of the cell length [3].

REFERENCES


Acoustic Studies of Magnetic Sensitive Polymer Gels

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The paper presents results of experimental studies of acoustic and magnetic properties of ferrogels. The absorption characteristics and dispersion of materials being studied for magnetic field free conditions and subjected to constant magnetic field are discussed.

INTRODUCTION

Ferrogels are soft materials belonging to a class of intelligent media which are studied in relation to their engineering or biomedical applications. Due to the large interest in the materials both experimental and theoretical work is necessary to promote their promising usage\cite{1}.

The purpose of the paper is to present the results of acoustic and magnetic studies of a poly (dimethyl siloxane) ferrogel. The influence of intensity of magnetic field and its direction on magnetic susceptibility and wave propagation parameters are determined and discussed.

EXPERIMENTAL PROCEDURE

Materials. Poly (dimethyl siloxane) gel (PDMS) is prepared from Elastosil 604 A and Elastosil 604 B (Walker Co.) with a magnetic filler added. The component A contains the polymeric material and the cross-linking agent, the component B provides the catalyst with Pt-content. The magnetite filler particles were syntehsised by coprecipitating aqueous solution of FeCl\textsubscript{2} and FeCl\textsubscript{3} in alkaline medium. The obtained precipitate was washed with distillated water. After washing with ethanol and acetone the precipitate was dried to obtain magnetic powder. The magnetite particles were stabilized in the Elastosil 604 A mixture by adding a 1 w/w% palmitic acid (MERCK) as a surfactant. The cross-linking reaction was carried out at ambient temperature for 24 hours to obtain gels. The concentration of the filler particles in the gel was 5, 10, and 15 w/w %. 

Methods. The cylindrical sample of ferrogel wounded with a coil is placed in constant magnetic field. The angle between the symmetry axes and the direction of magnetic field \(H_{dc}\) is controlled. The measurements of magnetic susceptibility as a function of intensity of magnetic field for longitudinal and transversal directions were done through digital electrical inductance meter where its working frequency was kept constant and equal to 1 kHz.

The studies of absorption coefficient versus frequency are performed for magnetic field free material using pulse transmission method and acoustic spectroscopy. The influence of magnetic field on absorption is determined by pulse transmission method in time domain. The changes of phase velocity due to variation of intensity of magnetic field were obtained by continuous wave method with tuned frequency \cite{2}.

RESULTS

The results for real susceptibility in longitudinal and transversal direction are shown in Fig. 1.

![FIGURE 1. Magnetic susceptibility of ferrogel.](image-url)
It is visible that there is no significant change of longitudinal susceptibility \( \chi_\parallel(H_{DC}) \) and in transversal direction the values of susceptibility \( \chi_\perp(H_{DC}) \) is constant up to about 400 kA/m and then sharply decreases. The magnetic characteristic of gel shows a qualitative similarity of its magnetisation with magnetisation of ferrofluids, which can be described by Langevin function.

The results for absorption coefficient as a function of frequency for samples studied without magnetic field are shown in Fig. 2. It is supposed that the observed increase of absorption is due to internal dissipation being the result of friction between elements of polymeric network as well as between pore fluid and the network.

![FIGURE 2. Absorption coefficient vs frequency for magnetic field free conditions.](image)

The influence of magnetic field on absorption for various time periods of the cycles – linear increase and decrease of magnetic field- is presented in Fig. 3.

![FIGURE 3. Changes of absorption vs magnetic field.](image)

For relatively broad range of lower values of intensity of magnetic field it does not influence the absorption coefficient while at about 400 mT it jumps significantly and hysteresis is observed.

The influence of magnetic field on variation of wave velocity is shown in Fig. 4.

![FIGURE 4. Changes of wave velocity vs magnetic field.](image)

Both the variation of absorption and wave velocity with changing magnetic field are probably related to evolution of internal structure of gel caused by rearrangement of magnetic particles within the polymeric network. Further studies of the materials are necessary to explain the observed behavior.

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