

# Application of Acoustic Waves to Investigate the Physical Properties of Liquids at High Pressure

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## 1. Introduction

Monitoring and studying the pressure effect on liquid physical properties are becoming increasingly important in the food (Le Bail et al., 2003), chemical (Schettino et al., 2008), cosmetic (Sonneville-Aubrun et al., 2004) and pharmaceutical industry (Masson et al., 2001). High-pressure research of the physical properties of liquids has been stimulated by the fast development of such technologies as biodiesel production (Demirbas, 2008), high pressure food processing and conservation (Bamberger et al., 1999). High pressure processing enables inactivation of pathogenic microorganisms without decreasing the nutritional values and organoleptic properties. Rheological data provide information on molecular structure of the processed food. The knowledge of viscosity changes with pressure is also very important for food-processing plant design. Viscosity measurement on-line is necessary for control of food quality at different stages of the process.

Knowledge of the effect of pressure on the viscosity of polymer melts containing dissolved gases and on the viscosity of carbonaceous materials used in the impregnation process (Kosinskii, 2009) is also very important. Acoustic measurements offer also a potentially practical manner for the in situ characterization of reservoir fluids (e.g., crude oil) under reservoir conditions of pressure (Ball et al., 2002). The rheological properties of liquid lubricants (Bair et al., 2001) under high pressure determine friction and wear and they are fundamental properties for tribological evaluation of rolling bearings, gears and traction devices. High-pressure technologies (up to 1 GPa) have proved a great potential in modern bioengineering as a method of modification of biotechnological materials. The knowledge of physical properties (e.g., viscosity, compressibility) of treated substance is essential for understanding, design and control of the process technology. Measurement techniques for “in-situ” determining of physical parameters of liquids under high pressure allow insight into the phenomena governing the microstructural modifications occurring in the treated substance. High-pressure transitions in liquids can be investigated by the measurement of the viscosity or the acoustic wave phase velocity in function of hydrostatic pressure.

Pressure is an important parameter in processes of glass making when pressures in regime of some hundreds of megapascals occur e.g., in injection molding or pressure-assisted sintering. Changes in the melt viscosity upon pressurization result in changes in the glass transition temperature and the working regime for glasses (Del Gaudio et al., 2009).

In earth science interesting information can be obtained from the high-pressure rheological investigations of molten minerals (Bingwell et al., 2004). Moreover, oil-based drilling fluids have become widely used in oil industry because of their distinct advantage over water-based drilling fluids. However, unlike water-based drilling fluids, oil-based drilling fluids show significant rheological properties dependence on temperature and pressure. It is highly recommended to measure rheology of the actual mud system at high pressures prior to drilling operations (Zhao et al., 2008).

The properties of water at high pressures are investigated for the purpose of studying the physical chemistry, geophysics, planetology, and the most diverse problems in science and engineering. At pressures lower than 1 GPa, the rheological properties of water, including viscosity, are essential for the investigation of hydrodynamic and heat transfer processes. At present, the rheological properties of water are used in designing power plants of some types, as well as in developing new technologies in the food industry and medicine where, in particular, the shock compression of water has come to be used to lithotripsy (Mineev & Funtikov, 2005).

Direct measurements of the physical properties such as density, compressibility and isobaric heat capacity are very difficult under conditions of very high pressure. The speed of sound is closely linked with these thermodynamic properties and can be measured relatively easily and with high accuracy over wide ranges of temperature and pressure. An understanding of the pressure dependence of sound speed, attenuation, and relaxation frequencies can provide valuable information as to transport quantities such as fluid viscosity and thermal conductivity along with ratios of specific heats. Additionally, sound speed is closely related to derivatives of the equation of state. Therefore, the precision of these derivatives is often substantially better when they are deduce from the speed of sound rather than obtained from the analysis of classical  $pVT$  data.

Up to date, high pressure viscosity measurements were performed only in laboratory conditions, using conventional mechanical methods (Kulisiewicz & Delgado, 2010), developed as early as in the second half of the nineteenth century (Shames, 2002), (Ferguson & Kembrowski, 1991). The conventional mechanical methods followed works of such eminent scientists as Stokes, Navier, Poiseuille, Couette, et al. The common factor of all conventional mechanical methods is their inability to measure the viscosity on-line, without interfering with the industrial process controlled. Since on-line monitoring is necessary in process automation a need for new real-time monitoring methods emerged.

In this work new ultrasonic methods for the measurement of the viscosity of liquids under high pressure are presented (Kielczyński et al., 2008a). These methods employ SH (shear horizontal) surface waves of the Love and Bleustein-Gulyaev (B-G) type. The energy of the SH surface wave is concentrated in the vicinity of the waveguide surface. Thus, the SH surface wave velocity and attenuation strongly depend on the boundary conditions on the waveguide surface which is viscoelastically loaded. Application of these SH surface waves extends considerably range of measuring pressures (up to 1 GPa). Moreover, the viscosity measurement is simplified and can be computerized. This enables on-line measurements of liquid viscosity.

## 2. Mechanical measuring methods for the measurement of liquid viscosity

Among the mechanical methods, the methods using rolling ball (King et al., 1992), falling ball (Nakamura et al., 2005), falling needle (Sha, 1997), and falling cylinder (Schaschke et al., 2008) are the most popular. Rotational viscometers of Couette type (Matveev et al., 2005) form another group of high-pressure viscometers. The critical parts of rotating viscometers are seals. The third group of viscometers is based on the Hagen-Poiseuille formula for capillary flow (Ripple, 1992). Similarly, a modified capillary tube viscometer is a high-pressure extrusion slit die viscometer (Lan & Tseng, 2002). Another type of viscometers is a sliding plate viscometer. In these viscometers, the medium to be tested is charged in between two parallel sliding plates. After shear rate and shear stress are measured, the viscosity can be readily evaluated according to the Newton equation of viscosity (Koran & Dealy, 1999). However, it is very difficult to extend conventional methods to determine the viscosity at high pressure. One of the problems is to control the trajectory of the falling (rolling) ball and to track its movements. The resetting of the sinker or rolling ball also present difficulties. An eccentric fall of the sinker can cause significant errors in determining viscosity based on sinker descent time. Falling sinker viscometers and rolling ball viscometers have very long measuring times at high viscosities. Moreover, capillary type viscometers pose problems with pressure gradients.

Conventional mechanical methods and devices for measuring viscosity of liquids possess many disadvantages:

1. presence of moving parts
2. measurements are tedious and time consuming
3. require special sophisticated equipment
4. large dimensions
5. difficult to computerize

The application of rotary viscometers is limited due to the problems with generated heat and leakage during the transmission of the rotation into high-pressure chamber. Due to inherent limitations, the conventional methods cannot operate in real-time, and are only laboratory methods.

There exist also other methods employing different physical phenomena, e.g., magnetic field (Mattischek & Sobczak, 1997), (Royer et al., 2002) and light scattering (Fukui et al., 2010), for measuring the viscosity of liquids at high pressure. However, they need very complicated equipment and specially developed high-pressure chambers.

This is why, their use for measuring liquid viscosity at high pressure is very limited.

## 3. Ultrasonic methods

### 3.1 Bulk acoustic waves

Due to the disadvantages of the mechanical methods a need for new measuring methods arose. To this end, ultrasonic methods for the measurements of the viscosity of liquids under high pressure were proposed. Ultrasonic waves are mechanical disturbances, propagating in a material medium, at frequencies above 20 kHz. Present day technology enables for routine generation and detection of ultrasonic waves in the frequency range from ~20 kHz to ~2 GHz. However, the frequency range used in acoustic viscosity sensors is usually limited to 1-20 MHz. The ultrasonic methods due to their accuracy and relative simplicity can be applied in the study of liquid state. Ultrasonic velocity and attenuation measurements have proved to be useful in investigations of structures of liquids and interactions between the molecules.

Standing waves (resonators) and travelling waves (waveguides) were used to investigate the rheological properties of liquids at high pressure. For example, a torsionally oscillating piezoelectric quartz rod was applied as an ultrasonic viscosity sensor (Phillippoff, 1963), (Collings & McLaughlin, 1971), (Ruttle & Stephenson, 1975). In this type of ultrasonic sensors bulk type waves were applied. The acoustic energy of bulk waves is distributed in the entire volume of the resonator. The contact with a measured liquid takes place on the surface of the resonator. This results in the moderate sensitivity of this type of viscosity sensors.

A high-pressure (up to 300 MPa) torsional shear wave rheometer has been developed by Kulisiewicz (Kulisiewicz et al., 2007). This measurement system uses transmission of small amplitude torsional shear waves generated and detected by piezoelectric elements. In order to determine the complex shear modulus the measurement of the time of flight of the bulk torsional acoustic wave travelling between driver and sensor plates (distance 0.3–1 mm) is used to assess the wave velocity. To perform the viscosity measurement a very complicated calibration procedure is needed.

Modified crystal plate (langasite) resonators were also used to measure the viscosity of liquids at high pressure (Andle et al., 2008). This attempt was not successful because of the enormous troubles in the construction of the resonator. The structure of the resonator is fragile and not robust. Moreover, the range of measuring pressures was very modest (up to 60 MPa).

To overcome the disadvantages of the bulk wave methods, the author has proposed to use the SH surface acoustic waves of the Love and Bleustein-Gulyaev (B-G) type (Kielczyński & Płowiec, 1989). At the beginning, the measurement of the liquid viscosity was carried out at the atmospheric pressure.

Subsequently, SH surface waves, i.e., Love waves and acousto-electric Bleustein-Gulyaev waves were used as a tool to measure the rheological parameters of liquids at high pressure (Kielczyński et al., 2008a), (Kielczyński et al., 2008b).

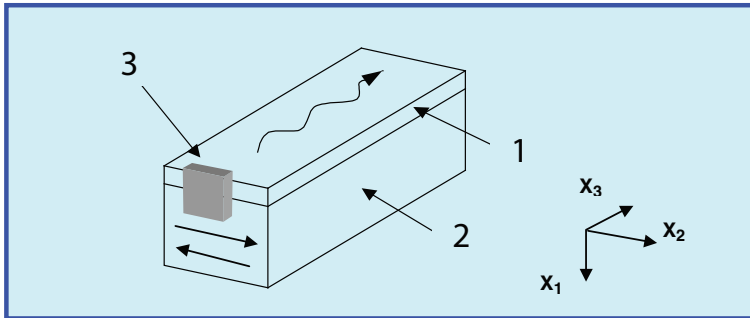
## 4. Surface acoustic waves

### 4.1 Love waves

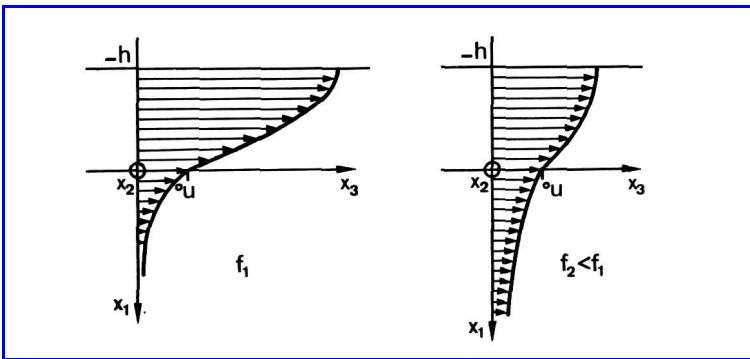
The Love wave propagates in a semi-infinite layered structure shown in Fig.1. Here, an elastic isotropic layer is rigidly attached to an isotropic and elastic half-space. Love waves can exist in special layered structures where phase velocity of the SH volume wave in the surface layer is smaller than that in the substrate, (Achenbach, 1973), (Farnell, 1978), (Royer&Dieulesaint, 2000). Mechanical vibrations of the shear horizontal surface wave are performed along the  $x_2$  axis parallel to the propagation surface ( $x_1 = 0$ ) and perpendicularly to the direction of propagation  $x_3$ . The energy of Love waves is concentrated in the vicinity of the surface. The amplitude  $f(x_1)$  of the surface Love wave should vanish for  $x_1 \rightarrow \infty$ . The penetration depth of the Love wave is of the order of the wavelength. At low frequencies the energy of the Love wave propagates mainly in the substrate. As the frequency increases the fraction of energy travelling in the surface layer increases. This improves sensitivity to surface perturbations like liquid viscous loading.

The propagation of Love waves in the layered waveguides is governed by the differential problem (Sturm-Liouville problem). Solving this problem, we obtain a set of pairs  $(\beta_i, f_i(x_1))$ , namely, the eigenvalue  $\beta_i$ , and eigenvector  $f_i(x_1)$  correspond to the propagation constant and distribution of the mechanical displacement with depth  $x_1$  of the Love wave. The index  $i = 1$  refers to the fundamental mode. Higher modes of Love waves

are labeled by  $i > 1$ . Similar Sturm-Liouville problem describes propagation of light waves in planar optical waveguides and motion of quantum particles in a potential well (Schrödinger equation).



(a)



(b)

Fig. 1. a) Excitation of the Love wave in the layered waveguide by means of the PZT plate transducer (3). Cu surface layer (1) is deposited on a steel substrate (2), b) Love wave amplitude distribution with the depth  $x_1$  for two different frequencies ( $f_1 > f_2$ ).

The Love wave has a multimode character. In the present paper, we have restricted our attention to the propagation of the fundamental mode of Love waves.

Love waves are excited by the plate transducer (3) attached to the waveguide face, see Fig.1. The sending-receiving transducer (3) is excited to shear vibrations parallel to the waveguide surface and generates impulses of the Love wave that propagate along the waveguide surface. Theoretical and experimental analysis of the generation of SH surface waves by means of a plate transducer is presented in (Kinh & Pajewski, 1980).

#### 4.2 Bleustein-Gulyaev (B-G) waves

Bleustein-Gulyaev (B-G) waves are shear horizontal acousto-electric waves, and they have no elastic counterpart (Royer & Dieulesaint, 2000), (Nakamura, 2007). If there is no piezoelectric effect, B-G wave degenerates to the shear bulk wave.

The distribution of the B-G wave mechanical displacement is similar to that of the Love wave. The B-G wave is capable of propagating along the surface of some crystals, e.g., with  $6mm$  or  $mm2$  symmetry (Zhang et al., 2001), as well as along the surface of properly polarized piezoelectric ceramics, see Fig.2.

Metallization of the PZT ceramic surface lowers the penetration depth of the B-G wave. In this case the penetration depth is of the order of a wavelength. Hence, in the metallized surface condition the B-G wave is more sensitive to liquid loading. B-G waves are excited similarly as Love waves, using the plate transducer (Kielczyński et al., 2004), see Fig.2.

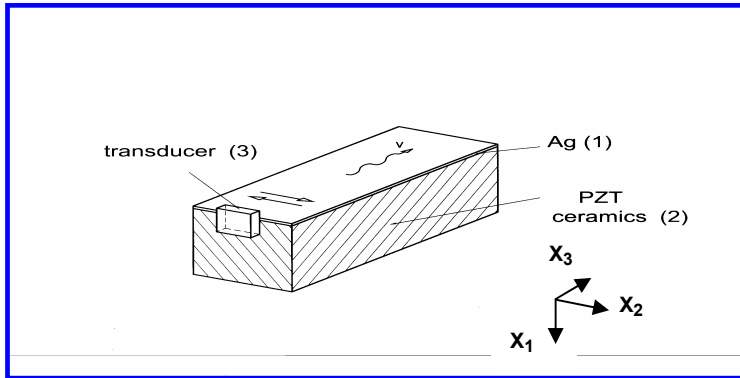


Fig. 2. Excitation of the B-G wave in a piezoceramic PZT waveguide (2) covered on the surface by a very thin metallic (Ag) layer (1) by means of the PZT plate transducer (3). PZT ceramics (both in the transducer and waveguide) is polarized along the axis  $x_2$ .

The Love wave is a dispersive wave (i.e., the phase velocity is dependent on frequency) and can exhibit higher waveguide modes than fundamental one. By contrast, the B-G wave is a nondispersive wave. Moreover, an advantage of B-G wave for liquid sensing application is that B-G wave has no multiple modes. This makes that inverse determination of liquid properties by utilizing B-G wave is easier than that by utilizing SH surface waves of the Love type. Both types of SH surface waves are widely used in resonators, sensors and delay lines.

## 5. Application of SH surface waves for determining the rheological parameters of liquids at atmospheric pressure

To overcome the drawbacks of the bulk wave method, shear horizontal (SH) surface acoustic waves (SAW) such as:

1. Love waves and
2. Bleustein-Gulyaev (B-G) waves

have been introduced for the viscosity measurements under ambient pressures (Kielczyński & Płowiec, 1989). These waves have only one SH component of mechanical displacement perpendicular to the direction of wave propagation and parallel to the waveguide surface. The energy of these waves is concentrated in the vicinity of the surface being in contact with a measured liquid. In consequence, the sensitivity of the viscosity sensors using SH surface acoustic waves (SAW) can be several orders larger than the sensitivity of the sensors employing bulk shear acoustic waves.

To measure the viscosity of liquid Rayleigh waves were also applied. Rayleigh waves have at least two components of vibrations i.e., longitudinal and vertical transverse, which cannot be separated. When Rayleigh waves propagate at a solid-liquid interface, the surface normal displacement radiates compressional waves into the liquid. Consequently, Rayleigh waves can be completely attenuated within the propagation range of the sensing device. Therefore, Rayleigh waves are impractical for use in the measurements of liquid viscosity. However, Rayleigh waves can be successfully applied in gas phase sensors.

In measurements of liquid viscosity, the effect of an investigated liquid on the properties of acoustic waves propagating in waveguides is primordial. The liquid presented on the waveguide surface loads it mechanically. The value of this load is proportional to the value of the mechanical impedance  $Z_L$  of a liquid medium (Kielczyński et al., 2004). The mechanical impedance of a layer of liquid loading the surface of the SH surface wave (i.e., Love or B-G wave) waveguide is equal to the characteristic shear impedance of the liquid  $Z_L$  for plane waves:

$$Z_L = (\rho_L \cdot G_L)^{1/2} \quad (1)$$

where:  $G_L = G' + jG''$  is the complex shear modulus of the liquid defined as the ratio ( $T/S$ ) of the shear stress  $T$  to the shear strain  $S$ ,  $\rho_L$  is the liquid density and  $j = (-1)^{1/2}$ .

In general, liquid loading of the sensor surface changes the phase velocity  $v$  and the attenuation  $\alpha$  of the SH surface wave. The complex propagation constant  $\gamma$  of the SH surface wave changes (Ballantine et al., 1997):

$$\frac{\Delta\gamma}{\beta} = \frac{\Delta\alpha}{\beta} - j \frac{\Delta v}{v_0} \quad (2)$$

where:  $\gamma = \alpha + j\beta$ ,  $\beta = \omega/v$ ,  $v_0$  is the phase velocity of the non-perturbed SH surface wave on the free surface, and  $\omega$  is the angular frequency of the SH surface wave.

Significant experimental indications result from Eq.2. Namely, (1) by measuring the time delay between two subsequent echoes, one can determine the relative change in phase velocity of the surface wave  $\frac{\Delta v}{v_0}$ , and (2) by measuring the amplitudes of the subsequent

impulses of the surface waves, we can determine the relative change in the surface wave attenuation  $\frac{\Delta\alpha}{\beta}$ . In this way, the relative change in the complex propagation constant  $\frac{\Delta\gamma}{\beta}$  of the surface wave is determined experimentally. Knowledge of the change in complex propagation constant  $\gamma$  is fundamental to the established nondestructive method used to determine the rheological parameters of a liquid medium.

By applying the perturbation method one can prove that the change in the complex propagation constant  $\gamma$  of the SH surface wave produced by viscoelastic liquid loading is as follows (Auld, 1973):

$$\Delta\gamma = -j \left( \frac{|v_2|_{x_1=0}^2}{4P} \right) Z_L = -jKZ \quad (3)$$

where:  $v_2$  is the SH surface wave amplitude on the waveguide surface ( $x_1 = 0$ ),  $P$  is the mean power on the unit width of the SH surface wave. The coefficient  $K$  is the characteristic quantity for each SH surface wave waveguide and depends solely on the material parameters of the waveguide and frequency (Kielczyński & Płowiec, 1989).

Knowing the change in the complex propagation constant  $\Delta\gamma$  from the experiment, we can calculate the complex shear impedance of a liquid  $Z_L = R_L + jX_L$ . Subsequently, by separating the real and imaginary parts of the Eq.1 we can calculate the real  $G'$  and imaginary  $G''$  parts of the complex shear modulus  $G_L$  of the liquid and, consequently, the rheological parameters of a viscoelastic liquid.

## 6. Application of SH surface waves for measuring the viscosity of liquids at high pressure

The Love wave and the Bleustein-Gulyaev (B-G) wave method for measuring the viscosity of liquids at high pressures have been established in the Laboratory of Acoustoelectronics of the Institute of Fundamental Technological Research, Polish Academy of Sciences in Warsaw, Poland (Kielczyński et al., 2008a), (Kielczyński et al., 2008b).

The SH SAW method for measuring the viscosity of liquids at high pressures possesses many advantages:

1. absence of moving parts
2. operation in real time
3. short measuring time
4. high sensitivity
5. low power consumption
6. small dimensions, simple and robust construction of the sensor
7. possibility of computerization
8. output signal is electrical
9. no leakage problems
10. no heating caused by shear

### 6.1 Measuring set up

High-pressure chamber was designed and fabricated in the Institute of Physics at Warsaw University of Technology (Rostocki et al., 2007). High pressure was generated in a thick-walled cylinder of 17 mm internal diameter with a simple piston and Bridgman II sealing system. The piston-cylinder assembly was working with a 20-tonne hydraulic press, driven by hand operated pump. The maximum pressure in this arrangement is limited to about 1.2 GPa due to the hydraulic press working range. For pressure measurement, a typical 500  $\Omega$  manganin transducer was used. Its resistance was measured with a precise HP 34970 multimeter. An accuracy of the pressure measurement was better than  $\pm 0.5$  MPa. All experiments were carried out at the temperature 293 K. Temperature was measured with the Cu - Constantan thermocouple placed inside the chamber. The described previously viscosity sensor (B-G or Love waveguide, see Figs.1, 2 and 4) was placed inside the high-pressure chamber, see Fig.3.

The piezoelectric transducer attached to the SH surface wave waveguide, manganin coil and thermocouple were connected with the external measuring setup by an electrical multichannel lead-through.



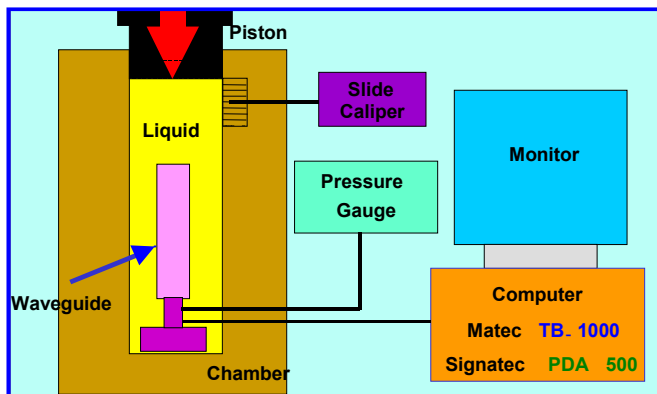


Fig. 3. Ultrasonic set up for measuring the viscosity and pressure of liquids under high pressure.

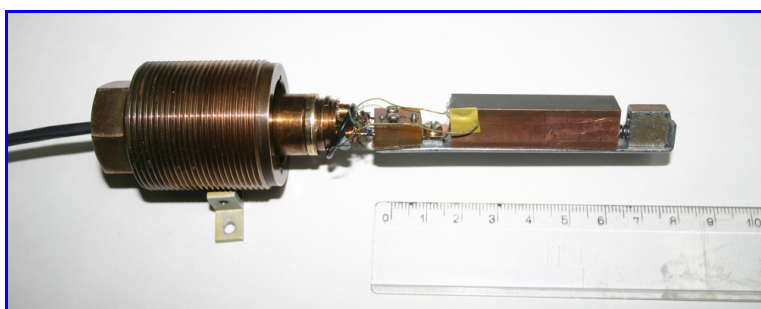


Fig. 4. Love wave waveguide (Cu surface layer on a steel substrate) connected to the high-pressure lead-through (on the left).

In the setup for measuring viscosity using the SH surface wave, see Fig.3, the sending-receiving piezoelectric transducer is driven by the TB-1000 pulser-receiver computer card (Matec, USA). The TB-1000 pulser generates the rf tone burst with a frequency  $f = 2$  MHz and length equal to  $0.5 \mu\text{s}$ . The repetition period equals 0.4 ms. The SH surface wave impulse generated by the transducer is reflected in multiple ways between two opposite edges of the SH surface wave waveguide (Fig. 4). The signals received by the transducer, see Figs.5a, b, are amplified by the TB-1000 receiver and sent into the PDA-500 digitizer card (Signatec, USA). This card samples and digitizes the input analog signals. The stored signals are then analyzed by computer software. For each measurement, the ultrasonic signal is averaged 1024 times in order to improve the signal - to - noise ratio. A computer program which controls the operation of the pulser-receiver card and digitizer card was written in C language.

## 6.2 Theoretical background

In this paper, the liquids investigated under high pressure are treated as the Newtonian liquids. The model of a Newtonian liquid was used by (Philippoff, 1963). He stated that the majority of oils in the considered shearing rate (about 1 MHz), and under high pressure are

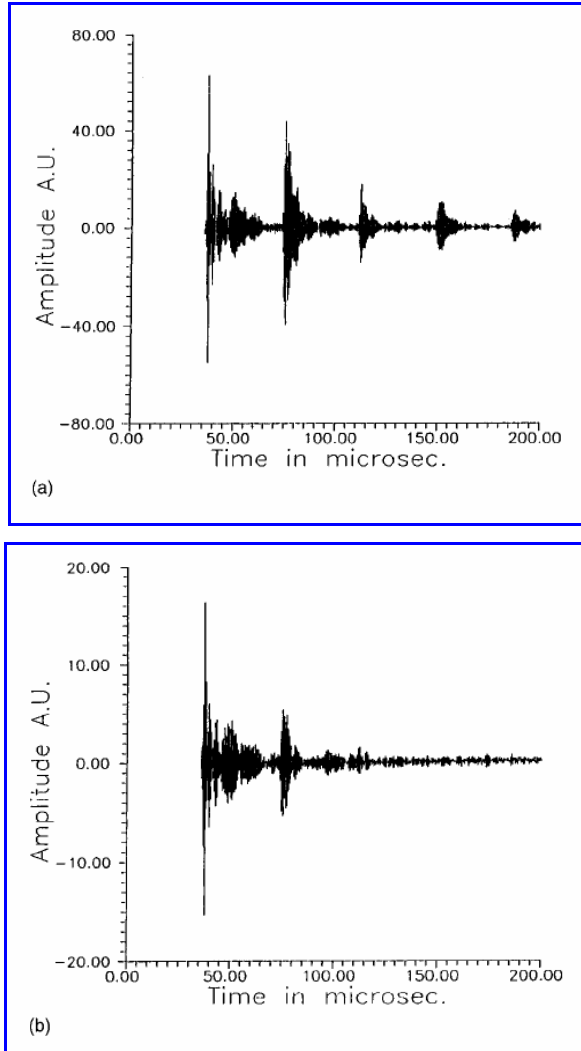


Fig. 5. (a) Oscillogram of the SH surface wave impulses reverberating in the waveguide unloaded with an investigated liquid, and b) Oscillogram of the SH surface wave impulses reverberating in the waveguide loaded with an investigated liquid.

the Newtonian liquids. This can justify the use of a Newtonian liquid model in our paper. For the case of a Newtonian (viscous) liquid, the shear mechanical impedance  $Z_L$  (defined as a ratio of the shear stress to the shear vibrational velocity) can be expressed as follows (Landau&Lifshitz, 1958):

$$Z_L = R_L + jX_L = \left( \frac{\rho_L \omega \eta}{2} \right)^{1/2} (1 + j) \quad (4)$$

where:  $\eta$  is the viscosity,  $\rho_L$  is the density of a liquid and  $j = (-1)^{1/2}$ . So that, we may regard formula (5) as holding for the liquids considered in the paper.

$$\eta = \frac{2R_L^2}{\omega\rho_L} = \frac{2X_L^2}{\omega\rho_L} \tag{5}$$

where:  $R_L$  and  $X_L$  is a real and imaginary part of the mechanical shear impedance of a liquid. The shear mechanical impedance of a liquid  $Z_L = R_L + jX_L$  can be determined from the measurement of the change in attenuation and time of flight of wave-trains that propagate in the waveguide loaded by a liquid (Kielczyński et al., 2004), see Fig.6.

The real part  $R_L$  of the shear mechanical impedance of a liquid can be expressed as, see Fig.6:

$$R_L = \frac{\ln(A_1^0/A_1^1)}{2KL} \tag{6}$$

where:  $A_1^0$  and  $A_1^1$  represent amplitudes of the first echo of the SH surface wave for an unloaded ( $A_1^0$ ) and loaded ( $A_1^1$ ) waveguide respectively,  $L$  is the length of the waveguide covered with an investigated liquid.

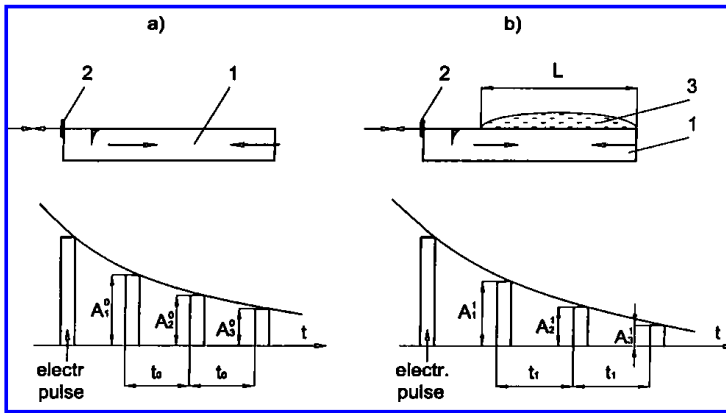


Fig. 6. Scheme of the SH surface wave measuring method, (a) free (nonloaded) waveguide surface and (b) waveguide surface loaded with a viscoelastic liquid. 1) waveguide of the SH surface wave, (2) sending+receiving transducer, and (3) layer of an investigated viscoelastic liquid.

### 6.3 Experimental results (Love waves)

An example of variations in viscosity of liquids as a function of hydrostatic pressure measured by the Love wave method is presented in Fig.7 (Kielczyński et al., 2008b), (Rostocki et al., 2010).

Castor oil is a vegetable oil, that is a triglyceride in which approximately ninety percent of fatty chains are ricinoleic acid. Oleic and linoleic acids are the other significant components. Castor oil and its derivatives have applications in the manufacturing of soaps, lubricants, hydraulic and brake fluids, paints, dyes, coatings, inks, cold resistant plastics, waxes and polishes, nylon, pharmaceuticals and perfumes.

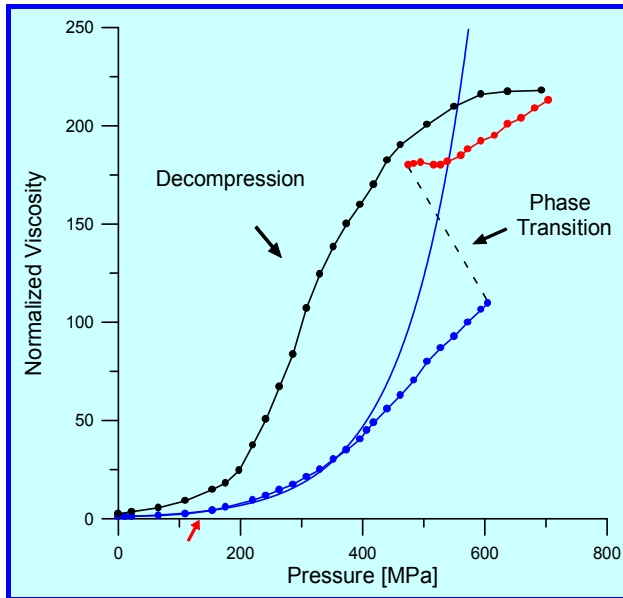


Fig. 7. Variations in viscosity of castor oil, as a function of hydrostatic pressure, measured by the Love wave method,  $f = 2\text{ MHz}$ . Red arrow indicates the hydrostatic pressure such as on the bottom of the Marianas Trench.

The pressure was generated in 10 MPa steps then kept constant for about 2-5 minutes. During that time the pressure was carefully observed. That allowed to identify pressure drop due to the first order phase transition and to observe whether the system is reaching thermodynamic equilibrium. After approaching 0.6 GPa the pressure was kept constant for about 20 hours to enable the phase transformation to occur. During the phase transition the small drop of pressure and increment of viscosity was observed.

As it can be seen in Fig.7, the experimental curve up to about 400 MPa is almost tangential to the exponential curve which represents the Barus formula  $\eta(p) = \eta_0 \exp(\alpha p)$ . (continuous curve in Fig.7), where:  $\eta_0$  is the viscosity at atmospheric pressure and  $\alpha$  is the viscosity - pressure coefficient. Above 400 MPa the experimental points are raising slower than the theoretical prediction. Finally, at 600 MPa when the pressure rise was stopped for about 20 hours the viscosity has risen to the new value characteristic for the high-pressure phase of castor oil. The further increment of viscosity was rather linear function of pressure.

#### 6.4 Experimental results (Bleustein-Gulyaev waves)

Similar as in the case of Love waves, measurements of high-pressure liquid viscosity were also performed using the Bleustein-Gulyaev wave method. Fabrication of the B-G wave waveguide is easy and its construction is simpler than that of the Love wave. On the other hand, Love wave waveguides are more robust and mechanically resistant.

A triglyceride and unsaturated fat: a triolein ( $\text{C}_{17}\text{H}_{33}\text{COO}$ ) $\text{C}_3\text{H}_5$  was investigated. Triolein is a model liquid in investigations of high-pressure phenomena in the natural oils that are very important in biodiesel technologies as well as in high-pressure food processing.

Most of the natural oils like castor oil, soybean oil, rapeseed oil, etc. consist of triglycerides of various fatty acids. The statistical characteristics of the molecular composition of these oils have made difficulties for the interpretation of the phenomena observed at high pressure. Therefore experiments have been concentrated upon well-defined triacylglycerol (triglyceride) structures. The triolein is very good model-liquid for the whole group of triglycerides since the phase transition takes place within only several dozen minutes after the application of sufficient pressure. That allows for more detailed and accurate studies than similar phase transition in vegetable oils taking even up to ten days from the application of sufficient pressure to the start of the phase transition.

Variations in viscosity of triolein as a function of hydrostatic pressure measured by the B-G wave method is presented in Fig.8 (Kielczyński et al., 2008a). Up to about 500 MPa the viscosity was increasing exponentially according to the known empirical Barus formula (continuous curve in Fig.8). After approaching 700 MPa the compression was stopped and the piston in the high-pressure chamber was fixed to enable the phase transformation to occur undisturbed. During the phase transition a pressure drop of about 100 MPa was observed in the chamber. The viscosity showed the further rise despite the pressure drop. It means that volume occupied by the resulting high-pressure phase diminishes. After the termination of the phase transformation process, the further increase of viscosity with increasing pressure was observed. The changes of viscosity during the decompression process inducing the high-pressure phase decomposition have shown large hysteresis (upper curve). Large hysteresis indicates existence of large internal friction forces. The phase transition in the case of triolein (Fig.8) lasts 1 hour. By contrast the phase transition in castor oil (Fig.7) is completed after 20 hours.

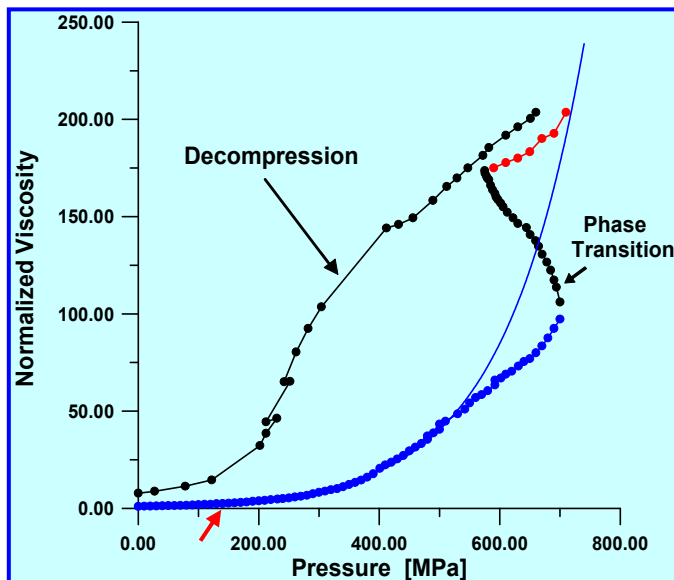


Fig. 8. Variations in viscosity of triolein, as a function of hydrostatic pressure, measured by the Bleustein-Gulyaev (B-G) wave method,  $f = 2 \text{ MHz}$ . Red arrow indicates the hydrostatic pressure such as on the bottom of the Marianas Trench.

## 7. Measurement of sound speed in liquids at high pressure

For the measurements of the phase velocity of longitudinal ultrasonic waves we have constructed the setup (Fig.9) especially designed to obtain a low level of parasitic ultrasonic signals (Kielczyński et al., 2009).

High-pressure chamber and computer cards are the same as in the viscosity measurements described previously. A special mounting of transducers in the high-pressure chamber was fabricated. The transducers were 5 MHz LiNbO<sub>3</sub> (Y<sub>36</sub> cut) plates (Boston Piezo-Optics Inc., USA). The phase velocity of the longitudinal ultrasonic wave was measured using a cross-correlation method (Sugasawa, 2002) to evaluate the time of flight (TOF).

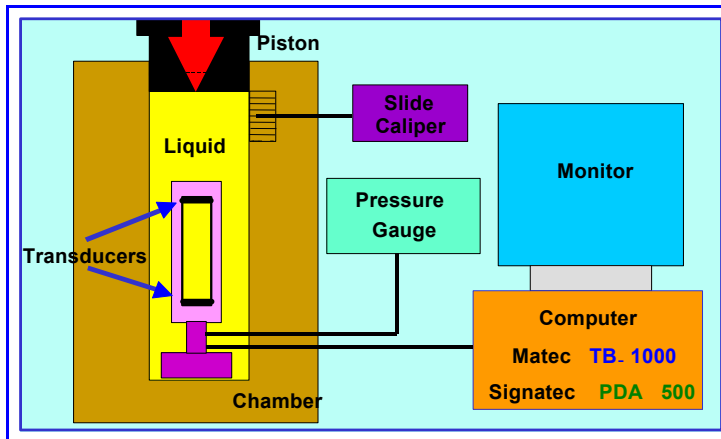


Fig. 9. Ultrasonic setup for measuring the phase velocity of longitudinal acoustic waves in liquids as a function of hydrostatic pressure.

For the sending and receiving of wave pulses the TB-1000 pulser-receiver computer card (Matec, USA) was used. The TB-1000 pulser generated the rf tone burst with a frequency 5 MHz and length equal to  $0.3 \mu\text{s}$ . The longitudinal wave impulse generated by the sending transducer propagated in investigated liquid and was detected by the receiving transducer. The PDA-500 digitizer card (Signatec, USA) sampled and digitized the signals received by the transducer and amplified by the TB-1000 receiver. The stored signals were then analyzed by computer software. For each measurement, the ultrasonic signal was averaged 1024 times in order to improve the signal-to-noise ratio. A computer program that controls the operation of the pulser-receiver card and digitizer card was written in C++ language. The time of flight of the ultrasonic pulses (see Fig.10) was evaluated by applying the cross-correlation method (Sugasawa, 2002), (Viola & Walker, 2003). The cross-correlation method is a global differential method. Due to this reason, the cross-correlation method does not depend on the trigger level and delays in cables and amplifiers. The change in the height of the column of a liquid caused by the piston movement was measured by a digital caliper. The piezoelectric transducers and manganin coil were connected with the external measuring setup by an electrical multichannel lead-through.

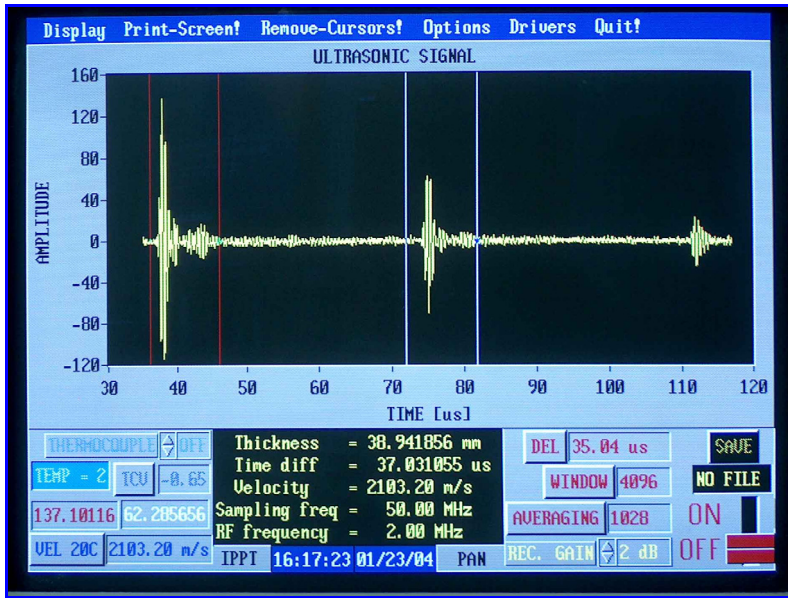


Fig. 10. Time of flight (TOF) between two ultrasonic impulses (delimited by cursors) is evaluated by using the cross-correlation method.

The sound velocity  $v_L$  was calculated using the formula:

$$v_L = \frac{l_0}{\Delta t} \quad (7)$$

where:  $l_0$  is the distance between sending and receiving transducer,  $\Delta t$  is time of flight (TOF) of the ultrasonic signal.

The isothermal compressibility  $\beta_T$  is given by the formula:

$$\beta_T = -\frac{1}{V} \frac{\partial V}{\partial p} \quad (8)$$

where:  $V$  is the volume of a liquid in the chamber for a given value of the hydrostatic pressure  $p$ .

## 7.1 Results

The measurements of the phase velocity (Fig.11) and isothermal compressibility (Fig.12) of triolein were carried out in function of hydrostatic pressure up to 650 MPa.

The pressure was generated in 20 MPa steps then kept constant about 2 min. that allowed to control whether the system was reaching equilibrium. Up to 450 MPa the phase velocity was increasing monotonically with pressure (arrow 1 in Fig.11). After approaching 450 MPa the compression was stopped, and the piston in the high-pressure chamber was fixed to enable the phase transformation to occur undisturbed. During the phase transition a pressure drop of about 150 MPa was observed in the chamber. It means that the volume occupied by the resulting high-pressure phase of triolein diminished. The phase velocity showed the further rise despite the pressure drop (arrow 2 in Fig.11). Finally the phase velocity has risen to the

new value characteristic for the high-pressure phase of triolein. Once the phase transition was completed the pressure was further increased up to about 650 MPa (arrow 3 in Fig.11). The phase velocity of longitudinal waves in high-pressure phase has increased monotonically. After approaching 650 MPa the decompression process was started (arrow 4 in Fig.11). At the point marked in Fig.11 by **a** the decomposition of the high-pressure phase started. Between points marked by **a** and **b** two phases coexisted in triolein.

Compressibility is an important property. It enters into many pressure-dependent thermodynamic expressions, and is an essential parameter for the design and use of any high-pressure equipment. Compressibility is dependent on the intermolecular forces acting within the substance, that is, it is the result of the balance between attractive and repulsive potentials. Compression results in decreasing the average intermolecular distance and reducing rotational and translational motion. Compressibility of liquids decreases with pressure, since the initial "free volume" has largely disappeared, and the repulsive potential is stronger than the attractive at high pressure. (Barbosa, 2003)

The isothermal compressibility of triolein presented in Fig. 12 was calculated using Eq.8. The volume changes  $\Delta V$  were determined from the changes of the height of the triolein column measured by the slide caliper. The arrows indicated by numbers 1, 2 and 3 in Fig.12 refer (similarly as in Fig.11) to the low-pressure phase, phase transition and high-pressure phase respectively.

It is worth noticing that the value of isothermal compressibility  $\beta_T$  during the phase transition is negative. Moreover, the isothermal compressibility of high-pressure phase is different than that of low-pressure phase.

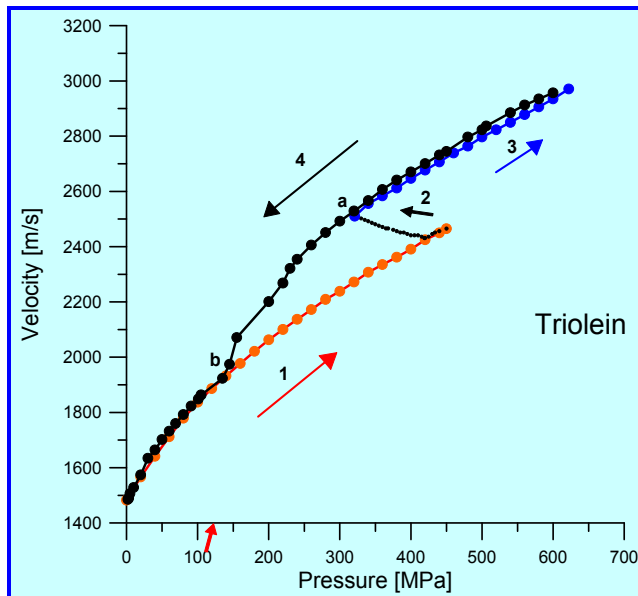


Fig. 11. Phase velocity  $v_L$  of longitudinal acoustic waves in triolein in function of hydrostatic pressure. (1) refers to low-pressure phase, (2) indicates the phase transition, (3) refers to high-pressure phase, and (4) indicates the decompression,  $f = 5\text{ MHz}$ . Red arrow indicates the hydrostatic pressure such as on the bottom of the Marianas Trench.



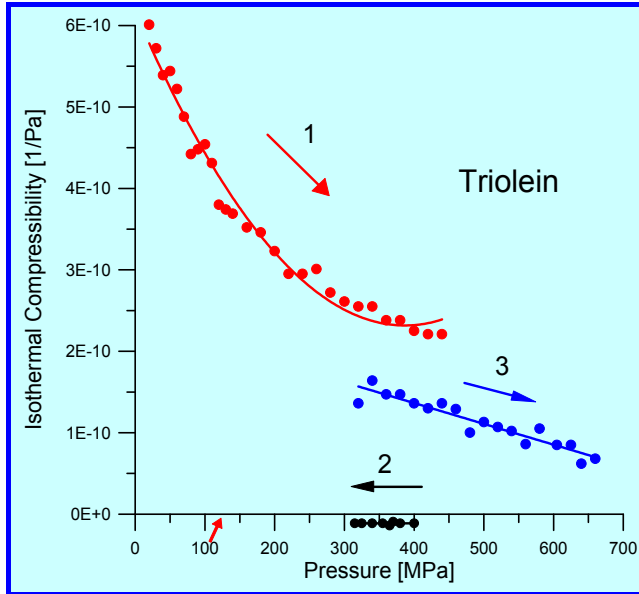


Fig. 12. Isothermal compressibility of triolein  $\beta_T$  as a function of hydrostatic pressure. During the phase transformation (arrow 2)  $\beta_T$  is negative.  $f = 5\text{ MHz}$ . Red arrow indicates the hydrostatic pressure such as on the bottom of the Marianas Trench.

## 7.2 Possibility of measurement of various physical (thermodynamic) parameters

The speed of sound is a particularly interesting property to study as it provides an indirect way to all of the observable thermodynamic properties of a single fluid phase. This way is a convenient one experimentally because sound speed measurements may be made quickly and accurately over ranges of temperature and pressure by means of largely automated apparatus.

The knowledge of the thermodynamic properties of pure organic liquids is of practical interest to industries in different fields, such as chemical, pharmaceutical industries, and food technology, because the applied industrial procedures are influenced by the temperature and pressure dependence of the used liquids.

The seven thermodynamic variables: pressure, volume, temperature, entropy, and the three components of the vector fluid velocity, can be related to one another through the equation of state, the equation of energy conservation, and also through the equation of continuity for mass and momentum, and the second law of thermodynamics. (Heydemann&Houck, 1969), (Stallard et al., 1969).

The densities, isobaric heat capacities, isobaric thermal expansions, isentropic compressibilities, isothermal compressibilities, and internal pressures as functions of temperature and pressure can be calculated using the experimental speeds of sound under elevated pressures together with the densities and heat capacities at atmospheric pressure (Oakley et al, 2003a), (Oakley et al, 2003b).

The bulk modulus of biodiesels determines the spray characteristics upon injection. As the fuel injection in the engine is approximately an adiabatic process, the adiabatic bulk modulus seems to be more useful than the isothermal one in estimation of the fuel injection

timing. The only experimental method that leads directly to adiabatic modulus is the acoustic one, based on the measurement of the speed of sound. The method is relatively simple tool for determination of thermodynamic properties, especially at high pressures (Dzida & Prusakiewicz, 2008).

The measurements of ultrasonic velocity can be applied for studying the nature of molecular systems and physicochemical properties of liquid mixtures and solutions. The results are interpreted in terms of molecular interaction between components of the liquid mixtures. A study of the thermophysical properties as a function of pressure and temperature in a homologous series of chemical compounds is of great interest not only for industrial applications (for example, the petroleum industry), but also for fundamental aspects for understanding the influence of the chain length of the components on the liquid structure and the developing models for an accurate representation of the liquid state. To this aim, ultrasonic speed measurements under pressure have been successfully applied (Daridon et al., 2002).

The experimental determination of the non-linearity parameter  $B/A$  is possible using the measurement of the ultrasonic wave velocity change due to an isentropic change of the static pressure (Khelladi et al., 2009), (Plantier et al., 2002).

## 8. Measurement of the physical properties of liquids during phase transition

High hydrostatic pressure can change molecular structure and intermolecular interactions in liquids. (Kulisiewicz et al., 2007), (Nithya et al., 2009). Rheological parameters describe macroscopic properties of a material. However, they are governed by molecular structure and mutual interactions of molecules in the material. Therefore, rheological parameters can be correlated with micro-structural parameters of a liquid (Delgado et al., 2010).

Investigation of phase transitions is important in lubricants, since rheological properties of lubricants can change during phase transitions. Investigations of the phase transitions in vegetable oils (e.g., castor oil or olive oil) and in the triglycerides (e.g., triolein) are of great importance. Vegetable oils are usually excellent boundary lubricants. They show higher viscosity index than mineral oils and they are environmentally friendly. In general, vegetable oils are highly attractive substitutes for petroleum based oils. Unfortunately their high-pressure behavior was not yet systematically investigated. The most important is to determine the range of pressures when phase transition (solidification) begins (Mia et al., 2007).

Investigation of phase transitions is also very important in food industry and in food conservation. Phase transitions can modify irreversibly the molecular structure and quality of food products. Media with high molar volumes like edible oils and fats exhibit phase transition at pressure levels about several hundred megapascals.

Investigation of phase transitions was impossible with conventional mechanical methods. By contrast, the proposed novel SH surface wave methods enable for the measurement of the rheological parameters of liquids during phase transitions.

As it is seen in Figs.7, 8, 11 and 12 during phase transitions a step change in liquid viscosity, phase velocity and compressibility occurs. This phenomenon is a clear indication that phase transitions in a liquid were initiated.

The kinetics of the phase transition, as a function of pressure, was investigated during phase velocity measurements in triolein. Pressure changes, occurring during phase transition, were registered with the piston locked in a fixed position, see Fig. 13. At stable pressure

conditions (450 MPa) the pressure remained constant in the first 30 minutes. Subsequently, a rapid decrease of pressure was observed, due to a phase transition in triolein. After about 60 minutes the pressure level stabilized on 330 MPa. This means that phase transition was complete. As a result, a new high-pressure phase in triolein with different microstructure has emerged. Physical properties of the new high-pressure phase are different than those in the low-pressure phase. The high-pressure induced phase transitions in vegetable oils are the phase transitions of first order.

To the author's knowledge, the measurement of the phase velocity of longitudinal acoustic waves in liquids during the phase transitions was not reported in the scientific literature and is a novelty. Measurement of the viscosity and sound speed in liquids during phase transitions is an original author's contribution.

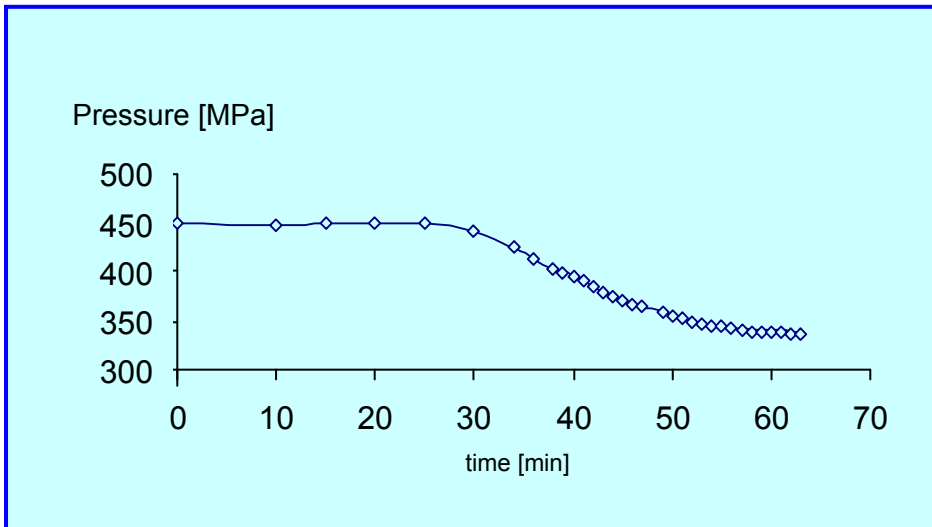


Fig. 13. Variation in pressure on time during the phase transition in triolein.

## 9. Summary

In this Chapter new methods for measuring the viscosity of liquids at high pressure are presented. Measurement of liquid viscosity at high-pressure is important in tribology in rolling bearings, in design and exploitation of ship diesel engines, in the chemical, pharmaceutical and cosmetic industries as well as in bio-fuels, and food conservation.

Based on the SH surface Love and Bleustein-Gulyaev waves, we designed novel methods and devices to characterize viscosity of liquids at high pressure. The SH SAW viscosity sensor is electrically responsive. Owing to this fact, modern methods of the digital signal acquisition and processing can be efficiently used. The measuring setup operates in real-time and can be employed for measuring liquid viscosity under high-pressure in the course of the technological processes. In general, the SH SAW method has high sensitivity and high reliability. The sensitivity of this method can be several orders larger than the sensitivity of the methods employing bulk acoustic waves. Application of this method will provide real-

time process monitoring and control thereby reducing down time and increasing product quality in food, chemical, cosmetic, pharmaceutical and petroleum industry.

The SH SAW method can be computerized. This enables continuous (on-line) monitoring of the rheological parameters of a liquid "in situ" in the processing line. Small dimensions of the viscosity sensor and the absence of moving parts are substantial advantages of this method. Only an electrical lead-through is needed. Therefore, it is very easy to assemble the sensor into the high-pressure chamber.

Ultrasonic methods using SH surface waves enable the measurement of the liquid viscosity in difficult access places such as pipelines and tanks.

In general, conventional mechanical methods enable the measurement of viscosity only up to about 200 MPa. In some cases, extending the measuring range up to 400 MPa may be possible after overcoming the enormous difficulties. Classical methods are in principle mechanical methods and can not be applied "in situ".

Application of ultrasonic waves extends considerably the range of pressures (up to 1 GPa) employed during the measurement of viscosity.

We measured the viscosity of liquid not only in the exponential range but also during the phase transitions, at high pressure phase and during the decompression. This is a novelty.

The measurements of the rheological properties of liquids during the phase transitions are not possible using conventional mechanical methods. On the other hand, application of the ultrasonic methods enables both the detection of phase transitions and investigation of their kinetics. This makes it also possible to determine the changes in microstructure occurring during the phase transitions.

To the author's knowledge, the measurements of liquid viscosity and sound speed under high-pressure during the phase transition and during the pressure decompression have not been reported in the scientific literature. This is an original author's contribution.

In future research it would be desirable to measure the physical properties of liquids in function of temperature and pressure. In this way, additional thermodynamic parameters could be determined (e.g., molar volume or adiabatic specific heat). The measurements should be extended into the non-Newtonian liquids (e.g., slurries, drilling fluids). In future the developed method could be applied in industry for on-line operation to investigate lubricants and bio-fuels (bio-diesels) and to control the food processing.

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