

# Ultrasonic Evaluation of Thermodynamic Parameters of Liquids Under High Pressure

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**Abstract**—In many technological processes (e.g., in the chemical, petrochemical, food, and plastics industries), liquids are subjected to high pressures and temperatures. Therefore, knowledge of their thermodynamic properties is essential for understanding, design, and control of the process technology. Direct evaluation of the thermodynamic parameters of liquids under high pressure, using conventional methods, is very difficult. Therefore, the application of these methods in industrial conditions, particularly in on-line control of the technological parameters of liquids, is practically impossible. Ultrasonic methods (e.g., sound speed measurements) are very suitable for this purpose because of their simplicity and accuracy. The sound velocity is closely related to numerous thermodynamic properties of liquids. The objective of this paper is to address the influence of temperature and pressure on the thermodynamic parameters of liquids, using the example of diacylglycerol (DAG) oil, employing ultrasonic methods. In this paper, we present ultrasonic velocity and density measurements (performed by the authors) in DAG oil over a range of pressures and temperatures. On the basis of experimental results (the sound velocity and liquid density versus pressure and temperature) a series of DAG oil thermodynamic parameters such as specific heat ratio, intermolecular free path length, Van der Waals constant  $b$ , surface tension, and effective Debye temperature were evaluated as functions of pressure and temperature.

## I. INTRODUCTION

IN many technological processes (e.g., in the chemical, food [1], petrochemical [2], [3], and plastics [4] industries), processed liquids are subjected to high pressures and temperatures. Therefore, knowledge of their thermodynamic properties is essential for the understanding, design, and control of the production processes, e.g., in high-pressure food processing and preservation. Knowledge of high-pressure thermodynamic properties of fuels and bio-fuels [5], [6] is also indispensable because of the increasing operating pressures ( $>200$  MPa) in modern fuel-injection systems. Research on thermodynamic properties of liquids under high pressure and elevated temperatures is an important area of application in the mining industry, e.g., in extraction of crude petroleum, and in exploration for gas and geothermal resources. Knowledge of the thermody-

namic parameters of liquid natural resources under high pressure and elevated temperatures is of paramount importance in the process of extraction, storage, and transportation of these liquid natural resources.

This paper was motivated by the lack of data in the literature on the thermodynamic parameters of liquids under high pressure and at elevated temperature. Knowledge of these parameters is necessary for the optimization and modeling of high-pressure technological processes in the food, chemical, and plastics industries, as well as in the mining industry in exploration for natural resources. Moreover, knowledge of the thermodynamic parameters under high pressure is of vital importance in the design and optimization of modern injection systems for diesel engines (common rail), where the fuel pressure exceeds 200 MPa.

The essential goal of this study is to evaluate the impact of temperature and high pressure on physicochemical properties of liquids, using the example of DAG oil. For this purpose, ultrasonic measurements of wave velocity and density are utilized. The speed of sound is directly associated with several thermodynamic parameters; therefore, measurements of ultrasonic wave velocity and density as functions of pressure and temperature allow the determination of several thermodynamic parameters in the investigated liquids, such as adiabatic compressibility, isothermal compressibility, intermolecular free path length, surface tension, etc.

Direct evaluation of thermodynamic parameters of liquids under high pressure, using conventional methods, is very difficult. By contrast, ultrasonic methods, because of their simplicity and accuracy, are very suitable for this purpose. In this regard, the measurement of speed of sound and density of liquids under high pressure ensures a relatively simple and accurate manner, to obtain a series of fundamental thermodynamic parameters of liquids as functions of pressure and temperature. In addition, the ultrasonic method is rapid, relatively inexpensive, noninvasive, and can be computerized.

Preliminary results of our research on the determination of the physicochemical parameters of liquids at high-pressure are included in our earlier papers [7]–[12]. The paper [7] concerned the study of phase transitions in oleic acid. The paper [8] involved the study of phase transitions in olive oil. In [9], the adiabatic compressibility, isothermal compressibility, and intermolecular free length for olive oil were defined. In [10], only isothermal and adiabatic compressibility for DAG oil were determined. In [12], the

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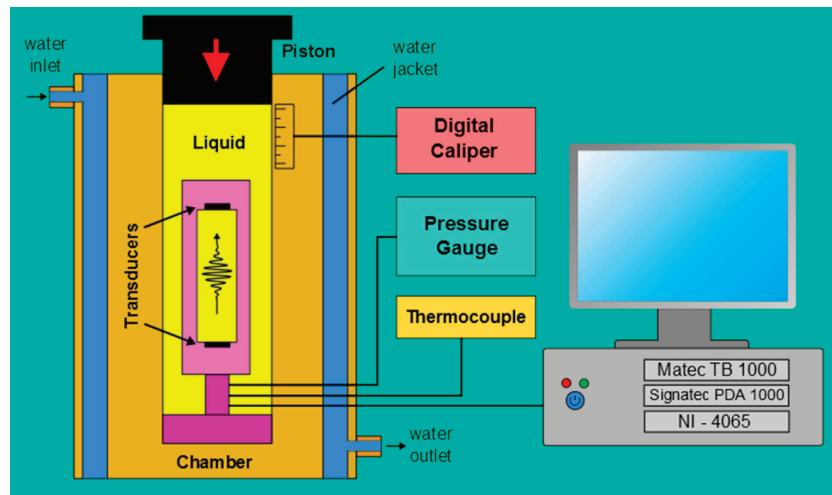


Fig. 1. Computerized ultrasonic setup for measuring the sound velocity in liquids at high pressure and various values of temperature.

isobaric thermal expansion coefficient  $\alpha_p$  and the specific heat capacity at constant pressure  $c_p$  were evaluated. In the present study, however, several isotherms of other thermodynamic parameters of DAG oil such as specific heat ratio  $\gamma$ , intermolecular free path length  $L_f$ , Van der Waals constant  $b$ , surface tension  $\sigma$ , and effective Debye temperature  $\theta_D$  are evaluated. This is an important extension of the research in relation to our previous works [7]–[12]. Ultrasonic wave velocity measurements are performed in a computerized measuring setup. The advantage of the designed and constructed measuring setup is that the measurement is carried out automatically and is operator independent. The computer controls the measurement process using specialized computer cards and a program written in C++.

The time of flight of ultrasonic wave pulses in DAG oil (and consequently the phase velocity) was measured using a cross-correlation method. Density values of DAG oil under high pressure were evaluated from the measurement of changes in the volume of a pressurized DAG oil sample. On the basis of experimental results (the sound velocity and liquid density versus pressure and temperature), specific heat ratio, intermolecular free path length, Van der Waals constant  $b$ , surface tension, and effective Debye temperature were calculated as functions of pressure and temperature.

The results obtained in this work can be applied to investigate other liquids to evaluate the influence of temperature and high pressure on their thermodynamic parameters. The results presented in this paper can be employed in mathematical modeling and optimization of new technological methods, as well as to design new fuel-injection systems in biodiesel engines.

The evaluated thermodynamic parameters of liquids can be also applied to determine the nonlinearity parameter  $B/A$  of liquids [11] often used in acoustics, from underwater acoustics to ultrasound in medicine, biology, and investigation of materials. To determine the nonlinearity parameter  $B/A$  by applying the thermodynamic method,

one must know the isobaric thermal expansion coefficient  $\alpha_p$  and isobaric specific heat capacity  $c_p$ , as well as changes in the speed of sound and density as functions of pressure and temperature [13]. The thermodynamic method for determining the nonlinearity parameter  $B/A$  is the most reliable and accurate measurement method. For this reason, knowledge of the thermodynamic parameters of the liquid (as functions of pressure and temperature) allows accurate determination of the nonlinearity coefficient  $B/A$  [14].

## II. MATERIALS AND METHODS

### A. Measuring Setup and Ultrasonic Measurements

In this paper, we present measurements of the time of flight of the longitudinal ultrasonic wave between the transmitting transducer and receiving transducer (through-transmission mode) by means of the cross-correlation method [15], [16]. In this way, we have determined the speed of sound in the investigated DAG oil sample as a function of pressure for various temperatures. The measurements were performed using a high-pressure measuring setup designed and constructed by the authors; see Fig. 1. From the change in position of the piston in the high-pressure chamber, sample volume changes were evaluated. The piston displacement was measured by a digital caliper gauge, with an accuracy of 0.01 mm. On this basis, knowing the density of the sample measured by pycnometer at atmospheric pressure, we determined the changes in density of the sample as a function of pressure for various temperatures. The pressure inside the chamber was measured by a 100- $\Omega$  manganin sensor [17]. The manganin sensor resistance was measured using an NI 4065 multimeter computer card (National Instruments Corp., Austin, TX, USA). Constant temperature in the chamber ( $\pm 0.01^\circ\text{C}$ ) was maintained by a thermostatic water bath and a precision thermostat (Julabo Labortechnik,

Seelbach, Germany). A copper-constantan thermocouple was placed inside the high-pressure chamber. All measurements were carried out at temperatures  $T = 20, 30, 40$ , and  $50^\circ\text{C}$ .

The piezoelectric transducers were  $\text{LiNbO}_3$  Y36 cut plates (Boston Piezo-Optics Inc., Bellingham, MA, USA), with diameter of 5 mm and resonant frequency  $f = 5$  MHz. The sending transducer was driven by a TB-1000 pulser-receiver computer card (Matec Instrument Companies Inc., Northborough, MA, USA). The pulser generated an RF tone-burst signal with a frequency of 5 MHz, with a length of  $0.3 \mu\text{s}$  and repetition time of 0.8 ms. The ultrasonic impulse generated by the sending transducer propagated in the investigated DAG oil sample and was detected by the receiving transducer and amplified by the TB-1000 receiver. The stored signals were analyzed by a computer program written in C++.

The measuring set-up and methods have been described in detail in our previous works [7]–[12].

The investigated DAG oil sample was composed of 82% DAGs and 18% triacylglycerols (TAG) with a vestigial amount of monoacylglycerols and free fatty acids [18]. The fractions were determined by means of the gas chromatography method. The volume of the investigated DAG oil sample was  $22 \text{ cm}^3$ .

### B. Uncertainty Analysis

The expanded relative uncertainty of the ultrasonic velocity  $\Delta U_v/U_v$  is given by

$$\frac{\Delta U_v}{U_v} = 2\sqrt{\left(\frac{\Delta U_L}{U_L}\right)^2 + \left(\frac{\Delta U_{t_d}}{U_{t_d}}\right)^2}, \quad (1)$$

where  $\Delta U_L/U_L$  is the relative standard uncertainty of the path  $L$ ,  $\Delta U_{t_d}/U_{t_d}$  is the relative standard uncertainty of the time of flight delay  $t_d$ .

The expanded relative uncertainty for the speed of sound ( $v = L/t_d$ ) in the liquid equals  $\pm 0.3\%$  at 95% confidence level. The total relative uncertainty of the density evaluation is  $\pm 0.05\%$ .

The distance between the transducers was determined from the calibration measurements in water as the reference liquid. At ambient temperature, the value of the distance is  $L = 10.278 \text{ mm}$ . The distance  $L$  was evaluated with uncertainty of  $\pm 10 \mu\text{m}$ .

Detailed analysis of the uncertainty of measurement is given in [10].

## III. EXPERIMENTAL RESULTS

### A. Sound Velocity

Fig. 2 shows the results of longitudinal ultrasonic wave velocity measurements (frequency 5 MHz) at temperatures  $20^\circ\text{C}$ ,  $30^\circ\text{C}$ ,  $40^\circ\text{C}$ , and  $50^\circ\text{C}$ . Pressure was applied in

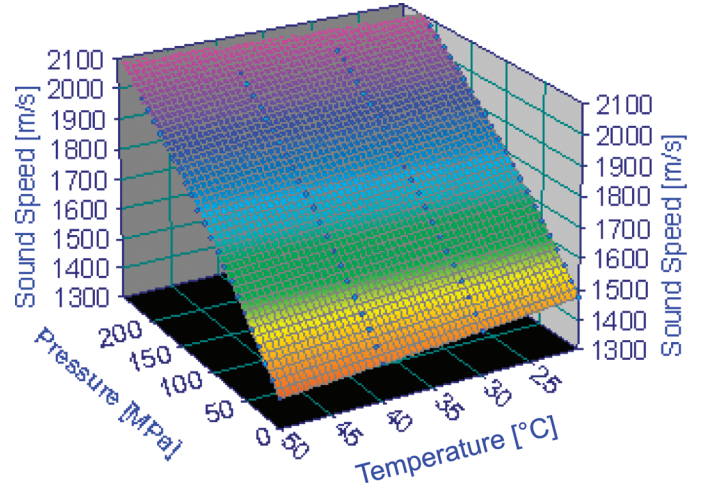


Fig. 2. Plot of sound velocity  $v$  in DAG oil as a function of pressure and temperature,  $f = 5$  MHz [12].

increments of 10 MPa up to 220 MPa. Each increase in pressure was followed by an interval of time (5 min) which allowed the DAG oil sample to achieve thermodynamic equilibrium conditions.

The experiment has shown (see Fig. 2 and Table I) that the speed of sound in DAG oil decreases monotonically with increasing temperature, and increases monotonically with pressure increase.

Generally speaking, the decrease in the speed of sound with temperature may result from the fact that the interatomic distance increases with temperature because of thermal expansion, which in turn reduces the sound speed. This is further supported by the fact that the sound wave propagates with higher velocity in the closely packed ar-

TABLE I. EXPERIMENTAL VALUES OF ULTRASONIC WAVE VELOCITY  $v$  IN METERS PER SECOND FOR DAG OIL AT VARIOUS TEMPERATURES AND PRESSURES.

Pressure [MPa]	Temperature [ $^\circ\text{C}$ ]			
	20	30	40	50
0.1	1474.5	1446.2	1421.7	1397.5
10	1511.1	1483.4	1459.5	1435.9
20	1546.7	1519.7	1496.4	1473.3
30	1581.5	1555.1	1532.4	1509.8
40	1615.3	1589.5	1567.3	1542.2
50	1648.2	1623.1	1601.4	1579.8
60	1680.3	1655.7	1634.6	1613.4
70	1711.6	1687.5	1666.9	1646.1
80	1742.0	1718.5	1698.3	1678.0
90	1771.7	1748.7	1728.9	1709.0
100	1800.6	1778.1	1758.7	1739.2
110	1828.7	1806.7	1787.8	1768.5
120	1856.1	1834.6	1816.0	1797.1
130	1882.9	1861.7	1843.6	1825.0
140	1908.9	1888.2	1870.4	1852.1
150	1934.4	1914.0	1896.6	1878.5
160	1959.2	1939.2	1922.0	1904.3
170	1983.4	1963.7	1946.9	1929.4
180	2006.9	1987.7	1971.1	1953.8
190	2030.0	2011.1	1994.7	1977.6
200	2052.6	2033.9	2017.8	2000.8
210	2074.6	2056.2	2040.3	2023.5

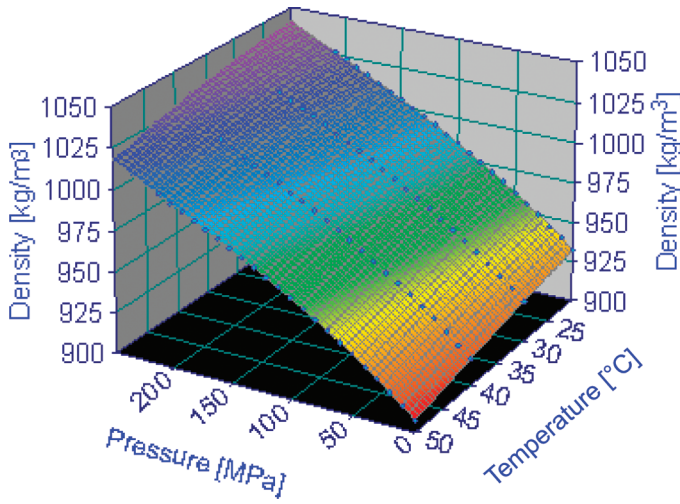


Fig. 3. Density  $\rho$  of DAG oil as a function of pressure and temperature [12].

range of atoms than in the loosely packed arrangement of atoms.

### B. Density

Fig. 3 and Table II demonstrate the results of measurements of the density of DAG oil versus pressure and temperature.

From measurements carried out by the authors, it follows that the density of DAG oil decreases monotonically with increase of temperature, and it increases with increasing pressure. Precise knowledge of the density changes of liquids under high pressure is relevant, e.g., in the

TABLE II. EXPERIMENTAL VALUES OF DAG OIL DENSITY  $\rho$  IN KILOGRAMS PER METER CUBED AT VARIOUS TEMPERATURES AND PRESSURES.

Pressure [MPa]	Temperature [°C]			
	20	30	40	50
0.1	932.32	925.22	916.70	907.67
10	938.48	931.53	923.07	914.02
20	944.39	937.58	929.19	920.12
30	950.06	943.40	935.06	925.97
40	955.52	948.99	940.71	931.59
50	960.76	954.36	946.13	936.98
60	965.80	959.54	951.36	942.17
70	970.66	964.53	956.39	947.16
80	975.35	969.34	961.24	951.97
90	979.88	973.99	965.93	956.61
100	984.27	978.49	970.46	961.10
110	988.52	982.85	974.85	965.44
120	992.65	987.10	979.12	969.64
130	996.68	991.23	983.28	973.74
140	1000.61	995.26	987.32	977.72
150	1004.46	999.21	991.29	981.62
160	1008.24	1003.08	995.17	985.43
170	1011.97	1006.90	999.00	989.18
180	1015.65	1010.67	1002.77	992.87
190	1019.30	1014.40	1006.51	996.53
200	1022.94	1018.12	1010.22	1000.15
210	1026.57	1021.83	1013.92	1003.76

optimization of operation of modern fuel-injection systems for diesel engines [5].

Tabulated values of physicochemical properties (i.e., specific heat ratio, intermolecular free path length, Van der Waals constant  $b$ , surface tension, and effective Debye temperature) evaluated by using the velocity and density of DAG oil are shown in Tables III–VII.

### C. Numerical Approximation of the Density and Sound Velocity

Empirical relationships  $v(p, T)$  and  $\rho(p, T)$  have been approximated by the appropriate functions of two variables ( $p, T$ ), i.e., the pressure  $p$  and the temperature  $T$ . The computer software package Table Curve 3D (Systat, San Jose, CA, USA) was used to perform the curve fittings. Sound velocity was approximated by using a third-order polynomial of two independent variables ( $p, T$ ) [12]:

$$v(p, T) = a + bp + cT + dp^2 + eT^2 + fpT + gp^3 + hT^3 + ipT^2 + jp^2T, \quad (2)$$

where  $a = 1556.1007$ ,  $b = 3.5558133$ ,  $c = -5.2591231$ ,  $d = -0.0046743392$ ,  $e = 0.070266476$ ,  $f = 0.0082758464$ ,  $g = 3.8777839e-6$ ,  $h = -0.0005704745$ ,  $i = -3.0256387e-5$ , and  $j = -9.7492135e-6$ .

A similar approximation was also performed for the density  $\rho(p, T)$  of DAG oil:

$$\rho(p, T) = a_1 + b_1p + c_1T + d_1p^2 + e_1T^2 + f_1pT + g_1p^3 + h_1T^3 + i_1pT^2 + j_1p^2T, \quad (3)$$

where  $a_1 = 938.58048$ ,  $b_1 = 0.57383355$ ,  $c_1 = 0.04310836$ ,  $d_1 = -0.0012712514$ ,  $e_1 = -0.020868499$ ,  $f_1 = 0.0035779617$ ,  $g_1 = 2.1460142e-6$ ,  $h_1 = 0.00015282847$ ,  $i_1 = -4.147052e-5$ , and  $j_1 = -1.8226879e-6$ .

### D. Adiabatic Compressibility

Adiabatic compressibility is of vital importance in the ultrasonic investigation of liquids and liquid mixtures because it is the measure of intermolecular arrangement and orientation of constituent molecules. Adiabatic compressibility is a key property of liquids in high-pressure technological processes, e.g., during high-pressure food preservation [19]. Moreover, adiabatic compressibility (and/or its reciprocal, the bulk modulus) is a crucial parameter that characterizes the behavior of fuels in the injection systems in diesel engines [5].

Adiabatic compressibility was determined using

$$k_s(p, T) = \frac{1}{\rho(p, T)v^2(p, T)} \quad [1/\text{Pa}], \quad (4)$$

where  $\rho$  is the density of DAG oil and  $v$  is the sound velocity in DAG oil.



The dependence of the adiabatic compressibility  $k_S$  on pressure and temperature, evaluated from (2)–(4), is presented in [12].

### E. Isothermal Compressibility

Compressibility (isothermal and/or adiabatic) of a liquid is an important physical parameter in fluid mechanics. It depends on the structure of the liquid. Compressibility is determined by the balance between attractive and repulsive forces and it enters into many pressure-dependent thermodynamic expressions. It decreases with pressure increase because the free volume between molecules decreases [20]. Furthermore, the isothermal compressibility to adiabatic compressibility ratio determines the specific heat ratio, which is a very important thermodynamic parameter.

Isothermal compressibility  $k_T$  is defined as

$$k_T(p, T) = \frac{1}{\rho(p, T)} \left( \frac{\partial \rho(p, T)}{\partial p} \right)_T \quad [1/\text{Pa}], \quad (5)$$

where  $T$  is the temperature in Kelvin.

Ref. [12, Fig. 5] shows the isothermal compressibility of DAG oil as a function of pressure for various values of temperature, derived from (3) and (5).

### F. Specific Heat Ratio $\gamma$

The specific heat ratio  $\gamma$  plays a crucial role in thermophysical characterization of oils and other organic liquids. The specific heat ratio is present in the equations of state that link pressure, temperature, and volume of investigated liquids:

$$\gamma(p, T) = \frac{c_p(p, T)}{c_v(p, T)} = \frac{k_T(p, T)}{k_s(p, T)}. \quad (6)$$

Fig. 4 shows the dependence of the specific heat ratio  $\gamma$  on pressure and temperature, evaluated from the (4)–(6). It appears from Fig. 4 that the specific heat ratio increases with increasing pressure and decreases as the temperature increases. See also Table III.

### G. Intermolecular Free Path Length

The intermolecular free path length is a significant physical parameter of a liquid which correlates the strength of interactions with sound speed and density. It is the distance between the surfaces of the neighboring molecules in a liquid. Changes in the molecular structure of DAG oil constituents alter the intermolecular free path length [21]. Temperature increase results in an increase of intermolecular distance. Therefore, the liquid becomes less packed, and consequently the intermolecular free path length and adiabatic compressibility increase. As a result, the density and ultrasonic longitudinal phase velocity decrease; see Figs. 2, 3, and 5.

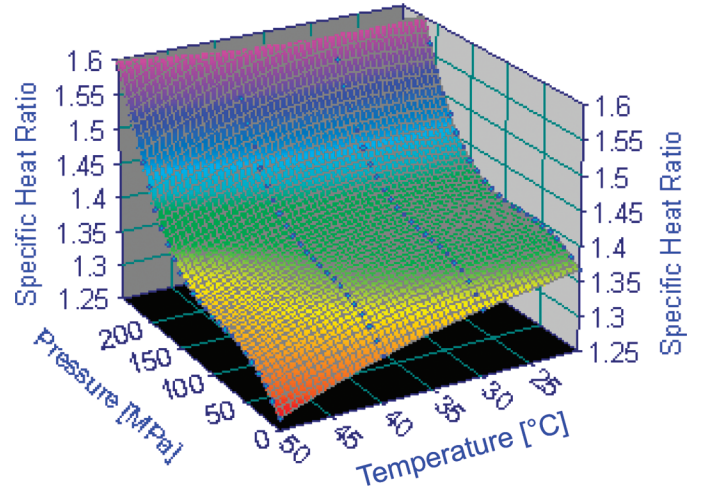


Fig. 4. The dependence of the specific heat ratio  $\gamma$  of DAG oil versus pressure and temperature.

The intermolecular free path length  $L_f$  is related to ultrasonic velocity and density as follows:

$$L_f(p, T) = K/[v(p, T) \cdot (\rho(p, T))^{1/2}] \quad [\text{m}], \quad (7)$$

where  $K$  is the Jacobson's constant, given by the relation:  $K = (93.875 + 0.345 \cdot T) \cdot 10^{-8}$ , and  $T$  is the temperature in Kelvin.

Fig. 5 shows the plot of intermolecular free path length  $L_f$  as a function of pressure and temperature, obtained from (2), (3), and (7). See also Table IV.

### H. Van der Waals Constant $b$

Van der Waals constant  $b$  represents the volume occupied by the molecules of a liquid. As seen in Fig. 6 and Table V, Van der Waals constant  $b$  decreases with increasing pressure and increases with increasing temperature. Van der Waals constant  $b$  is a useful parameter, e.g., in the polymer industry, for understanding the nature of interactions between polymer and solvent molecules [22].

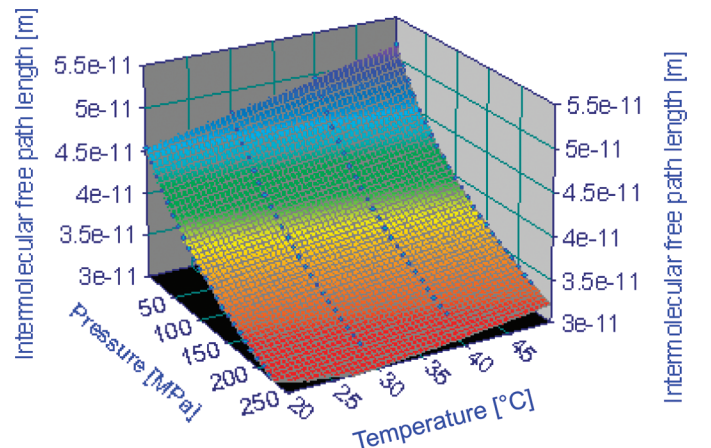


Fig. 5. The dependence of the intermolecular free path length  $L_f$  in DAG oil versus pressure and temperature.

TABLE III. EVALUATED VALUES OF THE SPECIFIC HEAT RATIO  $\gamma$  OF DAG OIL AT VARIOUS TEMPERATURES AND PRESSURES.

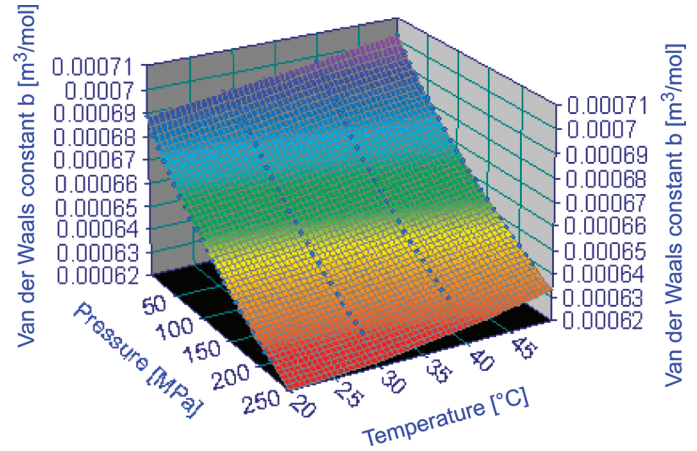
Pressure [MPa]	Temperature [°C]			
	20	30	40	50
0.1	1.3670	1.3465	1.3149	1.2676
10	1.3775	1.3599	1.3300	1.2834
20	1.3854	1.3705	1.3422	1.2962
30	1.3909	1.3787	1.3519	1.3064
40	1.3946	1.3848	1.3594	1.3142
50	1.3967	1.3892	1.3650	1.3200
60	1.3978	1.3924	1.3692	1.3243
70	1.3982	1.3947	1.3724	1.3274
80	1.3983	1.3966	1.3750	1.3297
90	1.3986	1.3985	1.3774	1.3317
100	1.3994	1.4007	1.3800	1.3338
110	1.4013	1.4037	1.3832	1.3363
120	1.4045	1.4080	1.3875	1.3397
130	1.4096	1.4138	1.3932	1.3444
140	1.4169	1.4218	1.4008	1.3508
150	1.4269	1.4322	1.4107	1.3593
160	1.4400	1.4454	1.4233	1.3704
170	1.4564	1.4619	1.4390	1.3844
180	1.4767	1.4820	1.4581	1.4017
190	1.5012	1.5062	1.4811	1.4227
200	1.5303	1.5347	1.5083	1.4477
210	1.5644	1.5680	1.5401	1.4772

Van der Waals constant  $b$  for the investigated DAG oil was calculated using the following expression:

$$b = \left( \frac{M}{\rho(p, T)} \right) \left[ 1 - \left( \frac{\gamma(p, T)RT}{Mv^2(p, T)} \right) \right] \times \left( \sqrt{1 + \left( \frac{Mv^2(p, T)}{3\gamma(p, T)RT} \right)} - 1 \right) \quad [\text{m}^3/\text{mol}], \quad (8)$$

TABLE IV. EVALUATED VALUES OF THE INTERMOLECULAR FREE PATH LENGTH  $L_f$  IN METERS OF DAG OIL AT VARIOUS TEMPERATURES AND PRESSURES.

Pressure [MPa]	Temperature [°C]			
	20	30	40	50
0.1	4.5357E-11	4.7395E-11	4.9488E-11	5.1715E-11
10	4.4146E-11	4.5851E-11	4.7589E-11	4.9486E-11
20	4.2940E-11	4.4603E-11	4.6196E-11	4.8091E-11
30	4.1776E-11	4.3429E-11	4.4801E-11	4.6721E-11
40	4.0791E-11	4.2320E-11	4.3686E-11	4.5235E-11
50	3.9791E-11	4.1312E-11	4.2636E-11	4.4272E-11
60	3.8918E-11	4.0313E-11	4.1614E-11	4.3223E-11
70	3.8137E-11	3.9507E-11	4.0746E-11	4.2290E-11
80	3.7369E-11	3.8762E-11	3.9825E-11	4.1404E-11
90	3.6650E-11	3.8002E-11	3.9069E-11	4.0597E-11
100	3.6005E-11	3.7284E-11	3.8381E-11	3.9803E-11
110	3.5376E-11	3.6621E-11	3.7686E-11	3.9045E-11
120	3.4831E-11	3.5964E-11	3.7019E-11	3.8355E-11
130	3.4245E-11	3.5367E-11	3.6420E-11	3.7692E-11
140	3.3727E-11	3.4847E-11	3.5837E-11	3.7089E-11
150	3.3263E-11	3.4332E-11	3.5288E-11	3.6502E-11
160	3.2769E-11	3.3831E-11	3.4769E-11	3.5976E-11
170	3.2328E-11	3.3285E-11	3.4305E-11	3.5457E-11
180	3.1874E-11	3.2829E-11	3.3819E-11	3.4968E-11
190	3.1484E-11	3.2423E-11	3.3378E-11	3.4479E-11
200	3.1076E-11	3.2002E-11	3.2932E-11	3.4015E-11
210	3.0718E-11	3.1610E-11	3.2453E-11	3.3550E-11

Fig. 6. The dependence of Van der Waals constant  $b$  for DAG oil as a function of pressure and temperature.

where  $M$  is the molecular mass ( $M = 0.65497$  kg/mol for the investigated DAG oil),  $R = 8.31446$  [J/(K·mol)] is the molar gas constant, and  $\gamma$  is the specific heat ratio.

Fig. 6 exhibits the dependence of the Van der Waals constant  $b$  on pressure and temperature, determined from (2), (3), (6), and (8).

### I. Surface Tension

The possibility to influence the value of the surface tension of a liquid is important in several technological processes in the chemical industry, for example, in processes of impregnation, flotation, and extraction. Control of surface tension is also important, e.g., in food high-

$$\theta_D(p, T) = \frac{h}{k} \left[ \frac{(9N/4\pi V(p, T))}{(\rho(p, T)k_s(p, T))^{3/2} \left\{ \left( \frac{1}{1+\gamma(p, T)} \right)^{3/2} + 2 \left( \frac{4}{3\gamma(p, T)} \right)^{3/2} \right\}} \right]^{1/3} \quad [\text{K}] \quad (10)$$

pressure processing. When the surface tension is reduced, an emulsion or foam can be formed easily [23].

Surface tension  $\sigma$  is defined as the energy  $dW$  that must be supplied to increase the surface area of a liquid by one unit  $dA$ , namely:

$$\sigma(p, T) = \frac{dW}{dA} = 6.33 \cdot 10^{-10} \cdot \rho(p, T) \cdot v(p, T)^{3/2} \quad [\text{N/m}]. \quad (9)$$

Fig. 7 displays the dependence of surface tension of DAG oil versus pressure and temperature computed from (2), (3), and (9). As illustrated in Fig. 7, the surface tension decreases with increasing temperature, and increases with increasing pressure, which is in accordance with expectations. See also Table VI.

#### J. Effective Debye Temperature $\theta_D$ :

The Debye temperature is helpful in the evaluation of heat capacity using the quasi-crystalline model for the liquids and the concept of phonons in terms of statistical thermodynamics. The Debye temperature is an important parameter for characterizing the properties of crude oil [24]; see (10), above, where  $h$  is the Planck constant,  $k$  is the Boltzmann constant,  $\gamma$  is the specific heat ratio,  $N$  is Avogadro's number, and  $V$  is the molar volume.

Fig. 8 shows the dependence of the effective Debye temperature of DAG oil versus pressure and temperature computed from (3), (4), (6), and (10). See also Table VII.

The quantum nature of the thermal oscillations in the liquid manifests itself below the Debye temperature.

#### IV. CONCLUSIONS

The goal of this work was to evaluate high-pressure thermodynamic parameters of liquids using the example of DAG oil, by using measurements of ultrasonic wave velocity and density in an investigated liquid. Longitudinal ultrasonic wave velocity and density measurements in DAG oil have been performed in the pressure range from atmospheric pressure to 220 MPa and at temperatures  $T = 20^\circ\text{C}$ ,  $30^\circ\text{C}$ ,  $40^\circ\text{C}$ , and  $50^\circ\text{C}$ . DAG oil is a ubiquitous fat in foodstuffs, e.g., in vegetable oils. Vegetable oils constitute a basic component of biofuels.

Using classical methods, direct measurement of the physicochemical parameters of liquids under high-pressure conditions is exceedingly difficult. To overcome this inconvenience, the authors employed an ultrasonic method that is based on the measurement of the speed of sound and density, which can be performed relatively easy and with high accuracy under high-pressure conditions.

TABLE V. EVALUATED VALUES OF VAN DER WAALS CONSTANT  $B$  IN METERS CUBED PER MOLE FOR DAG OIL AT VARIOUS TEMPERATURES AND PRESSURES.

Pressure [MPa]	Temperature [ $^\circ\text{C}$ ]			
	20	30	40	50
0.1	6.8847E-04	6.9306E-04	6.9778E-04	7.0263E-04
10	6.8190E-04	6.8665E-04	6.9285E-04	6.9637E-04
20	6.7805E-04	6.8261E-04	6.8864E-04	6.9277E-04
30	6.7454E-04	6.7901E-04	6.8471E-04	6.8910E-04
40	6.7119E-04	6.7560E-04	6.8128E-04	6.8487E-04
50	6.6781E-04	6.7209E-04	6.7783E-04	6.8202E-04
60	6.6468E-04	6.6872E-04	6.7422E-04	6.7875E-04
70	6.6194E-04	6.6572E-04	6.7114E-04	6.7574E-04
80	6.5885E-04	6.6270E-04	6.6772E-04	6.7279E-04
90	6.5605E-04	6.5972E-04	6.6497E-04	6.6989E-04
100	6.5353E-04	6.5694E-04	6.6198E-04	6.6705E-04
110	6.5056E-04	6.5422E-04	6.5910E-04	6.6420E-04
120	6.4800E-04	6.5161E-04	6.5639E-04	6.6148E-04
130	6.4556E-04	6.4872E-04	6.5370E-04	6.5890E-04
140	6.4318E-04	6.4624E-04	6.5126E-04	6.5644E-04
150	6.4088E-04	6.4387E-04	6.4877E-04	6.5405E-04
160	6.3859E-04	6.4146E-04	6.4612E-04	6.5179E-04
170	6.3635E-04	6.3902E-04	6.4401E-04	6.4953E-04
180	6.3405E-04	6.3677E-04	6.4175E-04	6.4733E-04
190	6.3198E-04	6.3465E-04	6.3941E-04	6.4505E-04
200	6.2966E-04	6.3240E-04	6.3729E-04	6.4292E-04
210	6.2779E-04	6.3027E-04	6.3514E-04	6.4071E-04

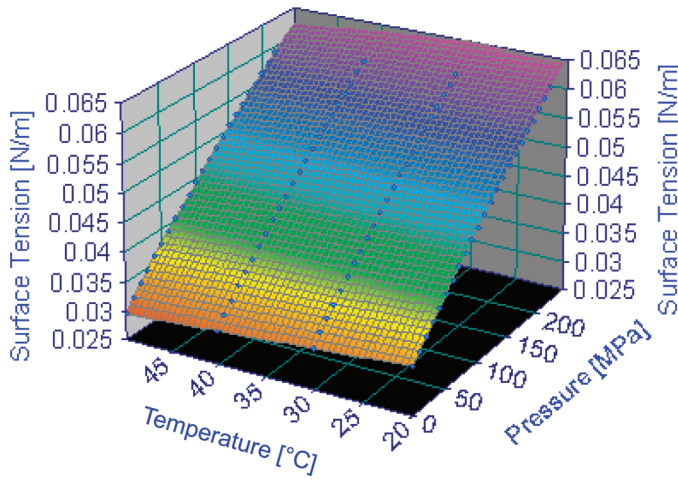


Fig. 7. Variation of surface tension  $\sigma$  of DAG oil on pressure and temperature.

The results of this work can be used in the numerical modeling and optimization of technological processes in the food and plastic industries (e.g., the injection process of molten polymers), as well as in the automotive industry in the construction and optimization of modern injection systems for diesel engines. Moreover, knowledge of reliable data of physicochemical properties of liquids under high pressure and various temperatures is indispensable in geophysics in exploration, refinement, and enhanced recovery of liquid natural resources (e.g., hydrocarbons) [25].

Ultrasonic wave velocity measurements conducted in a wide range of pressures and temperatures allow determination of the molecular dynamics of the liquid medium, and can provide information about the structural proper-

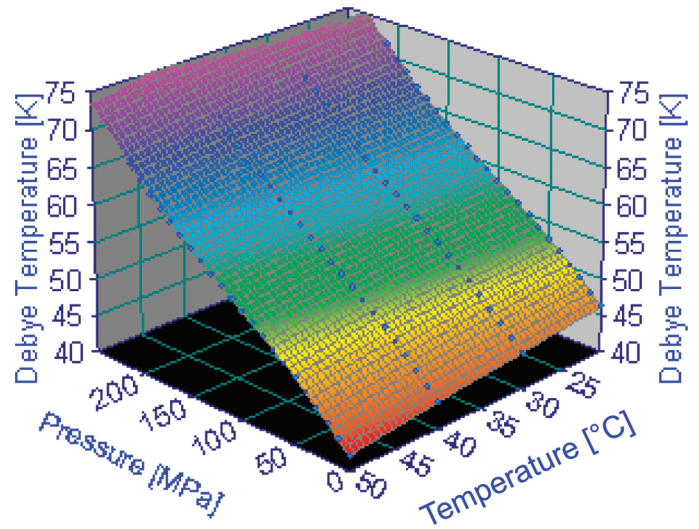


Fig. 8. The dependence of the effective Debye temperature  $\theta_D$  for DAG oil as a function of pressure and temperature.

ties of the investigated liquid. The key factors that determine the speed of sound are the adiabatic compressibility and the intermolecular free path length [26]. Using the measured speed of sound and density in a wide range of pressures and temperatures, the authors evaluated the following thermodynamic parameters: specific heat ratio, intermolecular free path length, Van der Waals constant  $b$ , surface tension, and effective Debye temperature as functions of pressure and temperature.

The results of this study are novel. The ultrasonic method presented in this paper can be applied to investigate (under high-pressure conditions and at elevated

TABLE VI. EVALUATED VALUES OF SURFACE TENSION  $\sigma$  IN MILLINEWTONS PER METER FOR DAG OIL AT VARIOUS TEMPERATURES AND PRESSURES.

Pressure [MPa]	Temperature [°C]			
	20	30	40	50
0.1	33.297	31.977	30.727	29.475
10	34.764	33.689	32.649	31.567
20	36.295	35.169	34.193	32.998
30	37.876	36.657	35.860	34.511
40	39.308	38.160	37.292	36.286
50	40.856	39.621	38.731	37.520
60	42.292	41.159	40.226	38.944
70	43.646	42.477	41.568	40.289
80	45.056	43.760	43.077	41.639
90	46.440	45.133	44.384	42.936
100	47.742	46.497	45.637	44.278
110	49.080	47.817	46.960	45.625
120	50.291	49.186	48.289	46.914
130	51.637	50.497	49.538	48.208
140	52.885	51.683	50.803	49.439
150	54.046	52.902	52.047	50.684
160	55.326	54.137	53.273	51.849
170	56.513	55.529	54.405	53.040
180	57.779	56.742	55.632	54.205
190	58.907	57.862	56.793	55.414
200	60.128	59.064	58.003	56.601
210	61.230	60.218	59.345	57.834

TABLE VII. EVALUATED VALUES OF THE EFFECTIVE DEBYE TEMPERATURE  $\theta_D$  IN KELVIN FOR DAG OIL AT VARIOUS TEMPERATURES AND PRESSURES.

Pressure [MPa]	Temperature [°C]			
	20	30	40	50
0.1	46.235	44.909	43.520	41.906
10	47.659	46.388	45.026	43.413
20	49.017	47.801	46.466	44.853
30	50.313	49.153	47.844	46.229
40	51.552	50.446	49.163	47.545
50	52.738	51.686	50.426	48.804
60	53.878	52.878	51.641	50.010
70	54.979	54.029	52.812	51.171
80	56.049	55.147	53.947	52.293
90	57.097	56.240	55.054	53.384
100	58.131	57.316	56.141	54.451
110	59.162	58.385	57.217	55.503
120	60.199	59.456	58.291	56.551
130	61.253	60.540	59.375	57.604
140	62.336	61.648	60.478	58.672
150	63.458	62.789	61.610	59.765
160	64.629	63.975	62.783	60.896
170	65.862	65.216	64.006	62.074
180	67.166	66.524	65.291	63.309
190	68.551	67.907	66.648	64.613
200	70.028	69.375	68.086	65.995
210	71.606	70.939	69.615	67.464



temperatures) thermodynamic parameters not only of oils and fats, but other liquids and mixtures (e.g., plastics, biofuels, drilling muds, and crude oil).

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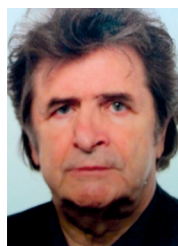


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