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LETTER TO THE EDITOR

Specific Heat of Olive Oil to 356 MPa

Bogdan M. Leu · Hasan Yavaş · Innokenty Kantor · Vitali B. Prakapenka

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Abstract We measured the velocity of sound in olive oil under pressure with the Brillouin light scattering technique. Using the values for the density and the thermal conductivity that have only recently been reported, we calculated the adiabatic compressibility and the isobaric specific heat up to 356 MPa and the thermal diffusivity up to 200 MPa. The specific heat displays a maximum at 124 MPa, suggesting a possible phase transition around this pressure. Apart from the theoretical and practical importance of these results for the food industry and beyond, this work shows that Brillouin light scattering and macroscopic methods are complementary and can be employed to measure thermophysical parameters of food liquids under pressure.

Keywords Olive oil · Pressure · Brillouin light scattering · Specific heat · Thermal diffusivity · Compressibility

B. M. Leu (✉) · H. Yavaş · I. Kantor
Advanced Photon Source, Argonne National Laboratory,
Argonne, IL 60439, USA
e-mail: leu@aps.anl.gov

H. Yavaş
Department of Geology, University of Illinois,
Urbana, IL 61801, USA

V. B. Prakapenka
GeoSoilEnviroCARS, University of Chicago,
Chicago, IL 60637, USA

Present Address:
I. Kantor
European Synchrotron Radiation Facility,
38000 Grenoble, France

Introduction

Due to its advantages with respect to the traditional thermal approach, high-pressure technology has become an attractive option for food processing [1]. Computer simulations are, like in many other fields, useful complementary investigative tools but they require physical parameters for food under pressure, information that is still scarce. For example, until recently, the density of some natural oils was known only up to 145 MPa [2], while the isobaric specific heat, thermal diffusivity, and thermal conductivity only up to 49 MPa [3]. These values are too low when compared to the pressures used in the food industry and offer only a limited insight into the properties of these materials, as demonstrated by later studies in which higher pressures were reached.

During the last 2 years, the density [4, 5] and the thermal conductivity [4] of some edible oils have been reported at several temperatures and pressures exceeding 400 MPa. This breakthrough allows one to derive the dependence of other physical parameters, such as the isothermal compressibility and the thermal expansion coefficient, on temperature and pressure [5]. However, the isobaric specific heat at higher pressures—a necessary parameter for feeding the models used to predict the heat transfer under pressure and microorganism inactivation [1, 5]—remains elusive.

Here, we apply the Brillouin light scattering (BLS) technique to measure the velocity of sound in olive oil at ambient temperature and high pressures and, using the values for the density [5] and the thermal conductivity [4] available in the literature, we calculate the adiabatic compressibility and the isobaric specific heat up to 350 MPa and the thermal diffusivity up to 200 MPa.

Experimental Procedure

Sample

We used commercially available olive oil (Mythology, Greece). According to the nutritional information provided, the ratio between monounsaturated fat, polyunsaturated fat, and saturated fat was 71/11/14%, which is typical for olive oil. The sample was loaded in a hole with a diameter of 100 μm laser-drilled in the center of a 250-μm-thick stainless steel gasket and was placed in a diamond anvil cell. The diamond culets were 800 μm in diameter.

Brillouin Light Scattering

The BLS spectrum of a liquid consists of a central (Rayleigh) band at the frequency of the incident light (f_0) and a doublet shifted to frequencies $f_0 \pm f_s$. Using the linearized Navier–Stokes equation, one can extract various properties of the liquid, including the adiabatic sound velocity [6]:

$$v_L = \frac{f_s}{Q} \quad (1)$$

in which $Q = 2\Lambda^{-1}\sin(\theta^*/2)$ is the size of the momentum transfer vector in the "platelet" symmetrical geometry (Λ is the wavelength of the incident light and θ* the predefined external scattering angle). The experiment was carried out at the GSECARS 13 BM-D beamline at the Advanced Photon Source, Argonne National Laboratory $\left(\Lambda = 532\,\text{nm}, \theta^* = 50^\circ, Q = 1.6 \times 10^6\,\text{m}^{-1}\right)$. Detailed information about the experimental setup can be found elsewhere [7]. The pressure was determined from the ruby characteristic R_1 luminescent line.

Results and Discussion

Select BLS spectra for olive oil are shown in Fig. 1, top panel. For convenience in the data analysis, we chose the sound velocity for the abscissa, rather than the frequency. The sound velocity as a function of pressure is shown in Fig. 1, lower panel. Although we reached pressures as high as 1,167 MPa, we included only the points up to 356 MPa in the present analysis (Fig. 2a) because the density of olive oil at ambient temperature has been measured only up to 350 MPa [5]. The error bars for the sound velocity are smaller than the size of the markers. We fitted the sound velocity with a second degree polynomial [8]:

$$v_L(p) = c_0 p^2 + c_1 p + c_2 \quad (2)$$

with $c_0 = 2.9 \times 10^{-4}$ ms^{-1} MPa^{-2}, $c_1 = 2.4$ ms^{-1} MPa^{-1}, $c_2 = 1{,}522$ ms^{-1}. Knowing the dependence of the specific volume on pressure and temperature [5]:

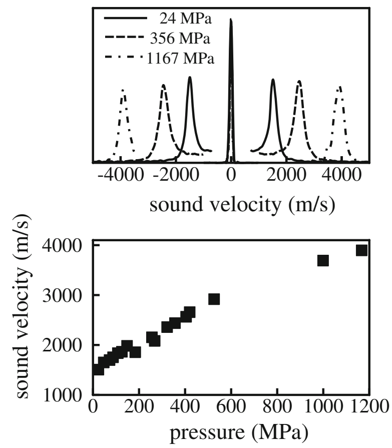

Fig. 1 *Top panel* select Brillouin light scattering spectra. The ordinate is not drawn on the same scale for the three data sets. The Rayleigh line was scaled down with respect to the corresponding Brillouin lines. *Lower panel* the sound velocity over the whole pressure range investigated

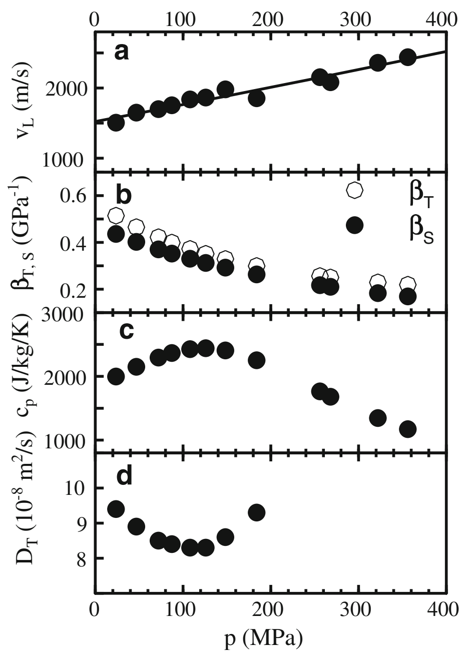

Fig. 2 **a** Sound velocity (including the fit with Eq. 2), **b** isothermal (Eq. 4; [5]) and adiabatic (Eq. 5) compressibility, **c** isobaric specific heat (Eq. 6), **d** thermal diffusivity (Eq. 8) as a function of pressure

$$v(p,T) = v_0(T)\left(1 - \frac{\Delta p}{B_0 + cT + dT^2 + e\Delta p + f(\Delta p)^2}\right) \quad (3)$$

allows one to calculate the isothermal compressibility (β_T) and the thermal expansion coefficient (α) from their respective definitions:

$$\beta_T = -\frac{1}{v}\left(\frac{\partial v}{\partial p}\right)_T, \alpha = \frac{1}{v}\left(\frac{\partial v}{\partial T}\right)_p \quad (4)$$

In Eq. 3, $v_0(T)$ is the specific volume at a reference temperature, $\Delta p = p - p_0$ ($p_0 = 0.1$ MPa), and B_0, c, d, e, and f are known constants [5]. We obtained the adiabatic compressibility at $T = 298$ K (Fig. 2b) from:

$$\beta_S(p) = \frac{v}{v_L^2} \tag{5}$$

and the isobaric specific heat from:

$$c_p(p) = \frac{T\alpha^2 v}{\beta_T - \beta_S} \tag{6}$$

in which v_L, v, β_T, α, and β_S are given by Eqs. 2, 3, 4, and 5. The presence of a maximum in c_p (Fig. 2c) is a characteristic of a phase transition from isotropic liquid to liquid crystal. X-ray diffraction studies on oleic acid showed that this fatty acid experiences a phase transition to a highly ordered smectic phase at 210 MPa [9]. This result confirmed previous light scattering studies which revealed an increase in the molecular order at that pressure [10]. We suggest that for olive oil the maximum in c_p may be a reflection of a similar phase transition occurring at approximately 124 MPa. With the help of a built-in camera, we noticed a change in the sample appearance around this pressure. This phase transition is not manifested in the density [5] or in the longitudinal sound velocity (Fig. 2a). This behavior contrasts with that of a semifluorinated alkane, a material for which several techniques, including pressure–volume–temperature and BLS measurements, revealed two different first-order phase transitions [11]. One way to describe the pressure dependence of c_p is through the following polynomials: $-0.045p^2 + 11.2p + 1{,}738$ ($p < 210$ MPa) and $0.016p^2 - 16p + 4{,}805$ ($210 < p < 356$ MPa). BLS has been previously used for investigations on liquids under pressure, such as relaxation processes in polymers [12], structural transformations in water [13], and physical properties of ammonia [14].

The thermal conductivity (λ) at ambient temperature has been measured with the transient hot wire method up to 200 MPa [4]. Because λ has a rather weak temperature dependence, very little error is introduced by using its value at 20 °C (rather than 25 °C) in our analysis. According to Ref. [4], $1/\lambda(\partial\lambda/\partial p)_T$ is approximately proportional to β_T, which leads to:

$$\lambda(p) = \lambda_0 \left(\frac{v}{v_0}\right)^a \tag{7}$$

where $a = -2.88$ is a proportionality factor, $\lambda_0 = 0.166$ Wm^{-1}K^{-1} is the thermal conductivity at ambient pressure, and the ratio v/v_0 is given by Eq. 3.

The thermal diffusivity:

$$D_T(p) = \frac{\lambda v}{c_p}, \tag{8}$$

is shown in Fig. 2d ($10^8 D_T = 1.64 \times 10^{-4}p^2 - 0.035p + 10.2$). According to the theory [6], the width of the Rayleigh peak (Γ_0) is equal to the product between the thermal diffusivity (D_T) and the square of the momentum transfer (Q^2). In practice, however, the central line is dominated by the laser width, often preventing one from measuring the actual Γ_0.

The olive oils used in different studies are not completely identical. There are hundreds of types of olive trees, whose fruits vary in size, chemical composition, etc. Furthermore, the fruit maturity and processing technique affect the characteristics of the final product. However, despite this variety, the same fatty acids account for 98% of the oil content making the oils remarkably similar, as demonstrated by Raman spectroscopy [15].

The significance of the results presented in this study is, in our opinion, two-fold: sample and technique-related. Regarding the liquid investigated, the importance of olive oil, and edible oils, in general, reaches beyond their traditional use (as food and cosmetic products). They are industrial fluids [16], fuel alternatives [17], substitutes for mineral oils [18], and low-viscosity magma mimics in models for the Earth's brittle crust [19]. For all practical and theoretical purposes, the quantities measured and calculated in this paper are important parameters for characterizing the dynamic and thermal properties of these materials under pressure, and for simulating their behavior. Perhaps more importantly, this study demonstrates that Brillouin light scattering and macroscopic (e.g. densimetric, transient hot wire) methods are complementary. Once the pressure-dependence of the sound velocity and the density is measured, several thermophysical parameters can be calculated. This relatively straightforward experimental approach has the potential of being employed for investigating other liquid foods.

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References

1. Rastogi NK, Raghavarao KSMS, Balasubramaniam VM, Niranjan K, Knorr D (2007) Opportunities and challenges in high pressure processing of foods. Crit Rev Food Sci Nutr 47:69–112
2. Acosta GM, Smith Jr RL, Arai K (1996) High-pressure *PVT* behavior of natural fats and oils, trilaurin, triolein, and *n*-tridecane from 303 K to 353 K from atmospheric pressure to 150 MPa. J Chem Eng Data 41:961–969
3. Safarov MM, Usupov S, Tagoev S (1999) Thermophysical properties of vegetable oils in a wide range of temperatures and pressures. High Temp High Pres 31:43–48
4. Werner M, Baars A, Eder C, Delgado A (2008) Thermal conductivity and density of plant oils under high pressure. J Chem Eng Data 53:1444–1452
5. Guignon B, Aparicio C, Sanz PD (2009) Volumetric properties of sunflower and olive oils at temperatures between 15 and 55 °C under pressures up to 350 MPa. High Pressure Res 29:38–45
6. Berne BJ, Pecora R (2000) Dynamic light scattering. Dover Publications, Inc., Mineola, NY
7. Sinogeikin S, Bass J, Prakapenka V, Lakshtanov D, Shen G, Sanchez-Valle C, Rivers M (2006) Brillouin spectrometer interfaced with synchrotron radiation for simultaneous X-ray density and acoustic velocity measurements. Rev Sci Instrum 77:103905
8. Fine RA, Millero FJ (1973) Compressibility of water as a function of temperature and pressure. J Chem Phys 59:5529–5536
9. Przedmojski J, Siegoczyński RM (2002) X-ray diffraction investigation of oleic acid under high pressure. Phase Transit 75:581–585
10. Siegoczyński RM, Wiśniewski R, Ejchart W, Jędrzejewski J (1994) Optical hysteresis in oleic acid and castor oil under pressure. High Pressure Res 13:93–97
11. Núñez E, Clark Jr CG, Cheng W, Best A, Floudas G, Semenov AN, Fytas G, Müllen K (2008) Thermodynamic, structural, and nanomechanical properties of a fluorous biphasic material. J Phys Chem B 112:6542–6549
12. Fytas G, Meier G, Dorfmüller T (1985) Rayleigh–Brillouin spectra of poly[(phenylmethyl)siloxane] under high pressures. Macromolecules 18:993–996
13. Li F, Cui Q, He Z, Cui T, Zhang J, Zhou Q, Zou G, Sasaki S (2005) High pressure–temperature Brillouin study of liquid water: Evidence of the structural transition from low-density water to high-density water. J Chem Phys 123:174511
14. Li F, Li M, Cui Q, Cui T, He Z, Zhou Q, Zou G (2009) The velocity, refractive index, and equation of state of liquid ammonia at high temperatures and high pressures. J Chem Phys 131:134502
15. López-Diez EC, Bianchi G, Goodacre R (2003) Rapid quantitative assessment of the adulteration of virgin olive oils with hazelnut oils using Raman spectroscopy and chemometrics. J Agr Food Chem 51:6145–6150
16. Aluyor EO, Obahiagbon KO, Ori-jesu M (2009) Biodegradation of vegetable oils: A review. Sci Res Essays 4:543–548
17. Demirbas A (2010) New biorenewable fuels from vegetable oils. Energy sources, Part A: recovery, utilization, and environmental effects 32:628–636
18. Amanullah M, Islam SM, Chami S, Ienco G (2005) Analyses of physical characteristics of vegetable oils as an alternative source to mineral oil-based dielectric fluid. In: IEEE Int Conf Dielectr Liq, pp 397–400
19. Galland O, Cobbold PR, Hallot E, deBremond d'Ars J, Delavaud G (2006) Use of vegetable oil and silica powder for scale modelling of magmatic intrusion in a deforming brittle crust. Earth Planet Sci Lett 243:786−804