

**ON AN OPTIMAL INTERVAL SELECTION FOR THE
REGRESSION OF MOLECULAR FREQUENCY VS.
DENSITY DATA AIMED AT DETERMINING
NONLINEARITY PARAMETERS OF ORGANIC LIQUIDS**

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INTRODUCTION

The nonlinearity parameter in thermodynamic consideration of liquids is defined by the ratio between the coefficients determining the density-pressure response at the second and the first-order perturbations respectively to the equilibrium state (ρ_0, P_0) :

$$P - P_0 = \rho_0 \left(\frac{\partial P}{\partial \rho} \right)_{X, \rho = \rho_0} \left(\frac{\rho - \rho_0}{\rho_0} \right) + \left(\frac{\partial^2 P}{\partial \rho^2} \right)_{X, \rho = \rho_0} \left(\frac{\rho - \rho_0}{\rho_0} \right)^2, \quad (1)$$

where $X = \{S, T\}$ means either adiabatic ($X \equiv S = \text{const}$) or isothermal ($X \equiv T = \text{const}$) compression.

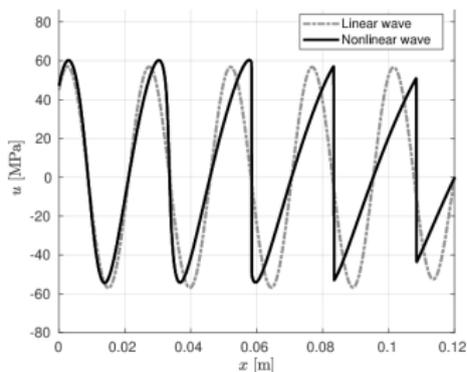
BAYER'S NONLINEARITY PARAMETER

The case $X \equiv S = \text{const}$ is realized by sound waves of finite amplitude and leads to the so-called Bayer nonlinearity parameter [1]

$$\frac{B}{A} = \rho_0 \left(\frac{\partial^2 P}{\partial \rho^2} \right)_{S, \rho=\rho_0} / \left(\frac{\partial P}{\partial \rho} \right)_{S, \rho=\rho_0} = 2\rho_0 c_0 \left(\frac{\partial c}{\partial P} \right)_{S, \rho_0, P_0}, \quad (2)$$

which defines:

- the distortion of a high intensity waveform;
- the occurrence of a shock wave.



[1] - Beyer, R.T. Parameter of nonlinearity in fluids. *Journal of the Acoustical Society of America* 1960, 32, 719–721. doi:10.1121/1.1908195

APPLICATIONS

The nonlinearity parameter B/A is a quantity, which plays the role of a promising indicator in the following areas:

- diagnostic ultrasound examinations;
- ultrasound tomography;
- physical chemistry of ionic liquids.

DEFINITION VIA THERMODYNAMIC PARAMETERS

Since the entropy in the expression (2) is not a measurable quantity, the non-linearity parameter B/A is expressed through directly determinable thermodynamic quantities:

$$\frac{B}{A} = 2\rho_0 c_0 \left(\frac{\partial c}{\partial P} \right)_{0,T} + \frac{2c_0 T \alpha_P}{C_P} \left(\frac{\partial c}{\partial T} \right)_{0,P} = \left(\frac{B}{A} \right)' + \left(\frac{B}{A} \right)'' , \quad (3)$$

where $\alpha_P = -\rho^{-1} (\partial\rho/\partial T)_P$ is the isobaric expansion coefficient, C_P is the isobaric specific heat capacity.

METHODS FOR DETERMINING B/A

Basic experimental methods:

- ① classical thermodynamic route;
- ② isoentropic thermodynamic route:
 - phase measurement;
 - transmission time measurement of an ultrasonic pulse;
 - frequency measurement;
- ③ analysis of a wave's shape:
 - respectively to the light diffraction;
 - by the comparison with wave profile modeling;
- ④ measurement of the amplitude of the second harmonic.

Theoretical methods:

- ① Nomoto model for Rao liquid;
- ② fluctuation model.

ISOTHERMAL NONLINEARITY PARAMETER

The case at $X \equiv T = \text{const}$ leads to the isothermal nonlinearity parameter:

$$k' = \rho_0 \left(\frac{\partial^2 P}{\partial \rho^2} \right)_{T, P=P_0} / \left(\frac{\partial P}{\partial \rho} \right)_{T, P=P_0}, \quad (4)$$

which allows the accurate prediction of the liquid's density up to ultrahigh pressures [1] when considering the initial problem for ODE along isotherms obtained within the framework of linear response theory:

$$(-1)^m \rho^n \left(\frac{\partial P}{\partial \rho} \right)_T = (\rho_0 \kappa_T^0)^{-1} [1 + k' \kappa_T^0 (P - P_0)], \quad (5)$$

where the pairs (m, n) define the type of equation.

[1] - Postnikov, E.B.; Belenkov, R.N.; Chorążewski, M. Combining the Tait equation with the phonon theory allows predicting the density of liquids up to the Gigapascal range. *Scientific Reports* 2023, 13, 3766. doi:10.1038/s41598-023-30917-0.

EXPLANATION OF THE COEFFICIENTS (N,M)

$(n, m) = (1, 0)$ gives the Murnaghan equation:

$$\rho_{Murnaghan} = \rho_0 [1 + k' \kappa_T^0 (P - P_0)]^{1/k'}, \quad (6)$$

$(n, m) = (2, 1)$ gives the Tait equation:

$$\rho_{Tait}^{-1} = \rho_0^{-1} \left(1 - k'^{-1} \ln [1 + k' \kappa_T^0 (P - P_0)] \right), \quad (7)$$

$(n, m) = (0, 0)$ gives the FT-EoS equation:

$$\rho_{FTEoS} = \rho_0 [1 + k' \kappa_T^0 (P - P_0)], \quad (8)$$

which is an approximation of Tait's and Murnaghan's equation for pressures up to 100 – 150 MPa.

RELATION BETWEEN PARAMETERS

It should be noted that the adiabatic and the isothermal nonlinearity parameters are not independent. In [1], the following expression is given for B/A (modified accordingly to the notation of Eq. (5))

$$\begin{aligned} \frac{B}{A} = & k' \gamma + (\gamma - 1) \left[k' - \frac{2}{\alpha_P \kappa_T} \left(\frac{\partial \kappa_T}{\partial T} \right)_P \right] + \\ & (\gamma - 1)^2 \left[1 + k' + \frac{1}{\alpha_P^2} \left(\frac{\partial \alpha_P}{\partial T} \right)_P - \frac{2}{\alpha_P \kappa_T} \left(\frac{\partial \kappa_T}{\partial T} \right)_P \right] + \\ & \frac{2c_0 T \alpha_P}{C_P} \left(\frac{\partial c}{\partial T} \right)_P, \quad (9) \end{aligned}$$

where γ , C_P , α_P are the heat capacity ratio, the isobaric heat capacity and the isobaric coefficient of thermal expansion. All terms except k' can be easily determined at atmospheric pressure (or along the coexistence curve of liquid and vapor before the boiling point).

[1] - Endo, H. Determination of the nonlinearity parameters for liquids using thermodynamic constants. *Journal of the Acoustical Society of America* 1982, 71, 330–333. doi:10.1121/1.387456

EXPRESSION FOR k' FROM PHONON THEORY

In [1], based on the phonon theory of liquids, it was shown that:

$$k' = \left(\frac{\partial (c_0(T)^3 \rho_0(T))}{\partial (\rho_0(T))} \right)_{P=P_0} \equiv 3 \left(\frac{\partial \ln \nu_{max}}{\partial \ln \rho_0} \right)_{P=P_0} = 3\Gamma, \quad (10)$$

where Γ is the microscopic (not thermodynamic) Grüneisen's parameter and ν_{max} is the characteristic frequency of the highest phonon mode in Debye's quasi-harmonic approximation.

In practice, this derivative is regarded as the slope coefficient of the approximating line $(c_0(T)^3 \rho_0(T))$ or $(\rho_0(T))$. However, the value of the k' coefficient is affected by the temperature range chosen for the approximation.

[1] - Postnikov, E.B.; Belenkov, R.N.; Chorażewski, M. Combining the Tait equation with the phonon theory allows predicting the density of liquids up to the Gigapascal range. *Scientific Reports* 2023, 13, 3766. doi:10.1038/s41598-023-30917-0.

OBJECTIVES

- to explore the point-wise dependence of k' on the temperature;
- to determine criteria for the optimal choice of k' ;
- to carry out tests with real liquids: methanol and toluene;
 - to check the predictive capacity of the model
 $\rho = (\rho_{Tait} + \rho_{Murnaghan}) / 2$ with the selected k' ;
 - to compare the value of the predicted acoustic nonlinearity parameter with the experimental.

LIQUIDS FOR TESTING

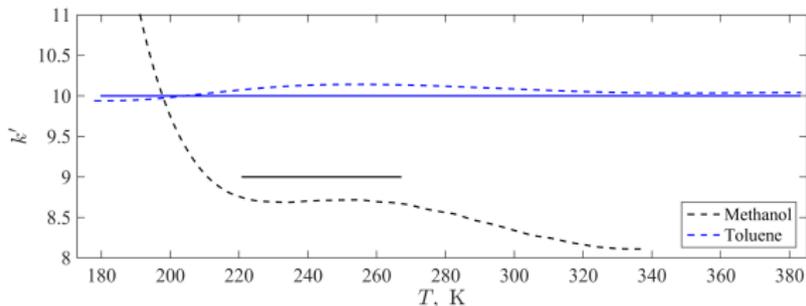
The following liquids were used to test the predictive hypothesis:

- methanol is a typical substance with strong hydrogen bonds;
- toluene is a standard molecular liquid with dispersion forces only.

The thermodynamic data of liquids in the saturated and compressed states used to study the isothermal nonlinearity parameter as well as to calculate the acoustic nonlinearity parameter thermodynamically were generated by NIST REFPROP 10.0 software.

DEPENDENCE OF k' ON TEMPERATURE

The isothermal nonlinearity parameters determined directly (dashed curve) as the derivative stated by Eq. (10) and their constant values rounded to integer values within intervals of negligible temperature dependence (solid lines).



It can be seen that the case of methanol actually requires consideration of a limited range of temperatures in order to consider k' approximately constant. For toluene, there is no such strong interval limitation, although linearity is best in the room temperature range, which agrees well with Rao's rule.

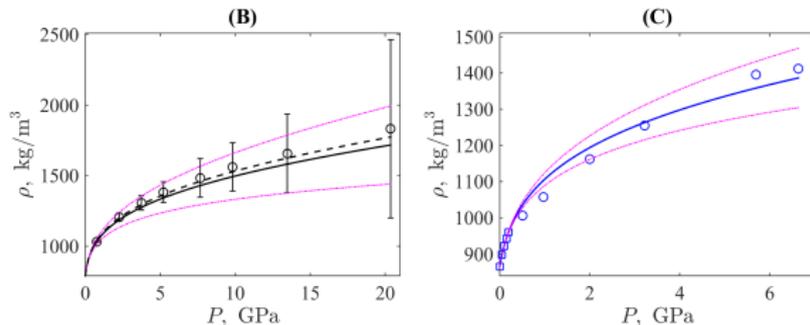
DISCUSSION OF RESULTS FOR k'

Key findings:

- the parameter k' can be influenced by the specifics of intermolecular interactions;
- the predictive approach to calculating the nonlinear properties of compressed fluids requires first identifying the interval of weak temperature dependence of k' .

DENSITY PREDICTION

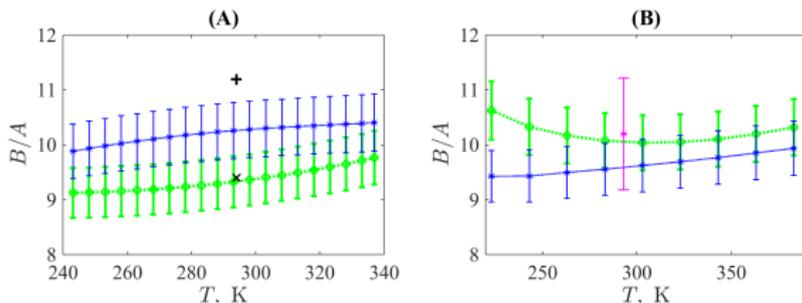
(B) The experimental compression curve for methanol at 298 K [1] (circles) and the density predicted (solid line with whiskers denoting extended experimental uncertainty) as the half-sum of Tait's (upper magenta curve) and Murnaghan's (lower magenta curve) equations. (C) Experimental data for toluene initially taken at 295 K: shock wave compression [2] (circles) and equilibrium isothermal compression from the REFPROP 10.0 (squares); lines marked as for the subpanel (B) denote predictions.



[1] - Zaug, J.M.; Slutsky, L.J.; Brown, J.M. Equilibrium properties and structural relaxation in methanol to 30.4 GPa. *Journal of Physical Chemistry* 1994, 98, 6008–6016. doi:10.1021/j100074a030.

[2] - Dick, R.D. Shock compression data for liquids. I. Six hydrocarbon compounds. *Journal of Chemical Physics* 1979, 71, 3203–3212. doi:10.1063/1.438767.

RESULTS ON B/A FOR METHANOL AND TOLUENE

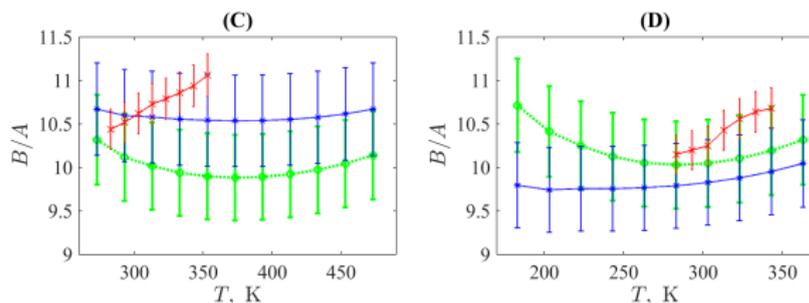


Blue curves with asterisks denote the thermodynamic value from Eq. (2), where adiabatic derivative computed using the isothermal and isobaric ones from the REFPROP EoS, green curves with circles use Eq. (9) with integer values of the isothermal nonlinearity parameter. The substances: (A) methanol, + and x denote experimental data obtained [1] by the finite amplitude loss and light diffraction methods; (B) toluene, magenta asterisk denote the experimental value obtained from the second harmonics generation [2].

[1] - Kashkooli, H.A.; Dolan Jr, P.J.; Smith, C.W. Measurement of the acoustic nonlinearity parameter in water, methanol, liquid nitrogen, and liquid helium-II by two different methods: A comparison. *Journal of the Acoustical Society of America* 1987, 82, 2086–2089. doi:10.1121/1.395653.

[2] - Shklovskaya-Kordi, V.V. An acoustic method of determining the internal pressure in a liquid. *Akusticheskii Zhurnal* 1963, 9, 107–111.

RESULTS ON B/A FOR HEPTANE AND DODECANE



The substances: (C) n-dodecane; (D) n-heptane. Red crosses mark (subpanels (C) and (D)) experimental data obtained by the fast adiabatic compression [1]

Based on the above plots, we conclude that the approach based on the phonon theory of liquids for calculating the acoustic nonlinearity parameter leads to quite reasonable estimates, which are within an inevitably wide range of experimental uncertainties.

[1] - Lu, Z.; Lagourette, B.; Daridon, J.L. Acoustic nonlinearity parameter of liquid alkanes as a function of temperature, chain length and isomerism. *Physics and Chemistry of Liquids* 2001, 39, 255–266.
doi:10.1080/00319100108030344.

CONCLUSIONS:

- a method for optimal selection of the isothermal nonlinearity parameter k' is proposed;
- the predicted density for pressures over 10 GPa including glassy and shock-compresses states for methanol and toluene accurately fits the experimental data;
- the isothermal nonlinearity parameter obtained via the above-mentioned way correpponds to the range following from different experimental methods

Thank you for your attention