Applied Problems of Nonlinear Oscillation and Wave Theory

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Approach to nonlinearity parameter in liquids calculation based on the scaling theory of thermodynamic fluctuations

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Abstract. The nonlinearity parameter B/A is a characteristic of liquids and soft matter, which gains growing attention due to its sensibility to the composition of materials. This makes it a prospective indicator for nondestructive testing applications based on the ultrasound sounding suitable for a variety of applications from physic chemistry to biomedical studies. At the same time, the thermodynamic definition of the nonlinearity parameter requires extensive measurements at elevated pressures that are not always available; in addition, there are known certain contradiction of such data with the data obtained by methods of nonlinear acoustics. *Objective.* In this work, we consider a recently proposed approach to the prediction of the speed of sound at high pressures, which uses the property of invariance of the reduced pressure fluctuations and the data obtained at normal ambient pressure only. The method generalises the classic Nomoto model, which however gives only a qualitative picture, and results in the quantitative correspondence to the experimental values within their range of uncertainty. *Methods.* Analytical methods of the theory of thermodynamic fluctuations applied to the parameters of equations of nonlinear acoustics as well as numerical simulation in the COMSOL Multiphysics® environment. *Results.* Expressions for calculating the nonlinearity parameter with acceptable accuracy were obtained using thermodynamic data obtained only at atmospheric pressure. Numerical calculations were performed for toluene. In addition, the discrepancy between values of the nonlinear parameter obtained via the thermodynamic and nonlinear acoustic routes is analysed based on the numerical solution of the Westervelt equation; it is revealed that this deviation emerges when the effects of absorption of finite-amplitude waves were not properly taken into account.

Keywords: nonlinearity parameter, high-intense ultrasound, thermodynamic fluctuations, nonlinear waves.

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Introduction

The nonlinearity parameter B/A (explicit expressions for the values A and B through the parameters of the state of the medium will be given below) as a characteristic of the waveform's

distortion for finite amplitude waves in liquids, [1] was introduced in [2] (although it was later noted [3] that this approach conceptually goes back to Rayleigh's work on acoustic pressure [4]).

A more general approach, linking the nonlinearity parameter with thermodynamic quantities that do not require working with powerful ultrasound to determine it, is based on the approach outlined in the article by R. T. Beyer [5] (because of this, in a number of sources, the parameter B/A is called «Beyer's nonlinearity parameter»). This approach is fundamental in the theory of nonlinear acoustics and its application to the study of a wide range of problems ranging from physical chemistry of liquids to biomedical applications. [6–8]. A detailed overview of the current state of research and the significance of the nonlinear parameter is presented in [9]. The significant sensitivity of the nonlinearity parameter to the composition and physico-chemical properties of liquids, colloids and soft media makes it an effective marker in the field of diagnostic ultrasound and ultrasound tomography [10, 11]. In the field of physics and physical chemistry of liquids, attention has been growing in recent years to the nonlinearity parameter as an important characteristic of the properties of ionic liquids and deeply eutectic solvents [12, 13]. Due to the growing interest in their use as media for chemical synthesis and heat transfer fluids at high pressures, the question arises about the behavior of the nonlinearity parameter under such conditions, which has not been practically studied experimentally. Accordingly, the question of the possibility of the predictive calculation of the value of B/A as a function of temperature and pressure from the data obtained under normal pressure conditions is open. In addition, there is also a fundamental problem of the relationship between the nonlinearity parameter B/A and the coefficients of the differential equations of nonlinear acoustics [14, 15].

The first attempt at a theoretical definition of the nonlinearity parameter B/A, universal with respect to temperature and pressure, is the work of O. Nomoto [16], performed under the assumption of the so-called «Rao liquid» (see also the work [17], which presented a deeper thermodynamic analysis), that is, the medium, for which an empirical power-law relationship between the density and the speed of sound (the Rao rule) [18] or density and isothermal or adiabatic compressibility (the Wada rule) is fulfilled [19]. Despite the fact that by now it is quite clear that the Rao-Wada rules are substantially approximate, they are still used as a practical method (with the introduction of empirical correction coefficients), see for example [20–24]. At the same time, the use of the Rao liquid model leads to a constant value of $B/A = 6$, which does not depend on temperature and pressure, which does not correspond to experiments and, moreover, the value itself demonstrates only qualitative agreement with reality (for various liquid and soft media, this value varies from 5 to 12).

Recently, it has been shown [25] based on the analogy between the analysis of differential equations of thermodynamics and dynamical systems that a more physically correct picture of the relationship between the density, the speed of sound and the fluid's temperature should be based on the consideration of thermodynamic fluctuations of density and pressure taken in the complex.

1. The nonlinearity parameter

The nonlinearity parameter B/A for sound waves of large amplitude is determined by the ratio of the expansion coefficients of the pressure change in the medium with respect to the adiabatic change (at constant entropy, which is further indicated by the index S in partial derivatives) of its density

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

where the following designations are introduced

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

Here ρ_0 and P_0 are the equilibrium (undisturbed) density and pressure, c_0 is the low amplitude speed of sound (thermodynamic (adiabatic) speed of sound).

Accordingly (hereafter the index 0 refers to derivatives taken with undisturbed parameters of the thermodynamic state),

$$\frac{B}{A} = \frac{\rho_0}{c_0^2} \left(\frac{\partial^2 P}{\partial \rho^2} \right)_{S,\rho=\rho_0} = 2\rho_0 c_0 \left(\frac{\partial c}{\partial P} \right)_{0,S}. \tag{1}$$

From this definition, it can be seen that the nonlinearity parameter can be found as based on the thermodynamic relations given by the equation of state of the liquid $\rho = \rho(P,T)$, from a practical point of view — from the functional relations linking the parameters of the state based on the regression of equilibrium thermodynamic experimental data. However, it should be noted that the direct application of the formula (1) is complicated by the fact that the entropy is not a directly measurable thermodynamic quantity (although there is a special phase-comparison method [26] that allows determining the adiabatic derivative of the speed of sound in an experiment, achieving a relative uncertainty of the nonlinearity parameter's value about 2.2%). Because of this, it is more practical to represent (1) through isobaric and isothermal derivatives of the speed of sound using standard relations between thermodynamic derivatives:

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

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

At the same time, the use of the expression (2) requires a sufficient amount of data on the speed of sound measured along the isotherms at elevated pressures, which are not always available (this is especially important for medical ultrasound diagnostics performed at atmospheric pressure). Accordingly, the question arises of how to calculate the isothermal derivative operating only with isobaric data.

2. Nomoto Model

The classical simple predictive model of the nonlinearity parameter referred to physico-chemical properties of a liquid is the Nomoto model [16] based on assumptions

$$\left(\frac{\partial c}{\partial T} \right)_P = \frac{3c}{2\rho} \left(\frac{\partial \rho}{\partial T} \right)_P, \tag{3}$$

$$\left(\frac{\partial c}{\partial P} \right)_T = \frac{3c}{2\rho} \left(\frac{\partial \rho}{\partial P} \right)_T, \tag{4}$$

which follow from the so-called Rao rule

$$\frac{M}{\rho} c^{1/3} = R_w, \tag{5}$$

where M is the molar mass, and R_w is a substance-specific constant (the molecular speed of sound), which can be calculated with acceptable accuracy by the method of group contributions respectively to interatomic chemical bonds or submolecular chemical groups either directly or through the compressibility of the liquid [19–21, 27].

However, this model leads to the constant value

$$\frac{B}{A} = 6, \tag{6}$$

which is not true for most liquids (with the exception of water, which has a weakly varying nonlinearity parameter [8] close in magnitude; it should be noted that for water, the value of R_w really weakly depends on both pressure and temperature [28]).

The quantitative and qualitative difference between Nomoto's result and the experimentally observed situation for the vast majority of molecular and ionic liquids can be attributed primarily to the violation of the condition of independence of the Rao parameter R_w from the choice of a thermodynamic path (isobaric or isothermal), which was discussed in the context of the study of the dependence of the speed of sound on the density along isotherms and along isobars [29, 30]. Thus, there is an emerging challenge of choosing a combination of thermodynamic parameters that satisfies the required invariance property with greater accuracy.

3. Fluctuation model

As the invariant mentioned above, which makes it possible to map the isobaric derivative of the speed of sound to the isothermal one, it was proposed in the work [25] to consider the squared thermodynamic pressure fluctuations in a liquid

$$\langle (\Delta P)^2 \rangle = \frac{RT}{M} \rho^2 \frac{1}{\rho \kappa_S}, \tag{7}$$

directly related to the speed of sound, by virtue of the expression of the latter $c = (\rho\kappa_S)^{-1/2}$ via the adiabatic compressibility $\kappa_S = \rho^{-1} (\partial\rho/\partial P)_S$, included in (7).

The used dimensionless value of the reduced pressure fluctuations is defined as the ratio of the actual value of the pressure fluctuations to the value of the pressure squared in a hypothetical medium having the properties of an ideal gas at the same density as the liquid in question ($P_{ig} = \rho RT/M$)

$$\nu_s \equiv \frac{\langle (\Delta P)^2 \rangle}{P_{ig}^2} = \frac{M}{R} \frac{1}{T \rho \kappa_s} \equiv \frac{M}{R} \frac{c^2}{T}.$$

In the work [25], the power-law dependence of the parameter of the reduced adiabatic fluctuations ν_s on the density was shown for a wide range of liquid hydrocarbons and their mixtures:

$$\nu_s \equiv \frac{Mc^2}{RT} = \Lambda \rho^{\lambda}, \tag{8}$$

where M/R, Λ, λ — constants (R — gas constant).

Let's do a procedure similar to the one that was performed when deriving the Nomoto model, and consider the combination

$$\frac{Mc^2}{RT^n} = \Lambda \rho^{\lambda},$$

in which an artificial exponent of n is introduced in order to explicitly trace the differences between the Nomoto model (for which $n = 0$, $\lambda = 6$, see (5)) and the fluctuation model for which $n = 1$ and λ is determined by regression of the expression (8) along the isobar of normal pressure.

After taking partial derivatives at constant pressure and temperature,

$$\left(\frac{\partial}{\partial T}\left(\frac{Mc^2}{RT^n}\right)\right)_P = \left(\frac{\partial}{\partial T}\left(\Lambda\rho^\lambda\right)\right)_P,$$

$$\left(\frac{\partial}{\partial P}\left(\frac{Mc^2}{RT^n}\right)\right)_T = \left(\frac{\partial}{\partial P}\left(\Lambda\rho^\lambda\right)\right)_T,$$

we get the following expressions:

$$\left(\frac{\partial c}{\partial T}\right)_P = \frac{\lambda c}{2\rho}\left(\frac{\partial \rho}{\partial T}\right)_P + \frac{nc}{2T}, \tag{9}$$

$$\left(\frac{\partial c}{\partial P}\right)_T = \frac{\lambda c}{2\rho}\left(\frac{\partial \rho}{\partial P}\right)_T. \tag{10}$$

It can be seen that for $n = 1$ in equality (9) there is an additional additive term in comparison to (3), which leads to a change in the value of the isobaric derivative compared to the Nomoto model; equality (10) retains the same functional form, which and (4) for the isothermal derivative.

Based on the definition of the nonlinearity parameter (1), revealing the adiabatic derivative

$$\left(\frac{\partial c}{\partial P}\right)_S = \left(\frac{\partial c}{\partial P}\right)_T + \left(\frac{\partial c}{\partial T}\right)_P \left(\frac{\partial T}{\partial P}\right)_S, \tag{11}$$

and substituting the expressions (9), (10) into (11), we get

$$\left(\frac{\partial c}{\partial P}\right)_S = \frac{\lambda c}{2\rho}\left(\frac{\partial \rho}{\partial P}\right)_T + \frac{\lambda c}{2\rho}\left(\frac{\partial \rho}{\partial T}\right)_P + \frac{nc}{2T}\left(\frac{\partial T}{\partial P}\right)_S = \frac{\lambda c}{2\rho}\left(\frac{\partial \rho}{\partial P}\right)_S + \frac{nc}{2T}\left(\frac{\partial T}{\partial P}\right)_S. \tag{12}$$

Taking into account the definition of the speed of sound, $(\partial\rho/\partial P)_S = c^{-1}$,

$$\frac{B}{A} = \lambda + \frac{n\rho_0 c_0^2}{T}\left(\frac{\partial T}{\partial P}\right)_S, \tag{13}$$

and as

$$\left(\frac{\partial T}{\partial P}\right)_S = \frac{T}{C_P}\left(\frac{\partial V_0}{\partial T}\right)_P \equiv \frac{VT\alpha_P}{C_P}, \tag{14}$$

then substituting (14) into (13), taking into account that the density is the inverse of the specific volume V_0, that is $\rho_0 V_0 = 1$, and reducing the temperature in the numerator and denominator, we get

$$\frac{B}{A} = \lambda + n\frac{c^2\alpha_P}{C_P}. \tag{15}$$

For $n = 0$, that is, for «Rao liquid», the expression (15) reduces to the well-known Nomoto formula (6) for the corresponding $\lambda = 6$, and when the power-law density scaling of fluctuations is fulfilled, $n = 1$, to the desired expression

$$\frac{B}{A} = \lambda + \frac{c^2\alpha_P}{C_P}. \tag{16}$$

Thus, it can be seen that the assumption of invariant power-law density scaling not of the speed of sound itself, but of the reduced fluctuations associated with it leads to the appearance in (16) of an additional term depending on the thermodynamic state of the liquid.

4. Results for the nonlinearity parameter in toluene

Toluene, which is a well-studied standard reference liquid [31], for which the Span-Wagner equation of state is known in the form of a multiparametric expression for the Helmholtz free energy with coefficients obtained by regression of the entire available set of critically evaluated experimental data in a wide range of state parameters. This makes it possible to use the corresponding analytical derivatives of free energy (using ThermoData Engine (TDE) — NIST [32]) to find all thermodynamic quantities required to calculate the nonlinearity parameter B/A by the formula (2). Relative uncertainties of the thermodynamic parameters obtained in this way, according to [31] and comparison with direct experimental data by TDE: 0.05% for the density, 0.5% for theisobaric heat capacity, 1% for the speed of sound, 2% for the isothermal compressibility, 1% for the isobaric coefficient of expansion. The corresponding values of the nonlinearity parameter are shown in Fig. 1 with markers – circles indicating the standard uncertainty interval $u_r(B/A) = 0.05$, found using the NIST Uncertainty Machine [33].

In addition, from the point of view of nonlinear wave dynamics, it is essential that the value of the nonlinearity parameter known for toluene, was determined not only by the indirect thermodynamic calculations, but also directly via the ratio of the amplitudes of the second and first harmonics for waves of finite amplitude [34]; the corresponding value is shown in Fig. 1 as an asterisk equipped with an uncertainty interval (of the order of 10% according to the cited experimental work).

The results of the model calculation (16) are shown in Fig. 1 with markers–squares. It can be noticed that at low temperatures they demonstrate a certain overestimation of the nonlinearity parameter value respectively to the value obtained on the basis of thermodynamic calculation; the difference reaches one and a half units, which exceeds the range of uncertainty intervals (although such a difference is still one and a half times less than for the Nomoto model). At temperatures above 263.15 K, the uncertainty intervals of the calculated and thermodynamic

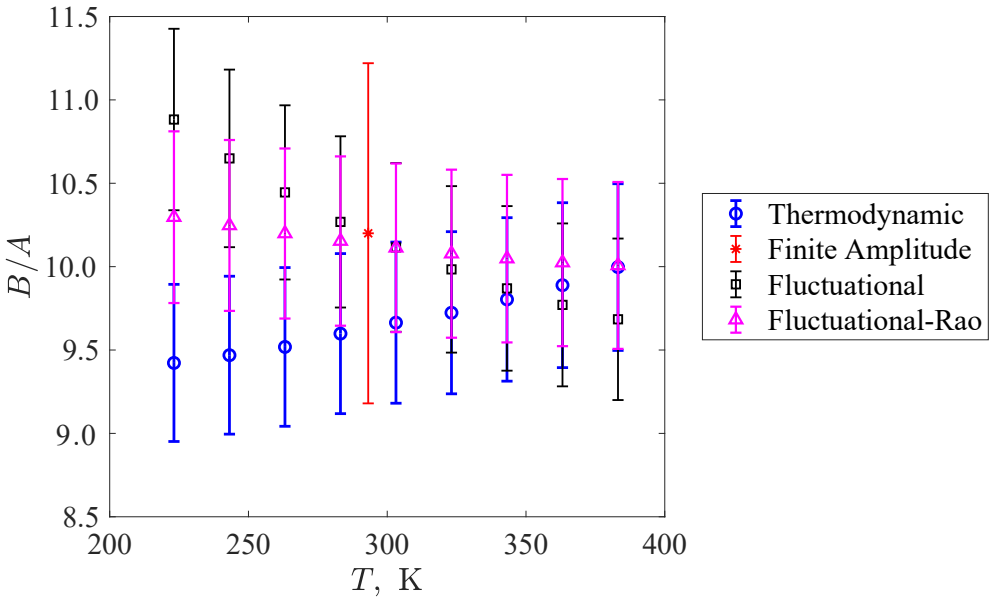

Fig. 1. Dependences of the nonlinearity parameter in toluene on temperature at atmospheric pressure, where "Thermodynamic" is calculated according to (2) from thermodynamic data; "Finite amplitude" is determined from the experiment directly using finite amplitude waves [34]; "Fluctuational" is calculated according to the equation (16); "Fluctuational-Rao" follows from a combined calculations, which uses the Rao rule along the isobar and the fluctuational model for isothermal derivatives

data begin to overlap further, up to the boiling point, they differ within these limits. At the same time, the trends of temperature dependence differ, although it should be remembered that the corresponding expressions (2) and (16) include derived thermodynamic quantities, the accuracy of which is significantly lower than that of the initial thermodynamic quantities.

It should also be noted that the experimental value obtained directly for finite amplitude waves lies very precisely on a line that can be drawn through the markers of data points obtained from the fluctuation model.

Let's consider the possible reasons for the deviation of the calculation by the formula (16) from thermodynamic expressions in more detail. Fig. 2 shows a scale dependency test for the expression (8) and for the Rao rule (5). The use of logarithmic coordinates serves as a linearizing transformation, with the slope of straight lines approximating the experimental data shown by markers corresponding to the scale indicator λ: $\lambda = 9.1$ (Fig. 2, *a*), and $\lambda = 6.0$ (fig. 2, *b*) corresponding to the Rao rule.

However, despite the acceptable linearity of both graphs, it can be noted that the deviations of the markers from the straight line in Fig. 2, *b* is clearly smaller. Hence the question arises about the reproducibility of the individual components of the nonlinearity parameter in the formula (2), for which the derivatives should mainly be considered (9), (10), the graphical representation of which is shown in Fig. 3. From Fig. 3, *a* it can be seen that the fluctuation expression gives a curve substantially closer to the experimental one than the one obtained from the assumption $R_w = \text{const}$ for the isothermal derivative. At the same time, for the isobaric dependence (Fig. 3, *b*), it follows that the Rao dependence (5) is fulfilled quantitatively over almost the entire temperature range, while the fluctuation dependence leads to a qualitatively incorrect temperature dependence. The latter is a consequence of only approximate linearity in Fig. 2, *a*, which affects the behavior of the derivative of the speed of sound.

Thus, it becomes possible to refine the computational model as follows: the isothermal part $(B/A)'$ of the formula (2) is calculated using the formula (10) with a scale indicator λ obtained by linear regression of the parameter defying the reduced pressure fluctuations (note that the latter

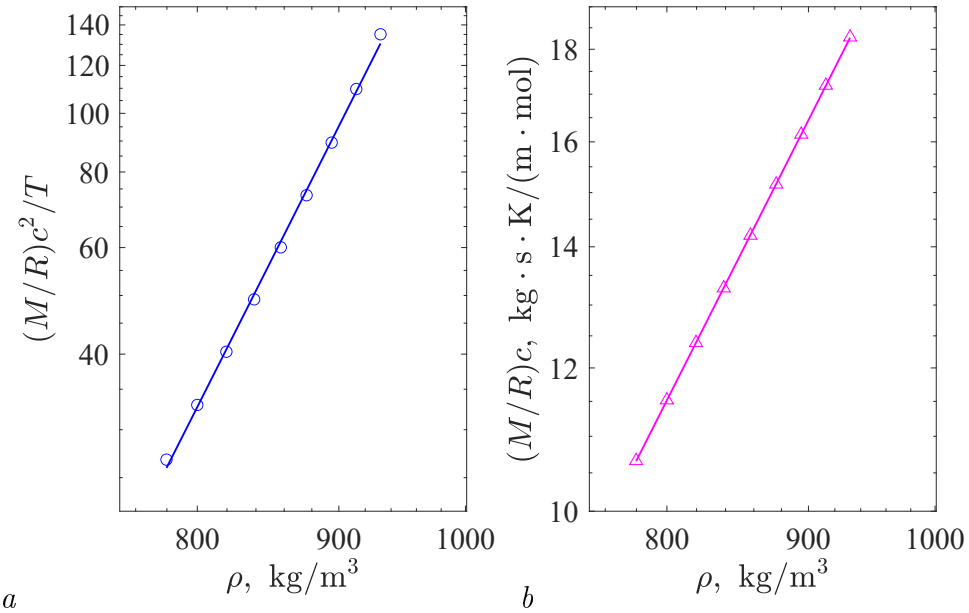

Fig. 2. Plots of the dependences of the parameter of reduced density fluctuations (*a*) and the relation expressing Rao's rule (*b*) in logarithmic coordinates as functions of the density along the isobar of normal atmospheric pressure

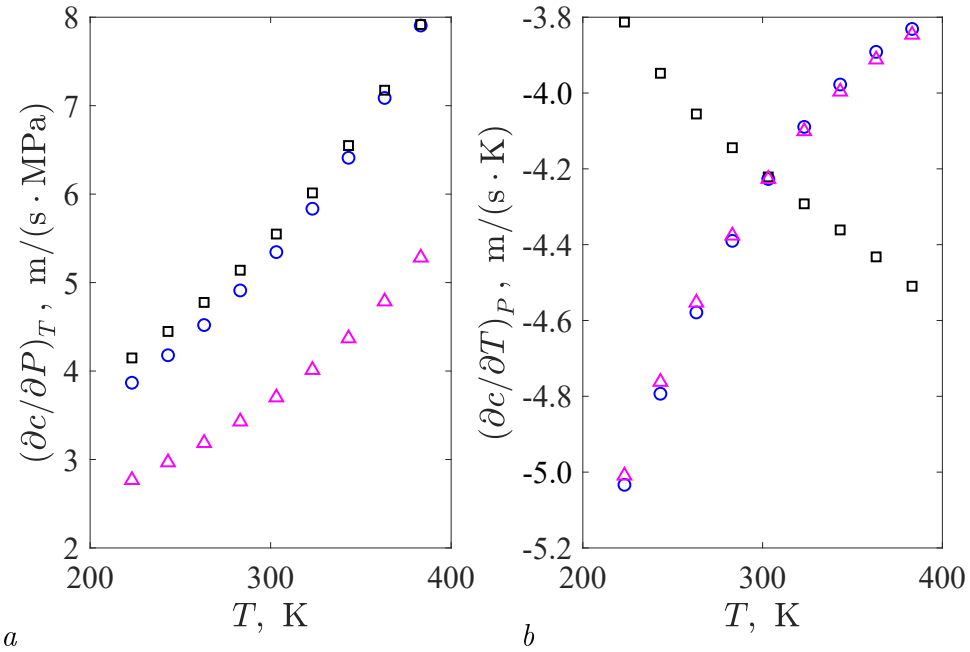

Fig. 3. The isothermal (a) and isobaric (b) derivatives of the sound speed in toluene at normal atmospheric pressure obtained from the experimental data (circles), the fluctuation model (squares), and the Rao rule (triangles)

corresponds to a successful predictive model for calculating the speed of sound along isotherms at high pressures, discussed in [25]), and isobaric (B/A)" — according to the Rao–Nomoto formula (4). The result of this combination is shown in Fig. 1 triangles. In this case, it can be seen that the change in the nonlinearity parameter as a whole as a function of temperature becomes small, which is typical for organic liquids, and despite some overestimation of the value of B/A (the average absolute deviation is 4.7%, which is consistent with the uncertainty of the data), the result indicates the possibility of estimating the nonlinearity parameter of ultrasonic waves in a liquid based on data of thermodynamic and acoustic values of small amplitude measured only at atmospheric pressure.

5. The difference in the magnitude of the nonlinearity parameter by nonlinear acoustic and thermodynamic changes

As shown above, there is a definite difference between the nonlinearity parameter in toluene determined by the stationary thermodynamic properties of the liquid and based on analysis of the attenuation of harmonics of a finite amplitude acoustic signal [34]. The technique implemented in the latter approach is based on the fact that the distortion of the wave directly depends on the nonlinearity parameter B/A. The amplitude of the second harmonic (P_2) at a distance from the source $x_2 = X < x_{\text{sh}}$ (x_{sh} is the distance of the shock wave formation) is calculated according to the expression

$$P_2 = \frac{n+1}{4}\left(P_1^2 \frac{X\omega}{\rho_0 c_0^3}\right), \tag{17}$$

where P_1 is the amplitude of the first harmonic near the sound source (measured at the distance of x_1), ω is the frequency of the signal, parameter $n = B/A+1$, from which the desired nonlinearity parameter B/A is determined.

To reproduce the conditions of this experiment, we will use numerical modeling simulating

the corresponding conditions of the measurement data using COMSOL Multiphysics®. The main standard equation of nonlinear acoustics [35], modeling the propagation and evolution of the sound wave form in the approximation of moderate (quadratic) nonlinearity, is the Westervelt equation, which is implemented in the model COMSOL Multiphysics® [36] in the form [37]

$$\frac{1}{\rho_0 c_0^2}\frac{\partial^2 p}{\partial t^2} - \nabla\left(\frac{1}{\rho_0}\left(\nabla p + \frac{\delta}{c_0^2}\frac{\partial(\nabla p)}{\partial t}\right)\right) = \frac{\beta}{\rho_0^2 c_0^4}\frac{\partial^2 p^2}{\partial t^2}, \tag{18}$$

where c_0 is the low-intensity sound velocity; ρ_0 is the density of undisturbed liquid; $\beta = 1 + B/(2A)$ is the coefficient taking into account the nonlinearity of the wave expressed in terms of the nonlinearity parameter; the coefficient taking into account relaxation phenomena (sound diffusion coefficient — sound diffusivity) has the from

$$\delta = \frac{1}{\rho_0}\left[\left(\frac{4}{2}\mu + \zeta\right) + \kappa\left(\frac{1}{C_V} - \frac{1}{C_P}\right)\right] \tag{19}$$

(μ and ζ are the shear and bulk viscosity coefficients, C_P and C_V are isobaric and isochoric specific heat capacities, κ is the thermal conductivity coefficient).

It should be noted that the possibility of using the Westervelt equation is currently being actively investigated not only for modeling the propagation of sound waves of finite amplitude, but also directly for finding the nonlinearity parameter of a liquid medium by comparing numerical solutions with the recorded signals. [15, 38].

In our case, the parameters for modeling were chosen as close as possible to the experimental ones [34, 39], namely: the emitter intensity $I = 288$ W/m^2, the emitter excitation frequency $f \equiv \omega/(2\pi) = 1.5$ MHz, $T = 20$°C. Thermodynamic parameters [31]: $\rho_0 = 866.89$ kg/m^3, $c_0 = 1324.3$ m/s; the next one is the «thermodynamic coefficient of nonlinearity» $\beta = 5.8$ (for $(B/A)_{\text{therm}} = 9.6$); viscosity coefficients [40] $\mu = 5.8714 \cdot 10^{-4}$ Pa·s, $\zeta = 0.0076$ Pa·s; the term (19), which depends on thermal conductivity, is neglected due to the smallness of the coefficient [41] $\kappa = (0.13088 \pm 0.00085)$ W/m/K and large values of the heat capacity.

Oscillation generation in the medium is produced by a flat radiator oscillating at a speed of $u(t) = u_0 \sin \omega t$ with an amplitude of $u_0 = 0.0224$ m/s, given by the equality $u_0 = p_0/(\rho_0 c_0)$.

The modeling interval was taken as $0 \leqslant x \leqslant 4.5x_{\text{sh}}$. The radiation source with the amplitude $p_0 = \sqrt{2I\rho_0 c_0} = 25715$ Pa is located at the point $x = 0$, the point $x = 4.5x_{\text{sh}}$ is terminated to exclude the signal's reflection. The distance of the shock wave formation

$$x_{\text{sh}} = \frac{c_0^2}{\omega\beta u_0} \tag{20}$$

in this case , it is equal to 1.43 m.

The pressure dependence $p(t)$ near the radiator was fixed at a distance $x_1 = 1$ cm, the point farthest from the emitter was considered $x_2 = 20$ cm, that is, at a distance much smaller than the distance of the shock wave formation. For the signals obtained by the numerical solution of the equation (18) at the corresponding points by means of a fast Fourier transform, spectra were obtained, the graphs of which are shown in Fig. 4.

The amplitude of the first harmonic near the emitter was $P_1 = 21825.2$ Pa, the amplitude of the second harmonic at a distance from the emitter was $P_2 = 1355.6$ Pa. Their substitution in the expression (17) leads to the value of the nonlinearity parameter $B/A = 10.2$, which practically coincides with the results given in [34], where the value $B/A = 10.4$ was obtained during the experiment. At the same time, this value is obviously overestimated in comparison with the «thermodynamic» value $(B/A)_{\text{therm}} = 9.6$ used as a parameter of the equation to be solved (18).

Thus, it can be concluded that the value given in [34] is due to the method of measuring and processing the data obtained.

In fact, the expression (17) is based on the simultaneous fulfillment of two assumptions: the smallness of the attenuation of the sound wave and the smallness of the distance from the source to the measurement point of the second harmonic, which can be shown analytically. Regarding the first assumption, the solution of the Westervelt equation for $\sigma = x/x_{\text{sh}} \leqslant 1$ can be represented [8] in the form of a series of Fubini solutions

$$p(x,t) = p_0 \sum_{n=1}^{\infty} B_n(\sigma) \sin\left(n\omega\left(t - \frac{x}{c}\right)\right), \tag{21}$$

where

$$B_n(\sigma) = \frac{2}{n\sigma} J_n(n\sigma). \tag{22}$$

Substituting $P_1 = p_0 B_1(\sigma_1)$ and $P_2 = p_0 B_2(\sigma_2)$, where $\sigma_1 = x_1/x_{\text{sh}}$ and $\sigma_2 = x_2/x_{\text{sh}}$ are the dimensionless distances from the emitter at which measurements are made, in (17), and leaving only the first term of the expansion of Bessel functions into the Taylor series ($J_1(\sigma) \approx \sigma$, $J_2(2\sigma) \approx \sigma^2/2$), that is, applying the second assumption mentioned above, we come to the identity.

The used value $\sigma_2 = 0.14$ can no longer be considered as small, as illustrated in Fig. 5, however, the deviation from the initial value of the nonlinearity parameter detected at $x_1 \to 0$, $x_2 \to 0$ is within one percent. More significant is the effect of the attenuation coefficient of nonlinear waves in a real liquid. This effect manifests itself as in the piston region for the fundamental harmonic, see a significantly lower value of the spectral peak at x_1 compared to the corresponding peak of the Fubini solution in Fig. 4, and at a distance of x_2 for the second harmonic. Since P_1 is squared by the formula when calculating the nonlinearity parameter and is in the denominator, this makes a significant contribution to the overestimation of the value of B/A. In addition, comparing Fig. 5 and fig. 4, it should be noted that the realistic value of the amplitude of the first harmonic of the acoustic signal is noticeably lower at a distance of x_2 than

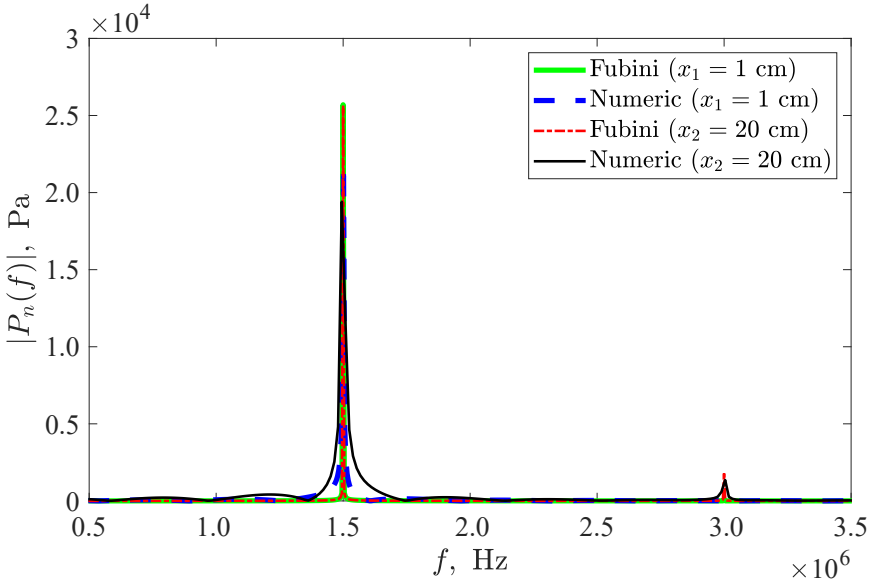

Fig. 4. Spectra of signals near the wave source and at a distance from the transmitter according to numerical simulations and from the Fubini solution (color online)

at a distance of x_1, which indicates the contribution of attenuation in toluene at such distances, in contrast to the ideal medium corresponding to the Fubini solution, for which the reduction of the first harmonic only for the account of the development of the second can be neglected.

Thus, it can be concluded that the initial experimental data obtained in [34] themselves have a sufficiently high accuracy to find the nonlinearity parameter. However, their correct processing should not refer to the formula (17), but to the numerical solution of the nonlinear equation (18), which significantly depends on the magnitude of absorption and the position of experimental acoustic pressure sensors, with different sets of the parameter β included in the equation, followed by the identification of its numerical value, which best matches the harmonics of the numerical solution with the experimental ones.

Conclusion

The main message of this work is the conclusion that the parameter expressing the magnitude of the reduced density fluctuations allows us to estimate with acceptable accuracy not only the speed of sound as a function of changing pressure (that is, the first adiabatic derivative of density), as it is currently shown in practical application to various types of liquid media [25,42], but also the nonlinearity parameter associated with the second derivative, which is significantly more sensitive to the course of the original differentiable functions.

In addition, it is revealed that the contradiction existing in various sources regarding the value of the nonlinearity parameter determined during thermodynamic and nonlinear acoustic measurements is based on an oversimplified analytical approximation to the solution of the nonlinear Westervelt equation modeling the propagation of a nonlinear wave of large amplitude. At the same time, the agreement of the numerical solution with the measurable values of the

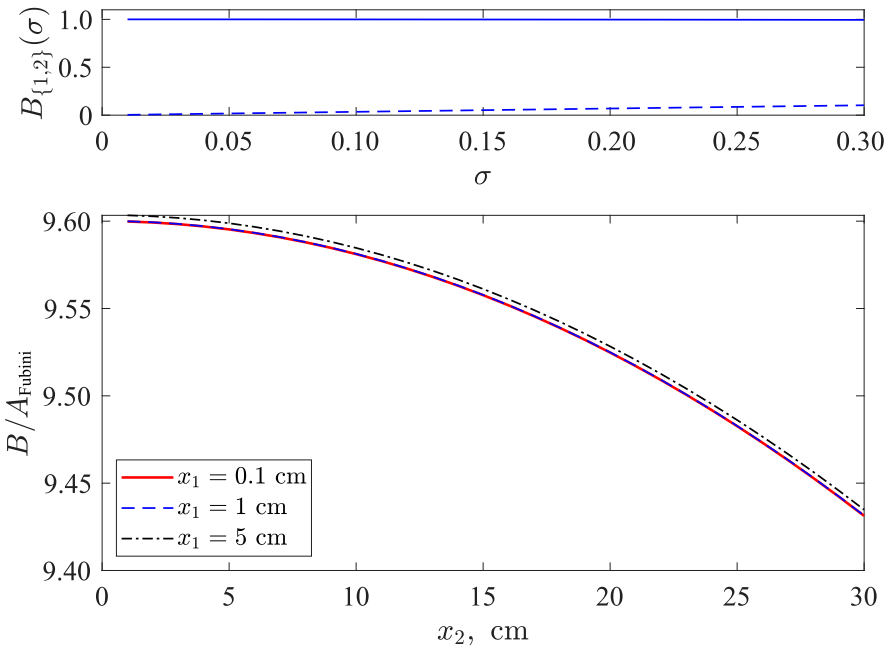

Fig. 5. The coefficients $B_1(\sigma)$ and $B_2(\sigma)$ in the series representing the Fubini solution (21), (22) shown with solid and dashed lines, respectively (upper panel), and the nonlinearity parameter according to the formula (17) for the Fubini solution measured at different initial and end points (lower panel)

amplitudes of the first and second harmonics of the nonlinear wave makes it possible in principle to find the nonlinearity parameter included in the original differential equation consistent with the thermodynamic value of the nonlinearity parameter.

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