LIQUID WATER. ANALYTICAL EQUATION OF STATE AND ACOUSTIC PARAMETERS EVALUATION

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The analytical equation of state for liquid water, proposed by Jeffery and Austin, is discussed and used for calculating of the sound velocity and the parameter B/A in the paper. These acoustic quantities, obtained for the theoretical model, are compared with experimental data. Some corrections to the equation of state, resulting from the comparison, are proposed.

INTRODUCTION

An analytical equation of state for liquid water is interesting problem for many of physicists, for the sake of wide applications. The trials of building universal theoretical model of liquid water were made in the past. It is obviously, the problem still is not closed.

The one of the groups, which deals with the subject of liquid water is Poole *et al.* They proposed to extend the van der Waals equation of state for that medium [1], in order to incorporate, in approximate fashion, the effects of the network of hydrogen bonds. The model they obtained predicts in a qualitatively way the special thermodynamic properties of water. They gave the formula for Helmholtz free energy F_{HB} which is responsible for the hydrogen bonds behavior.

The other group is Song, Mason and Ihm, which elaborated the analytical equation of state for molecular fluid, based on an perturbation theory for hard convex bodies [2,3]. They obtained a fifth-order polynomial in the density, that seems to be valid for the many of real fluids, what was tested with experimental data, hovewer the mentioned equation not shows density anomaly around $4\,^{o}C$ in liquid water.

1. ANALYTICAL EQUATION FOR LIQUID WATER

In 1999 year, C. A. Jeffery and P.H. Austin proposed an analytical equation of state for liquid water [4] that was a modification of the Song-Mason-Ihm equation but for the polar fluid, with taking into considerations the hydrogen bonds effect, such in Poole *et al.* paper. In that approach the equation of state has form:

$$\frac{p}{\rho RT}=1-b_0\rho-\frac{a\rho}{RT}+\frac{\alpha\rho}{1-\lambda b\rho} \tag{1}$$

where ρ is expressed in mol/m^3 unit and function $b(T)$ has form :

$$b(T)=v_B\left(0.25e^{1/(2.3T/T_B+0.5)}-b_1e^{2.3T/T_B}+b_2\right)=v_B(e^{T_1(T)}-b_1e^{T_2(T)}+b_2)$$
$$T_1(T)=-\ln 4+\left(2.3\frac{T}{T_B}+0.5\right)^{-1},\qquad T_2(T)=2.3\frac{T}{T_B}. \tag{2}$$

The constants in the equation have the following values: $a=a_{VDW}=0.5542$ *Pa* m^6/mol^2;

$\lambda=0.3159$; $\alpha=2.145\ v_B$; $b_0=1.0823\ v_B$; $b_1=0.02774$; $b_2=0.23578$, Boyle volume: $v_B=4.1782*10^{-5}\ m^3/mol$; Boyle temperature $T_B=1408.4\ K$, R – universal gas constant. The equation of state for free energy proposed by these same authors is:

$$F=G(\rho,T)-RT\Psi(T), \tag{3}$$

with additional formulas:

$$G(\rho,T)=RT\,log\rho-RTb_0\rho-a\rho-\frac{RT\alpha}{\lambda b(T)}log(1-\lambda b(T)\rho)-RT(-3\ log\ \Lambda(T)+1)+G_0, \tag{4}$$

$$\Lambda^2(T)=\frac{R^{5/3}h^2}{2\pi mK_B^{8/3}T},\qquad \Psi(T)=\Psi_1+\Psi_2\frac{T_B\lambda b(T)}{T\alpha}+\Psi_3\frac{T_B}{T}. \tag{5}$$

The new symbols are denote by authors as: $G_0=21470\ J/mol$, $\Psi_1=5.13$, $\Psi_2=20.04$, $\Psi_3=2.73$ and Λ means temperature wavelength.

Some of estimated constants, given below, differ from those in a theoretical water model which takes into account influence of hydrogen bonds [Sec.III of Ref.4]. However, we limited ourselves to this approach (without hydrogen bonds), because we compare theoretical and experimental data in higher than characteristic for the hydrogen bonds effect temperatures.

2. SOUND VELOCITY AND B/A FOR NEW MODEL OF LIQUID WATER

The presented theoretical model of liquid water can be used to calculate the theoretical values of the sound velocity and the nonlinearity parameter *B/A* .

The general expression for the sound velocity c is given by:

$$c^2 = \left(\frac{\partial p}{\partial \rho}\right)_S . \tag{6}$$

Index "S" means that process is isoentropic, but we can assume reversible adiabatic process, in this case. For *B/A* we use the general expression (see, e.g., [5]):

$$\frac{B}{A} = \frac{\rho_0}{c_0^2}\left(\frac{\partial^2 p}{\partial \rho^2}\right)_S = \frac{\rho_0}{c_0^2}\left(\frac{\partial c^2}{\partial \rho}\right)_S . \tag{7}$$

In order to find the acoustic wave propagation velocity, in the discussed medium, according above formula, we put $dS = 0$ for adiabatic process and use the known formula of thermodynamics: $U = F - T\left(\frac{\partial F}{\partial T}\right)_V$. We make the following transformations: (bottom index means partial differential, for example F_T means $\frac{\partial F}{\partial T}$)

$$dU = dF - dTF_T - TdF_T .$$

$$dF = dG - RdT\Psi - RT\Psi_T dT, \qquad F_T = G_T - R\Psi - RT\Psi_T, \tag{8}$$

$$dF_T = dG_T - Rd\Psi - RdT\Psi_T - RT\Psi_{TT}dT, \qquad dG = G_T dT + G_\rho d\rho$$

Next, we obtain the equation:

$$d\rho\left(G_\rho - TG_{T\rho} + \frac{\mu p}{\rho^2}\right) + dT\left(-TG_{TT} + 2RT\Psi_T + RT^2\Psi_{TT}\right) = 0 , \tag{9}$$

where *dT* we treat as an element of the expression: $dp = p_T\, dT + p_\rho d\rho$, and finally the required formula is: (we remind that: $p = p(\rho,T)$, $G = G(\rho,T)$ and $\Psi = \Psi(T)$)

$$c^2 = \frac{\beta_1\left(G_\rho - TG_{T\rho} + \frac{\mu p}{\rho^2}\right) + T\beta_2\left(G_{TT} - 2R\Psi_T - RT\Psi_{TT}\right)}{T\left(G_{TT} - 2R\Psi_T - RT\Psi_{TT}\right)} . \tag{10}$$

In order to make shorter the above formula we have introduced some new symbols:

$$\beta_1(\rho,T)=\frac{\partial p}{\partial T}, \qquad \beta_2(\rho,T)=\frac{\partial p}{\partial \rho}$$

$$\beta_1 := \frac{\rho R\left(1-\frac{b_0\rho}{\mu}-\frac{a\rho}{\mu R T}+\frac{\alpha\rho}{\mu-\lambda b\rho}\right)}{\mu}+\frac{\rho T R\left(\frac{a\rho}{\mu R T^2}+\frac{\alpha\rho^2\lambda\left(\frac{\partial}{\partial T}b\right)}{(\mu-\lambda b\rho)^2}\right)}{\mu}$$

$$\beta_2 := \frac{T R\left(1-\frac{b_0\rho}{\mu}-\frac{a\rho}{\mu R T}+\frac{\alpha\rho}{\mu-\lambda b\rho}\right)}{\mu}+\frac{\rho T R\left(-\frac{b_0}{\mu}-\frac{a}{\mu R T}+\frac{\alpha}{\mu-\lambda b\rho}+\frac{\alpha\rho\lambda b}{(\mu-\lambda b\rho)^2}\right)}{\mu}$$

$$\frac{\partial b(T)}{\partial T}=-2.3\frac{v_B}{T_B}\left(\frac{\exp\left((2.3\cdot T/T_B+0.5)^{-1}\right)}{4\left(2.3\cdot T/T_B+0.5\right)^2}+b_1\exp\left(2.3\cdot T/T_B\right)\right)$$

We consider this expression as valid in the same range as the general equations of state we used. Hence we differentiate it, taking into account the adiabaticity condition when evaluate derivatives $dT/d\rho$. The expression of the nonlinear parameter B/A has a complicated form, however one can calculate some values of it using a computer program.

It must be underlined, the derived formulas for c and B/A are general in the sense that only the thermodynamical relations for the simple medium had been used.

3. COMPARISON OF THEORETICAL AND EXPERIMENTAL DATA

Today, pure liquid water is described in the experimental studies very well. We have plenty of information about special and amazing properties of water. The dependence of the sound velocity on temperature seems to be one of these very interesting characteristics. It must be notice, that the sound velocity grows due temperature to *74°C* and next becomes smaller. The peculiarity of the water results probably from long-range order, strong polarity and strong association of water molecules.

Fig.1 shows the mentioned dependence and presents, simultaneously, the theoretical curves, obtained for analytical equation (Jeffery and Austin model). Figure 3, in similar way shows *B/A* dependence. Next, fig.2 and fig.4 present some changes of the sound velocity *c* and the nonlinearity parameter *B/A* when pressure of measurements grows to 50 *MPa*.

It must be emphasized, the presented corrections (λ = 0.2442 instead of 0.3159 , b_o = - 0.000026 instead of 0.000045 and ψ_2 = 22.044 instead 20.04) to the constants must be treated as an example only, not necessarily quite right, what Fig.3 and 4 shows. There are a few constants, which are estimated for water with using experimental measurements, in Jeffery and Austin paper. So, some changes of these constants theoretically are still possible. The important question is which corrections are sensible.

In general, using the acoustic parameters we have an effective tool for testing some new equations of state. A fact seems to be interesting is, the density values, calculated by using the presented analytic equation of state, are not agree with the experiment data [7]. So, in this paper we calculate sound velocity for the known experimental densities. Hovewer, during the *B/A* (C/A, D/A...) calculation process, some possible errors increase, so could be found that the higher parameters are more sensitivity and more helpful in testing some equations of state.

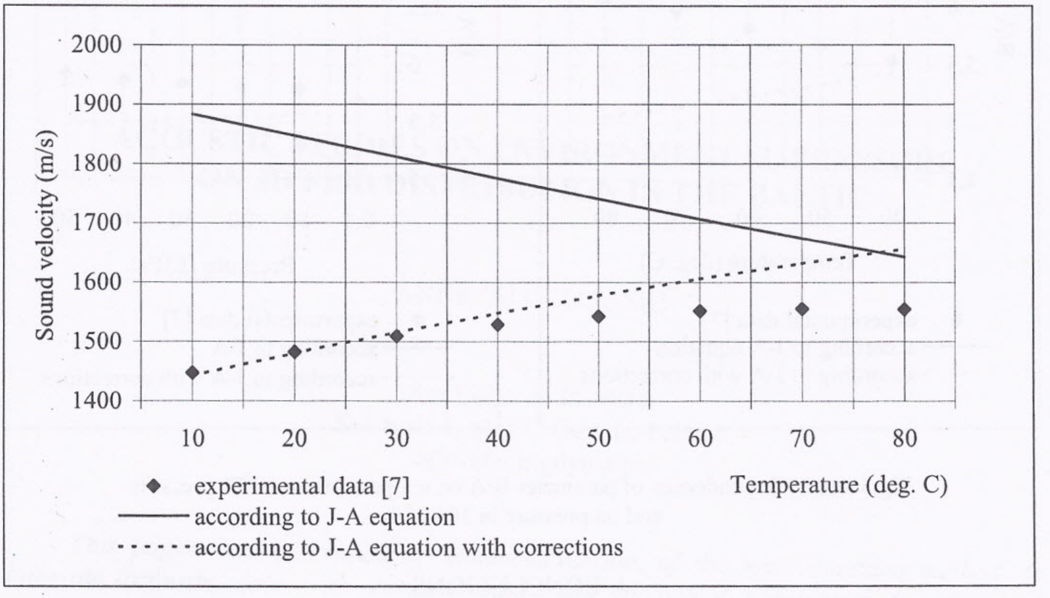

Fig.1. Dependence of sound velocity on temperature in $10^5 Pa$ pressure

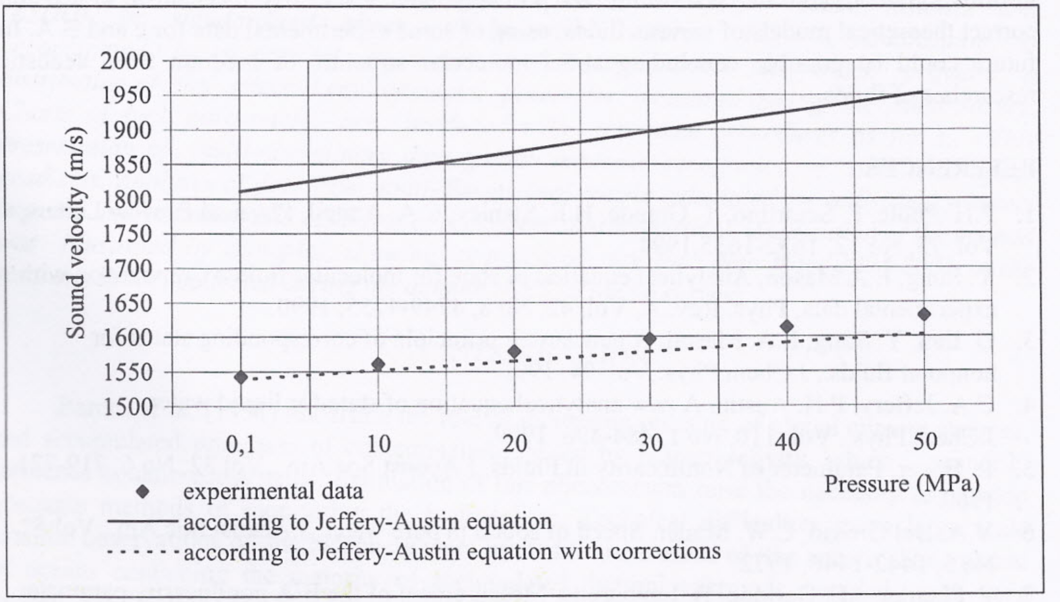

Fig.2. Dependence of sound velocity on pressure, $T = 303.15\ K$

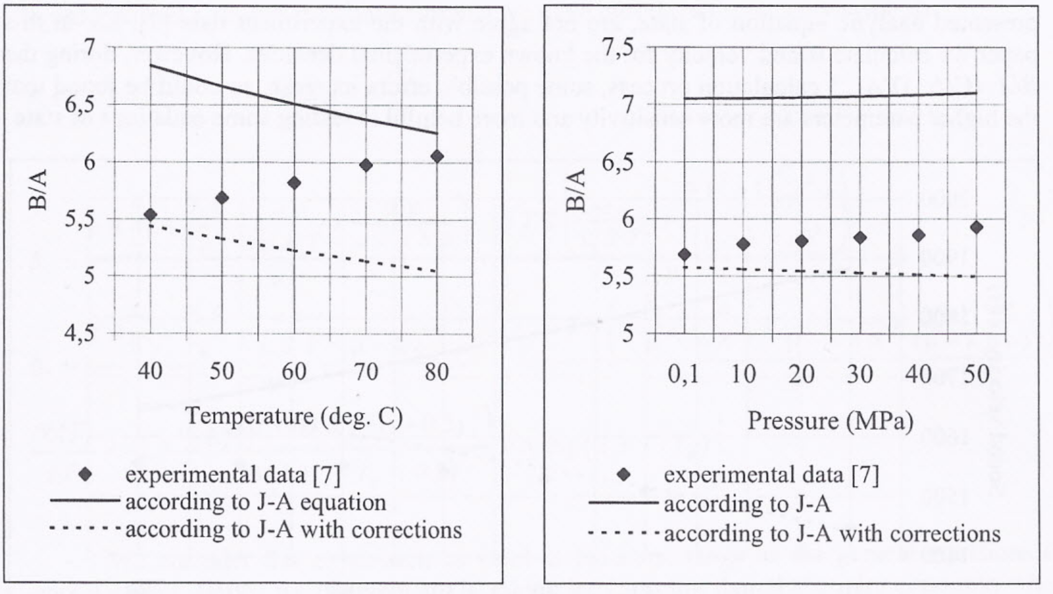

Fig.3 and 4. Dependences of parameter B/A on temperature in 10^5Pa pressure and on pressure in 303.15 K

4. CONCLUSIONS

Connecting thermodynamic physics and acoustics seems to be an interesting source of information about considered medium. We probably make a sensitive mechanism to test and correct theoretical models of various fluids, using of some experimental data for c and B/A. In future could be possible concluding about molecular structure of medium from acoustic researches of fluids.

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