SOME ACOUSTIC PROPERTIES OF WATER OBTAINED BY THE JEFFERY-AUSTIN EQUATION OF STATE

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Abstract

Application of a new analytical thermodynamic equation of state for liquid water, gived by Jeffery and Austin is applied to evaluation of some acoustic parameters. The values of sound velocity and nonlinear constant from the theoretical model and the experimental data are compared. Some aspects of connecting between thermodynamic and acoustic properties of medium are discussed.

Introduction

The today's theoretical methods of search of the expressions for some acoustic parameters of fluid medium, such as the sound velocity c and the nonlinearity parameters (B/A, C/A, ...), use the thermodynamic equations of state. This is the way of introduction of microscopic information about kind of gas or liquid. The equation of state, the thermic or the caloric, can be written in the form containing the expression for the intermolecular potential of medium. As the first example we can take the virial form of the state equation for van der Waals model gas.

The next models, are more and more complicated, but the mentioned van der Waals one is treated as a starting point to developing of the majority of theories.

It seems interesting, that one have chance to connect the information about fluid medium on the microscopic, and macroscopic levels, especially, information about the intermolecular potential and some acoustic properties. However, the problem, is not so simple, what we could notice in the liquid water example.

The model of liquid water, to be considered, is based on the analytical equation of state, given by Jeffery and Austin [1].

There are many of groups of scientists concentrated on the liquid water equation of state for various fields of physics and chemistry. Some analytical equations which are interesting for our thermodynamic/acoustic approach are:

- Song, Mason and Ihm analytical equation for nonpolar fluid based on perturbation theory for hard convex bodies [2,3];
- Poole et al's model of free energy of strong tetrahedral hydrogen bond (which is taking into account for water cooled below 4^oC) [4];
- and finally, the analytical equation of state for liquid water, given by Jeffery and Austin, composed from the upper approaches with taking into account some polar properties of fluid [1].

Analytical Equation for Liquid Water by Jeffery and Austin

The equation of state to be used has the form (where ρ is expressed in mol/m^3 unit)

$$\frac{p}{\rho RT} = 1 - b_0\rho - \frac{a\rho}{RT} + \frac{\alpha_1\rho}{1-\lambda b\rho} \qquad (1)$$

where b is the function

$$b(T) = v_B\left(0.25e^{1/(2.3T/T_B+0.5)} + -b_1e^{2.3T/T_B} + b_2\right)$$

and a, λ, α_1, b_0, v_B, b_1, b_2, v_B, T_B are some constants (see in original paper[1]).

The equation of state for free energy, proposed by these same authors, is found by integration of the thermic equation and has form

$$F = A_1(\rho, T) - RT\Psi(T), \qquad (2)$$

where A_1 and Ψ are functions

$$A_1 = RTlog\rho - RTb_0\rho +$$

$$-a\rho - \frac{RT\alpha_1}{\lambda b(T)} log(1 - \lambda b(T)\rho) +$$

$$-RT(-3log\Lambda + 1) + A_0,$$

$$\Psi = \Psi_1 + \Psi_2 \frac{T_B \lambda b(T)}{T\alpha_1} + \Psi_3 \frac{T_B}{T},$$

and A_0, Ψ_1, Ψ_2, Ψ_3 are also constants, tabulated in [1]. Λ means the thermal wavelength. The form of $\Psi(T)$ and the parameters A_0, Ψ_1, Ψ_2, Ψ_3 are established empirically.

Sound Velocity and B/A for Water

The authors use the new way of calculation the sound velocity and B/A, for adiabatic process, without using Taylor series expansion. In order to find the acoustic wave propagation velocity, in discussed medium, we put $dU + pdV = 0$ for adiabatic process and use the known connection

$$U = F - T\left(\frac{\partial F}{\partial T}\right)_V.$$

After some transformations the expression for c is (indexes T or ρ mean the partial differentials)

$$c^2 = \left(A_{1\rho} - TA_{1T\rho} + \frac{mp}{\rho^2} + \frac{\beta_2}{\beta_1} TA_{1TT} + \right.$$

$$\left. -\frac{\beta_2}{\beta_1} 2RT\Psi_T - \frac{\beta_2}{\beta_1} RT^2 \Psi_{TT}\right)\beta_1 \cdot$$

$$\cdot\left(TA_{1TT} - 2RT\Psi_T - RT^2\Psi_{TT}\right)^{-1}$$

where

$$\beta_1 = \left(\frac{\partial p}{\partial T}\right)_\rho, \qquad \beta_2 = \left(\frac{\partial p}{\partial \rho}\right)_T.$$

The formula for B/A is well-known and written as a derivative $c^2 = c^2(\rho, S)$. However, the finding of the function S needs the solution of a complicated differential equation (it follows from the condition $dS = 0$). Even if the solution of the equation is found, one could has no an explicit form for the function S. In our case it seems impossible to solve the problem of an explicit expression for the function c^2 for ρ and S as the independent variables. We, however, can use the differential connections between the variables to express the B/A coefficient via the derivative of $c^2(\rho, T)$ by the variable ρ, taking into account the fact that for the fixed (adiabatic) process the temperature T depends on the density ρ. The derivative $dT/d\rho$ is found from the equation $dS = 0$ in the corresponding variables ρ and T. Finally, both of these, c and B/A parameter, have the complicated but algebraic forms, so one can calculate some values of it using a computer program.

As the first result we observe that using the Jeffery - Austin equations of state, which the constants are chosen by means of the thermodynamic measurements, gives rather bad values of the acoustic parameters for water. We then consider some alternative values at parameters of the final expressions for c and B/A to obtain the better approximation of the experimental data. For the figures below, we made some little changes of a few constants in Jeffery and Austin equation, in order to correct the theoretical sound velocity dependence on temperature and pressure. The modifications we treat only as the example.

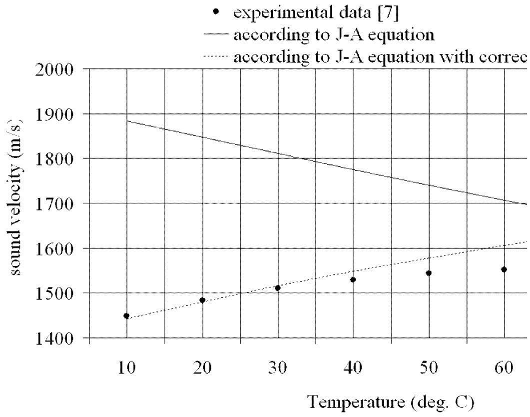

Figure 1:
Water. Dependence of sound velocity on temperature in 10^5 Pa pressure.

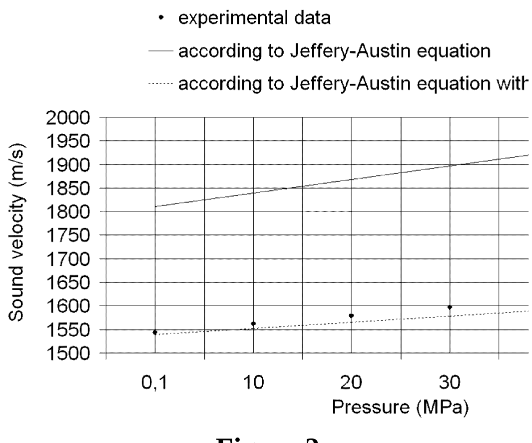

Figure 2:
Water. Dependence of sound velocity on pressure, T = 303.15 K.

Conclusions

Connecting thermodynamic physics and acoustics seems to be an important source of information about considered medium. A comparison of the theoretical (via Jeffery-Austin equation of state) and experimental data (from [5]) shows the significant difference in the sound velocity values (the same remark for B/A). Changing of constants in equations of state leads to rather big variations in acoustic parameters (c^2, B/A) values. Such phenomenon points to a possible instability of the mathematical description based on the choice of the state equation. We propose perhaps 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 a medium from acoustic researches of fluids.

References

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