

## NONLINEAR PARAMETERS AND SOUND SPEED IN ACOUSTICS AND ITS EVALUATION FOR REAL GASES AND LIQUIDS.

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*Values of nonlinear parameter  $B=A$  and sound velocity are calculated in the theory of real (van der Waals) and semi-ideal gases and compared with experimental data. Both thermic and the caloric equations of state are revisited and used in Taylor series coefficients evaluation. The equations describe the non-adiabaticity of the process of the sound wave propagation.*

### INTRODUCTION

The main idea of the present investigation is to use appropriate equations of states to derive expressions for the parameter of nonlinearity and the sound speed in real fluids, as functions of equilibrium temperature  $T$  and mass density  $\rho$  ( $T_0, \rho_0$ ). There are two equations of state, for energy  $E(T, \rho)$  and pressure  $p(T, \rho)$  for isotropic fluids, which close the dynamic system of equations. It is known from thermodynamics and statistical physics, that the form of these equations is defined by the potential energy of molecules interaction. Generally, both equations may be thought as series of corrections due to non-ideality of fluid. Up to date, physical chemistry does great efforts to account these correction terms, the difficulties are mainly concern with numerical investigation. The results of physical chemistry may be applied to evaluate the acoustic parameters. The advantages of such approach are obvious: the wide range of background parameters may be accounted. Further, the final formulas are analytic. It is also desired to start from the partition function of ensemble in order to satisfy a relation

$$\left[ -\rho \left( \frac{\partial E}{\partial \rho} \right)_T + p \right] = T \left( \frac{\partial p}{\partial T} \right)_\rho \quad (1)$$

that appears as a condition for compatibility of caloric and thermal equations of state. If both internal energy and pressure are found from partition function, the equation (1) satisfies automatically. We should complete a standard gas dynamics system with relation  $E = E(p, \rho)$  that follows from  $E(T, \rho)$  and  $p(T, \rho)$ . There is a very narrow class of models with equations of state in the form of concrete functions: ideal and semi-ideal gases, for example. For the majority of other substances, even homogeneous, there are no general-purpose equations of state. Generally, equation of state should be expanded in the Taylor series in the vicinity of equilibrium state (disturbed values are primed):

$$\rho_0 \dot{E} = E_1 \dot{p} + \frac{E_2 p_0}{\rho_0} \dot{\rho} + \frac{E_3}{\rho_0} \dot{p}^2 + \frac{E_4 p_0}{\rho_0^2} \dot{p}^2 + \frac{E_5}{\rho_0} \dot{p} \dot{\rho} + \dots \quad (2)$$

For example, an ideal gas treated by  $E = p/(\rho(\gamma - 1))$  yields in coefficients:

$$E_1 = E_4 = 1/(\gamma - 1), \quad E_2 = E_5 = -1/(\gamma - 1), \quad E_3 = 0 \quad (3)$$

The parameters of nonlinearity are defined by [1]:

$$p = p_0 + A \frac{(\rho - \rho_0)}{\rho_0} + \frac{B}{2} \frac{(\rho - \rho_0)^2}{\rho_0^2} + \frac{C}{6} \frac{(\rho - \rho_0)^3}{\rho_0^3} + \left( \frac{\partial p}{\partial s} \right)_{\rho, s=s_0} \quad (4)$$

The equivalent system  $(v_*, \dot{p}_*, \dot{\rho}_*, r_*, t_*)$  in non-dimensional variables:  $v = \alpha c v_*$ ,  $\dot{p} = \alpha c^2 \rho_0 \dot{p}_*$ ,  $\dot{\rho} = \alpha \rho_0 \dot{\rho}_*$ ,  $x = \lambda x_*$ ,  $t = t_* \lambda / c$  where  $c$  is adiabatic sound velocity  $c^2 = p_0(1 - E_2)/(\rho_0 E_1)$ ,  $\lambda$  means characteristic scale of disturbance and  $\alpha$  – coefficient responsible for amplitude of acoustic wave, may be written in the matrix form (asterisks for dimensionless variables will be later omitted):

$$\frac{\partial \Psi}{\partial t} + L\Psi = \tilde{\Psi} + \tilde{\tilde{\Psi}} + O(\alpha^3) \quad (5)$$

where:  $\Psi^T = (v, \dot{p}, \dot{\rho})$  is variables column and  $L$  is the linear matrix operator.

$$\tilde{\Psi} = \alpha \begin{pmatrix} -v v_x + \dot{\rho} \dot{p}_x \\ -v \dot{p}_x + v_x (D_1 \dot{p} + D_2 \dot{\rho}) \\ -v \dot{\rho}_x - \dot{\rho} v_x \end{pmatrix}, \quad \tilde{\tilde{\Psi}} = \alpha^2 \begin{pmatrix} -\dot{\rho}^2 \dot{p}_x \\ v_x (D_3 \dot{\rho}^2 + D_4 \dot{p}^2 + D_5 \dot{\rho} \dot{p}) \\ 0 \end{pmatrix} \quad (6)$$

Down index "x" means  $\partial/\partial x$  and symbols  $D_1 \dots D_5$  mean dimensionless coefficients, depending on  $E_1 \dots E_5$ : The constants  $A, B, C$  relate to coefficients from (6) in the following way:

$$A = [(1 - E_2)/E_1] p_0, \quad B = -(D_1 + D_2 + 1)[(1 - E_2)/E_1] p_0, \quad (7)$$

$$C = (D_1 + D_2 + 1)(D_1 + 2) - 2(D_3 + D_4 + D_5)[(1 - E_2)/E_1] p_0. \quad (8)$$

For ideal gas we find the coefficient to be  $D_1 = -\gamma$ ,  $D_2, D_3, D_4, D_5 = 0$  (where  $\gamma = c_p/c_0$ ), so  $A = \gamma p_0$ ,  $B = \gamma(\gamma - 1)p_0$ ,  $C = \gamma(\gamma - 1)(\gamma - 2)p_0$ .

#### STATISTICAL MECHANICS ASPECTS. GASES OBEYING THE VAN DER WAALS EQUATION OF STATE AND SEMI-IDEAL ONES.

It is known that the interacting forces between the molecules of nonideal gases and liquids cannot be neglected except first approximation. The more a gas is condensed, the

rougher this approximation becomes. For a system comprised of interacting particles, the partition function must be written for the ensemble of molecules, since the potential energies of molecules cannot be split [2]. If the kinetic energy is small compared with the atomic and nuclear energies, the energy of the ensemble may be considered to be a function of only the positions of the molecules. If the equations of state would be found through the partition function, the equation (1) were satisfied automatically. Generally, the partition function for the ensemble looks

$$\bar{Z} = \bar{Z}_{\text{trans}} \bar{Z}_p (Z_{\text{vib}} Z_{\text{rot}} Z_{\text{elec}})^N \tag{9}$$

where  $\bar{Z}$  refer to the partition functions of the ensemble,  $N$  is the number of particles in the ensemble,  $Z$  refer to the partition function for each particle.  $\bar{Z}_{\text{trans}}$ ,  $\bar{Z}_p$  mean the translation partition function and that for the potential energy. Here, vibrational, rotational, electronic, and nuclear contributions to the total partition function are involved. In the case of an ideal gas, the potential energy term  $E_p(q) = \sum_{i>j}^N \sum_{j=1}^{N-1} e_p(r_{ij})$ ;  $e_p(r_{ij})$  is potential energy due to interaction between pair of molecules  $i$  and  $j$  equals to zero. Then,  $\bar{Z}_p$  from (9):

$$\bar{Z}_p = V^N \left( 1 + \frac{1}{2} N^2 \frac{\beta}{V} \right), \quad \beta = \int f_{ij} d\tau_i = \int_0^\infty 4\pi r^2 f(r) dr \tag{10}$$

From statistical mechanics, the thermic equation of state is given by:

$$pV = kT \left( \frac{\partial \ln \bar{Z}}{\partial \ln V} \right)_{T,N} = kT \left( \frac{\partial \ln \bar{Z}_p}{\partial \ln V} \right)_{T,N} \tag{11}$$

(where  $k$  is Boltzmann's constant) while the only factor of the partition function  $\bar{Z}$  dependent on volume is  $\bar{Z}_p$  (10). If we assume that  $\frac{1}{2} N^2 \frac{\beta}{V}$  is very small compared with unity, the proceeding equation becomes:  $pV = NkT(1 - \frac{1}{2} N^2 \frac{\beta}{V})$ . The internal energy  $U$  for a system of  $N$  particles and internal energy  $E$  per unit mass ( $E = (UN_0)/N\mu$ ), where  $N_0$  - Avogadro number,  $\mu$  - molar mass, are:

$$U = - \left( \frac{\partial \ln \bar{Z}}{\partial (1/kT)} \right)_V, \quad E = \frac{f}{2} \frac{RT}{\mu} + \frac{\rho}{2} \left( \frac{N_0}{\mu} \right)^2 \frac{\partial \beta(T)}{\partial (1/kT)} \tag{12}$$

Here dependence on  $T$  of only  $\bar{Z}_p$  is assumed in (9). Symbol  $f$  notes number of degrees of freedom of each molecule (sum of translation and rotational movements).

When we assume that  $\langle e_p(r) \rangle$  is small in comparison with  $kT$ , for Van der Waals gas model we find:  $\beta = -2(b - aN_0/(RT))$  where  $a, b$  - the known VdW constants,  $R$  - universal gas constant. The internal energy per unit mass follows from (12). To find some corresponding coefficients for the semi-ideal gas, we have take into account  $Z_{\text{vib}}$  from (9), so [3]:

$$E = E_{\text{id}} + (R/\mu) \sum_1^{f_{\text{osc}}} \theta_i / (e^{\theta_i/T} - 1)$$

where:  $C$ ,  $f$ ,  $\theta_i$  – vibrational specific heat, number of degrees of freedom of a molecule, characteristic temperatures of oscillation.

Gas	Model of ideal gas		Model of semi-ideal gas		Experimental data	
	$B/A$	$c[m/s]$	$B/A$	$c[m/s]$	$B/A$	$c[m/s]$
<i>He</i>	0.67	972.9	0.67	972.9	0.66	971
<i>N<sub>2</sub></i>	0.40	336.9	0.40	336.9	0.401	334.0
<i>CO</i>	0.40	337.0	0.40	337.0	0.40	336.338
<i>CO<sub>2</sub></i>	0.33	262.2	0.24	255.0	0.31	256.7
<i>CH<sub>4</sub></i>	0.33	434.7	0.29	431.3	0.30	430

TABLE 1. All values in table are obtained for  $T = 273,15K$ .

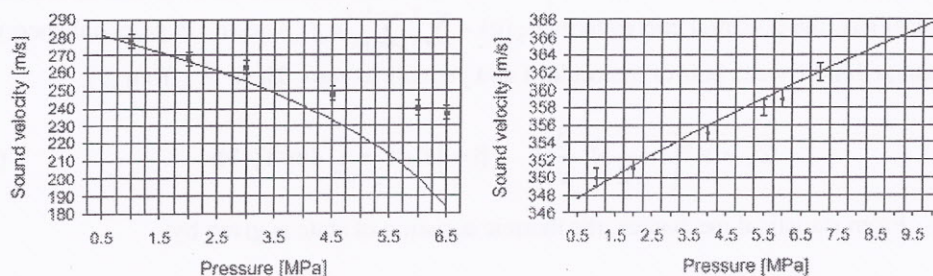


FIGURE 1. Comparison of theoretical (Van der Waals) and experimental values of sound velocity: a)  $CO_2$  gas, 323.95 K, 0.3 MHz, [4]; b) air gas, 298 K, 486 kHz, [5].

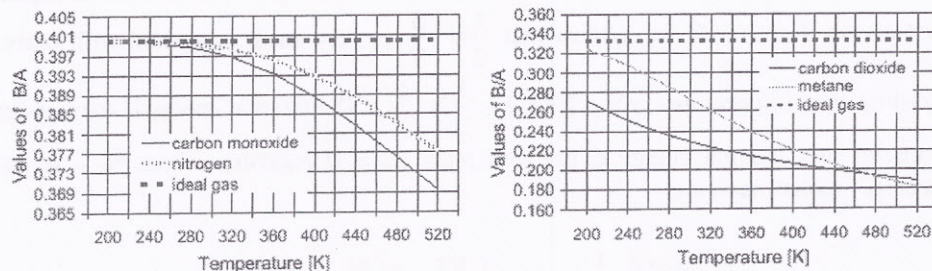


FIGURE 2. Temperature dependence of  $B/A$  parameter for some semi-ideal: a) diatomic and b) polyatomic gases.

#### REFERENCES

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