IOP Conf. Series: Journal of Physics: Conf. Series **792** (2017) 012035 doi:10.1088/1742-6596/792/1/012035

An approach to get thermodynamic properties from speed of sound

M A Núñez and L A Medina
Departamento de Física, Universidad Autónoma Metropolitana Iztapalapa, A. P. 55-534, C.P. 09340, D. F., México. e-mail: manp@xanum.uam.mx

E-mail: manp@xanum.uam.mx

Abstract. An approach for estimating thermodynamic properties of gases from the speed of sound u, is proposed. The square u^2, the compression factor Z and the molar heat capacity at constant volume C_V are connected by two coupled nonlinear partial differential equations. Previous approaches to solving this system differ in the conditions used on the range of temperature values $[T_{min},T_{max}]$. In this work we propose the use of Dirichlet boundary conditions at T_{min}, T_{max}. The virial series of the compression factor $Z = 1+B\rho+C\rho^2+\ldots$ and other properties leads the problem to the solution of a recursive set of linear ordinary differential equations for the B, C. Analytic solutions of the B equation for Argon are used to study the stability of our approach and previous ones under perturbation errors of the input data. The results show that the approach yields B with a relative error bounded basically by that of the boundary values and the error of other approaches can be some orders of magnitude lager.

1. Introduction

The knowledge of thermodynamic properties of gases is of interest in molecular physics and its industrial applications. Generally, heat capacities are measured with uncertainties which can be orders of magnitude larger than those of thermal properties. The speed of sound u yields a way to estimate caloric properties with an accuracy exceeding that of direct measurements [1]. In this work an approach to estimate thermodynamic properties from speed of sound data, is proposed. The stability of this approach under perturbations is studied together with that of two other approaches [2]-[6], by means of the virial series for gases. Accurate estimation of virial expansions is of interest yield a connection between microscopic and macroscopic gas theories, e. g., to constraint multiparametric equations of state and develop models of intermolecular interactions [7], [8]. The approach and the stability analysis are given in section 2 and section 3 is devoted to some concluding remarks.

2. The new approach and its stability

Hereafter partial derivatives will be indicated as follows $\partial Z/\partial T=Z_T$, $\partial^2 Z/\partial T\partial\rho=Z_{T\rho}$. A closed system of equations that connect the speed of sound u with the compression factor $Z=p/RT\rho$ and the molar heat-capacity at constant volume C_V is

$$\rho Z_\rho = - Z - (R/C_V)(Z + TZ_T) + F , \quad F = Mu^2/RT , \tag{1}$$

$$\rho C_{v,\rho} = - R(T^2 Z_{TT} + 2TZ_T) ,$$

where T, R, ρ, M, p, are the temperature, the universal gas constant, the molar density and mass, and the pressure. Several approaches have been proposed to solving this system in a rectangular region $\{T_{min}\leq T\leq T_{max},\ 0\leq\rho\leq\rho_{max}\}$ where the speed-of-sound data u are known. Since this is a system of first order in ρ, it is usually solved with initial conditions given by the perfect-gas limit, namely,

$$Z=1, \quad C_V=C_V\,??\,(T) \quad \text{at} \quad \rho_{min}=0 . \tag{2}$$

The main difference between previous approaches lies in the conditions used on the interval of temperature values $[T_{min}, T_{max}]$. A first approach, which will be referred to as the initial value method (IVM) [5], has used initial conditions in the temperature

$$Z=Z^{min}(\rho) , \ Z_T=Z_T^{min}(\rho) \ \text{at } T_{min} . \tag{3a}$$

Although this approach can provide accurate thermodynamic properties some inaccuracies in the surface of C_V have been reported and it was pointed out that a source of error is the estimation of the derivative Z_T at T_{min}, whose relative error is one order of magnitude larger than that of Z at T_{min} [5]. In order to avoid the estimation of Z_T in [6] it was proposed to solve the problem with Dirichlet boundary conditions (DBC's) on two isotherms in the lowest range of temperature values T_{min}, T_b,

$$Z=Z^{min}(\rho) \text{ at } T_{min}, \quad Z=Z_b(\rho) \ \text{ at } T_b , \tag{4a}$$

e. g, in a range with $T_{max} - T_{min} = 140$ K it was used $T_b\sim T_{min}+5$ K. In this work we propose the use of the initial conditions (2) and the following DBC's

$$Z=Z^{min}(\rho) \ \text{ at } T_{min}, \quad Z=Z^{max}(\rho) \text{ at } T_{max} . \tag{5a}$$

A way of studying the stability of these formulations is given by the virial series

$$\begin{aligned} Z &= 1 + B\rho + C\rho^2 + D\rho^3 + \ldots \\ C_V &= C_V\,??\,(T) + C_{V,1}\rho + C_{V,2}\rho^2 + \ldots \\ F &= \gamma_0(u^2/u_0^2) = \gamma_0 + \gamma_0\beta_a\rho + \ldots , \qquad u_0^2 = (\gamma_0 RT)/M , \end{aligned}$$

which lead to linear ordinary differential equations for B, C, …. . The equation for B is

$$B_{xx} + (1+2C_0) B_x + 2(C_0+1)C_0 B = C_0^2\gamma_0\beta_a \tag{6}$$

where we set $C_0 = C_V$??/R, $x = \ln \tau$, $\tau = T/T_r$, and T_r is a reference value. To get analytic solutions of equation (6) we consider the gaseous Argon with C_V ?? = $3/2R$, $\gamma_0 = 5/3$, and reference values of B are obtained from the equation of state (eos) reported in [8]. Experimental speed-of-sound data u with T between T_{min}=110 and T_{max}=450 yield T_r=280 K yield β_a values reported in [9] with which we get the least-squares estimation

$$\beta_a = -117.7019\tau^{-2} + 210.5188\tau^{-1} - 666.2851 + 1174.822\tau - 839.8723\tau^2 + 314.1316\tau^3 - 48.3716373\tau^4 \quad (7)$$

Hereafter values of B and β are in $cm^3 mol^{-1}$. The conditions corresponding to (3a), (4a), (5a), are

$$B = B^{min}, \quad B_x = B_x^{min} \text{ at } T_{min}, \quad (3b)$$
$$B = B^{min} \text{ at } T_{min}, \quad B = B_b \text{ at } T_b, \quad (4b)$$
$$B = B^{min} \text{ at } T_{min}, \quad B = B^{max} \text{ at } T_{max}. \quad (5b)$$

The eos [8] yields $B^{min} = -153.47835$, $B_x^{min}=280.7384$, $B^{max}=3.59194$, with which the equation (6) is solved analytically. The solution of equation (6) with the conditions (3b), (4b), (5b), will be denoted by B^{IVM}, $B^{DBC(4)}$, $B^{DBC(5)}$, respectively.

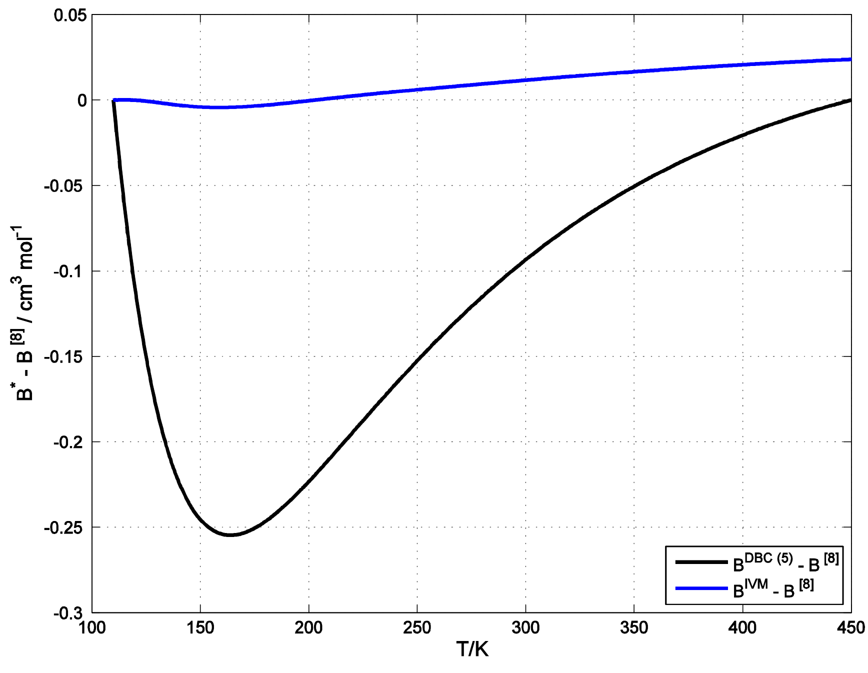

Figure 1. Deviations with respect to the eos for Argon of Ref. [8].

The plot of the difference B^{IVM}-$B^{[8]}$, $B^{DBC(5)}$-$B^{[8]}$, v.s. T is given in figure 1, where $B^{[8]}$ are the values from the eos [8]. The IVM yields B^{IVM} a closer $B^{[8]}$ than the $B^{DBC(5)}$ given by our approach, although $B^{DBC(5)}$-$B^{[8]}$ is of order 0.25, the uncertainty of B values reported in Table 16 of [8]. To study the stability under perturbations of the input data we solve analytically the equation

IOP Conf. Series: Journal of Physics: Conf. Series **792** (2017) 012035 doi:10.1088/1742-6596/792/1/012035

$$B_{xx}^{e} + (1+2C_0)\, B_x^{e} + [(1+k)C_0+2]C_0\, B^{e} = C_0^2\gamma_0\, \beta_a^{e} \tag{8}$$

where the superscript *e* indicates a solution with errors in the input data. The errors e_j are defined by the following expressions

$$\begin{aligned} B^e(T_{min}) &= (1+10^{-2}e_1)\, B(T_{min}) , \quad B_x^e(T_{min}) = (1+10^{-2}e_2)\, B_x(T_{min}) , \\ B^e(T_{max}) &= (1+10^{-2}e_3)\, B(T_{max}) , \quad \beta_a^e(T) = (1+10^{-2}e_4\ \sin 9x)\, \beta_a(T) . \end{aligned} \tag{9}$$

Thus e_j yields the percentage error $e_j = 100(q^e-q^{e=0})/q^{e=0}$. The factor $\sin 9x$ introduces a nonuniform error distribution in β_a (7). The effect of an error e_j in the perturbed solution B^e is measured by means of the percentage error

$$\%\Delta B^e=100\times[(B^e-B^{e=0})/(B^{e=0}-7.5)] \tag{10}$$

where the denominator $B^{e=0}$-7.5 is used to avoid the singular value B=0 at T∼408 K and $B^{e=0}$ denotes the virial coefficient obtained by without input data errors. The relative uncertainty of the velocity data $\Delta u/u \sim 10^{-4}$ yields e_4 of order 0.3%, so that the errors in B are dominated by the error in complementary conditions (3), (4), (5).

The graph of $\%\Delta B^{IVM,e}$ with e_1=e_4=0.3 and increasing values of the error e_2=0.3, 1, 5, in B_x, is given in figure 2 and shows that the monotonic growing of the absolute value of $\%\Delta B^{IVM,e}$ is faster as the error in the derivative increases. In contrast, figure 3 shows that the error $\%\Delta B^{DBC(5),e}$ is bounded basically by e_j. The second DBC in (4a) is defined with T_b=120 K and $B^{DBC(5),e=0}$= -130.8880 at T_b. The perturbation of this value is

$$B^{DBC(4),e}\,(T_b) = (1+10^{-2}e_b)\, B^{DBC(5),e=0}(T_b) .$$

For e_b=e_j the absolute value of the error $\%\Delta B^{DBC(5),e}$ is bounded by that of e_j only in the interval $[T_{min},T_b]$ and grows monotonically as T increases in the complementary region $[T_b,T_{max}]$. Figure 4 shows that this absolute error can grow rapidly when the sign of e_1 and e_b is different. Hence, the DBC's (4a) can yield a very unstable solution.

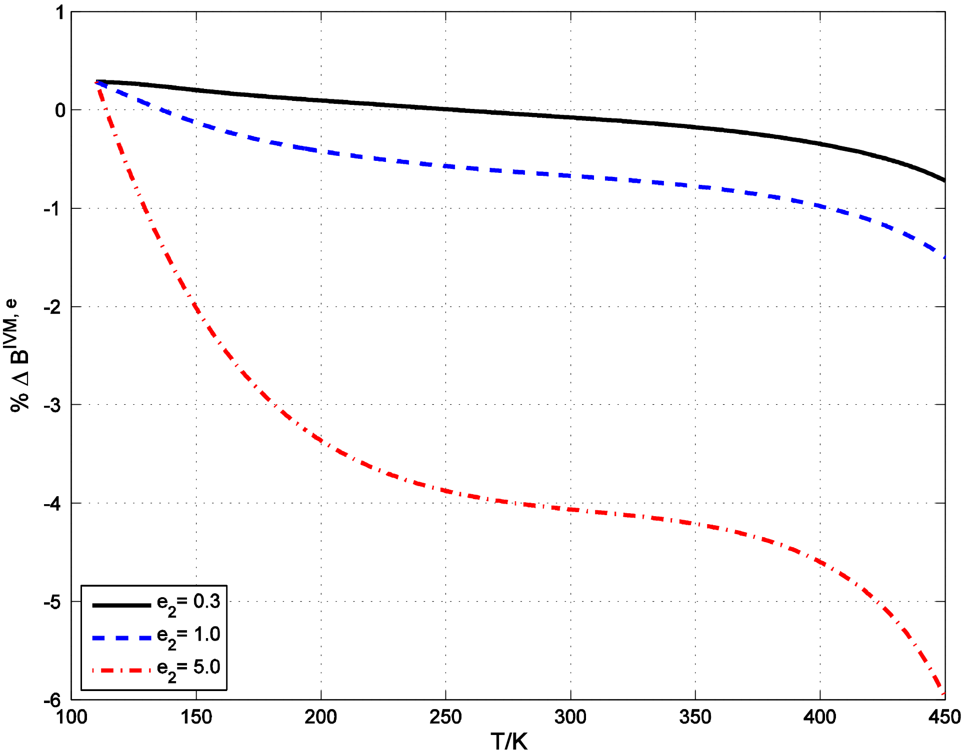

Figure 2. Relative error with e_1=e_4=0.3 and increasing values in the error e_2 of the derivative B_x at $T_{\min}$.

IOP Conf. Series: Journal of Physics: Conf. Series **792** (2017) 012035 doi:10.1088/1742-6596/792/1/012035

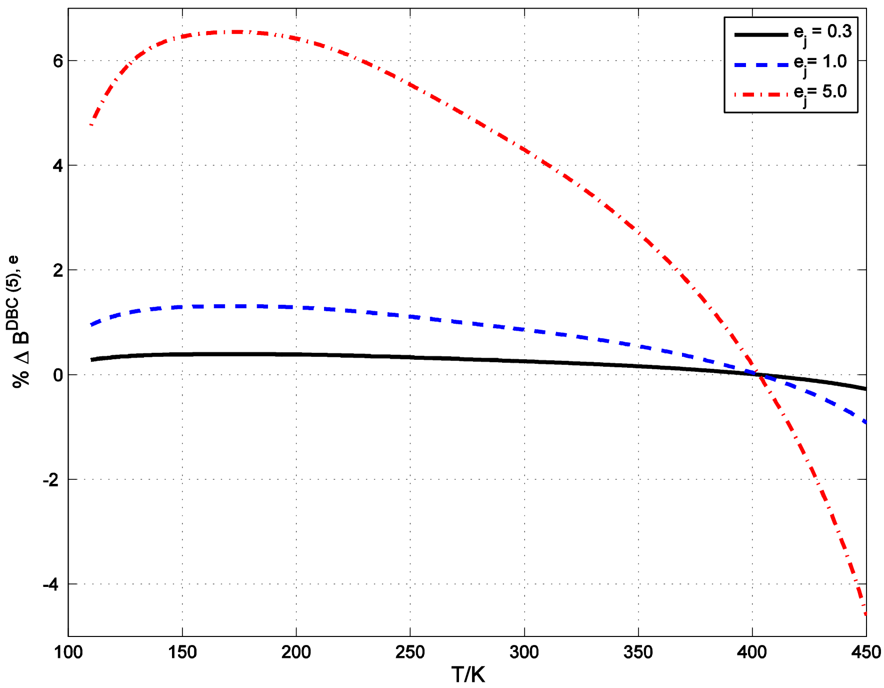

Figure 3. Relative error of $B^{DBC(5)}$ with increasing values of e_1= e_3=e_4.

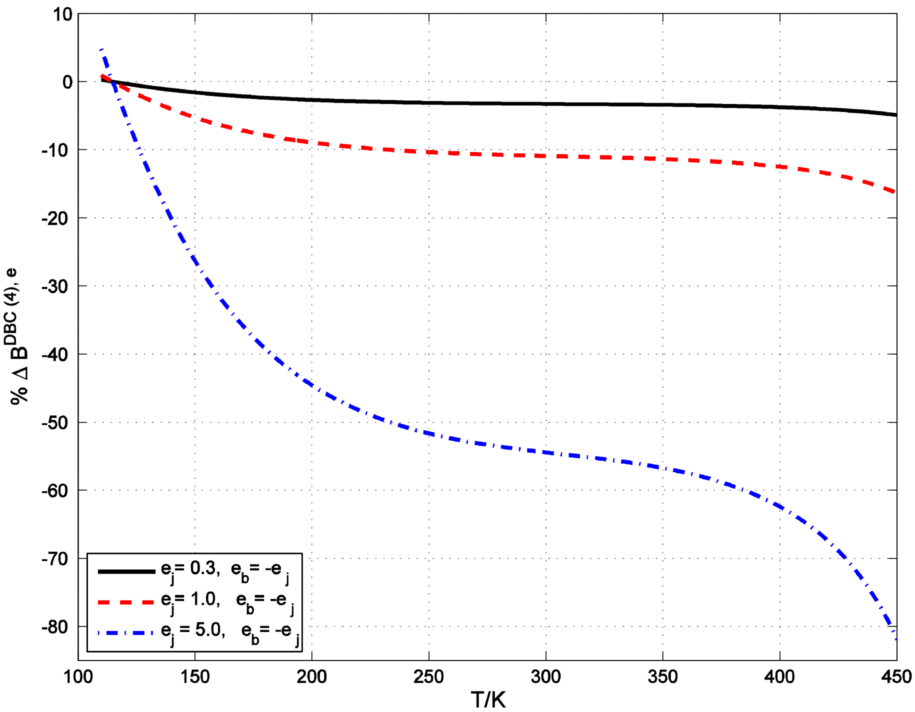

Figure 4. Relative error of $B^{DBC(4)}$ determined by DBC's (4a).

3. Conclusions

This work proposes an approach to compute thermodynamic properties from speed of sound data by solving equations like (1) by means of DBC's (5). Analytic calculations of the virial coefficient B show that these boundary conditions yield stable calculations with an error bounded approximately by that of the DBC's, in contrast with the other approaches whose error can grow rapidly as T increases.

4. References

[1] Trusler J P M 1991 *Physical Acoustics and Metrology of Fluids* (Adam Hilger, Bristol).
[2] Trusler J P M and Zarari M J 1992 *J. Chem. Thermodynamics* **24** 973.
[3] Dayton T C, Beyerlein S W and Goodwin A R H 1999 *J. Chem. Thermodynamics* **31** 847.
[4] Estrada-Alexanders A F, Trusler J P M and Zarari, M P 1995 *Int. J. Thermophys*. **16** 663.
[5] Estrada-Alexanders A F and Trusler J P M 1996 *International Journal of Thermophysics* **17** 6.
[6] Bijedi´c M and Neimarlija N 2013 *Latin American Applied Research* **43** 393.
[7] Maitland G C, Rigby M, Smith E B and Wakeham W A 1981 *Intermolecular Forces* (Clarendon Press, Oxford).
[8] Tegeler C, Span R and Wagner W 1999 *J. Phys. Chem. Ref. Data* **28** 779.
[9] Estrada-Alexanders A F and Trusler J P M 1995 *J. Chem. Thermodyn*. **27** 1075.