Data analysis method for estimating virial acoustic virial coefficients of Argon from speed of sound data in the pressure-temperature domain

Marco A. Núñez, Luis 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

Abstract. Virial series of imperfect gases yield a way for study the reliability of potential interaction models by means of high precision the speed-of-sound data, which are measured as function of pressure and temperature. However, a theoretical study for Argon showed that the third acoustic virial coefficient estimated from by high precision velocity data for Argon, can be inconsistent with ab initio calculations in density-temperature domain. In this work we propose a data analysis method to solving this apparent contradiction. The results show that speed-of-sound data for Argon in the pressure-temperature domain can indeed yield reliable estimations of the third and fourth acoustic virial coefficients in the density-temperature domain.

1. Introduction

Mayer's theory for imperfect gas [1] shows the existence of the virial series

\[ pV / RT = 1 + B_2(T)V^{-1} + B_3(T)V^{-2} + \ldots + B_k(T)V^{-k+1} + \ldots \]

\[ = 1 + B'_2(T)p + B'_3(T)p^2 + \ldots + B'_k(T)p^{k-1} + \ldots \]

where \( p, V, R, T, \) are the pressure, molar volume, the universal constant and the temperature, respectively. These yield the series of the speed of sound \( u \) as a function of \( p, T, \) and \( V, T, \)

\[ f = \left[ u^2(p,T) / u_0^2 - 1 \right]RT / p = A'_2(T)V + A'_3(T)p + \ldots \]

\[ = [u^2(V,T) / u_0^2 - 1]V = A_2(T) + A_3(T)V^{-1} + \ldots \]

The acoustic coefficients \( A_2 \) and \( A'_2 \) are obtained from \( B_2 \) and \( B'_2 \) via differential relations [2]. For Argon \( u_0^2 = \gamma_0 RT / M \) is constant, \( \gamma_0 \) and \( M \) are the heat-capacity ratio in the limit of perfect gas and the molar mass. Since \( B_3 \) depends of potential interaction models, virial expansions yield a theoretical connection between microscopic and macroscopic descriptions [3]. This connection was used in [4] to study the sensitivity of virial coefficients to Argon interaction models. The study shows a good agreement between ab initio and experimental results, except by a significant disagreement with the third acoustic virial coefficient \( A'_3 \) reported in [5], whose authors claim that their approach can yield accurate virial coefficients. The main aim of this work is to show that this disagreement can be solved by means of a suitable data analysis method, which can yield reliable values of \( A'_2, A'_3, \) and \( A'_4, \) the latter being not reported in [5].
2. Previous methods of acoustic data analysis for Argon

Experimental speed-of-sound data $u_y = u(p_y, T_i)$ are measured with a given temperature $T_i$ and increasing pressure values $p_y (p_y < p_{ij+1})$. The corresponding values $f_y = (u_y^2 / u_y^2 - 1)RT_i / p_y$ (2) are analysed with a truncated series of the form

$$f^{(k)}(p, T) = A'_1(T) + A'_2(T)p + A'_3(T)p^2 + ... + A'_k(T)p^{k-2}. \quad (4)$$

It is generally accepted that the series (4) is a correct model of the data set $T_i, p_y, f_y$, on each isotherm [6,7]. Under this assumption the acoustic coefficients $A'_k$ are estimated by minimizing the sum of squares

$$\chi^2 = \sum_i [f^{(k)}(p_y, T_i) - f_y]^2 d_y^{-2} \quad (5)$$

where $d_y = df(T, p_y, u_y) / du \Delta u$ are errors with the high accuracy $\Delta u/u \sim 10^{-4}$ of velocity data [2,6]. To study the validity of model we computed the following quantities with the Argon velocity data reported in [6]. Let $A'_k(n)$ be the coefficients obtained by least-square fit of set $DS_i(n)$ with the first $n$ data $p_y, f_y$, for isotherm $T_i$ and the parabolic model

$$f^{(2)}(p, T) = A'_1(T) + A'_2(T)p + A'_3(T)p^2. \quad (6)$$

Details of the fit are given below. Figure 1 shows the graph of $n$ vs. $A'_4(n)$ for isotherm $T=148$ K. If the range of pressure values were "sufficiently" small, the coefficients $A_k(n)$ should be near a constant value. However, we see that $A'_4(n)$ moves away monotonically from the value $A'_4(3)$. This behaviour shows that model $f^{(2)}(p, T)$ is not suitable to represent the velocity data $u_y$ in the range of pressure values $p_y$ for isotherm $T=148$ K. The same conclusion is obtained with each isotherm $T_i$ reported in [6]. The correct model has the following form

$$\tilde{f}(p, T) = \tilde{A}_1(p, T) + \tilde{A}_2(p, T)p + \tilde{A}_3(p, T)p^2. \quad (7)$$

In [5] it was assumed that model (6) is correct at each isotherm and the "lowest" reported value and two more pressures between 1 and 2 MPa. Model (6) was used in two steps to estimate acoustic coefficients, details are given in [6]. In the first step the coefficient $A'_4$ is estimated. Once $A'_4$ was obtained, the quantity $Y_5 = [f^{(2)}(p, T) - A'_1] / p$ is calculated from which $A'_1$ and $A'_3$ are obtained from
the zero-pressure intercept and slope. Wiebke et. al. [4] studied the sensitivity of the thermal and acoustic virial coefficients of Argon to the models of interaction potentials. These models are worked in density-temperature domain and yield coefficients $B_z$ and $A_z$. They conclude that several theoretical and experimental acoustic results are in very good agreement among themselves, but they reported an incompatibility with the third acoustic coefficient $A_{3}$ from [5], which was obtained from the virial series (2) by means of the relations

$$A_z = A_z'$$  \hspace{1cm} (7) \\
$$A_i = A_i B_z + (RT) A_i'$$  \hspace{1cm} (8) \\
$$A_i = A_i B_z + 2(RT) A_i' + (RT)^2 A_i''.$$  \hspace{1cm} (9)

Wiebke [4] found that there is a good agreement between several experimental and theoretical coefficients $A_i$ and that reported in [5]. However, using a theoretical $B_z$ Wiebke found a significant disagreement between several results of $A_i$ and that given by $A_i'$ of [5] via equation (8), see Fig. 6 of [4]. In this work we used coefficients $B_z$ from Jager [8] since these include improvements of interaction potentials from quantum mechanical calculations. Figure 2 confirms the disagreement between the $A_i$ of Jager [8] and the $A_i$ given by $A_i'$ of [5] via equation (8). Wiebke [4] remark that contrastingly, there is excellent agreement between experimental and \textit{ab initio} data set, all of which are mutually independent, except by the discrepancy of $A_{3}$ from [5].

This poses the following problem that we shall attempt to solving in this work: The discrepancy in Figure 2 between $A_{3}$ of [8] and $A_{3}$ from [5] is generated by the inaccuracy of the acoustic data or the method of data analysis. The results reported below show that our data analysis method yields $A_z$ and...
$A_i$ in agreement with \textit{ab initio} calculations. It should be noted that the data analysis method of [6] and used in [5] yields the three acoustic coefficients $A'_i$, $A'_i$, $A'_i$, but in [5] the values $A'_i$ were not reported. In contrast our proposal yields values of $A'_i$ congruent with \textit{ab initio} calculations.

3. Proposed data analysis

The starting point of our data analysis method is the chi-square function $\chi^2_i$ (5). It is well known that the parameters given by least squares are very sensitive to the presence of outliers [9]. Numerical experiments with synthetic data to check the importance of the errors $d_j = df / du\Delta u$, show that the fit is robust when the number of data is \textit{at least} 50. Unfortunately, the number of acoustic data reported for each isotherm is 11 or 12 [6]. This motivated us to seek a criterion independent of $d_j$ to measure the goodness of a fit. A widely accepted measure of the goodness of a fit is the correlation coefficient

$$r_i^2 = \frac{\sum [f_j^i - \bar{f}_i]^2}{\sum f_j^i},$$

where $\bar{f}_i = n^{-1} \sum f_j$, (10)

whose ideal value is $r_i = 1$ [10]. The feature of $r_i$ is its independence of $d_j$. For each isotherm $r_i$ was computed with the errors $d_j = df / du\Delta u$ and $d_j = 1$. The results showed that the best correlation coefficient is obtained with $d_j = 1$ and, therefore, such a value was used to get the results reported below. In order to explore a method for estimating virial coefficients $A'_i$ we used the analytic function

$$f_i = (A'_i + a_1 x + a_2 x^2) \exp(-70x) = A'_i + A'_i p + A'_i p^2 + ...$$

with $x = p / RT$, $A_i = -145$ and coefficients $a_1, a_2$, such that $f_i$ takes the values $f'(0) = A'_i = -2.3 \times 10^4$, $f''(0) = A'_i = -9.49 \times 10^6$, which are similar to the Argon values for $T = 110 K$. This function provides exact eleven synthetic data $f_j$ whose graph is very similar to that obtained with the eleven data reported in [6]. These data were perturbed to get $f_j^i = f_j + e_j$ with a given error $e_j$. We used a uniform mesh $p_j$ with values similar to those of the experimental data with $T = 110 K$ [6]. Let $A^\prime\prime_i(n)$ be the coefficients given by least-square fit of the first $n$ data set $DS(n)$ with $n$ from 3 to 11. The graphs of $p$ vs. $A^\prime\prime_i(n)$ with $e = 0$ show that $A^\prime\prime_i(n)$ change monotonically. As expected, the model (6) is not suitable for the data, but these graphs show that the desired coefficients $A'_i$ can be obtained by extrapolation of such graphs toward $p = 0$. The problem appears when the error $e_j$ is not zero, as occurs with real data. We studied the estimation of the data and their derivatives by means the Savitzky-Golay (SG) smoothing filters [9]. The results showed that reasonable approximations of the true $A'_i, A'_i$, can be obtained by extrapolation to $p=0$ but $A'_i$ is not well estimated. In this work we study some variations of the SG-smoothing filters. Consider the data set $DS(n)$ given by the first $n$ data of a given isotherm $T_i$ and let $A'_i(n)$ be the coefficients given by least-squares fitting of the model (6). The question is: what is the representative value $p_j^{(n)}$ of $p$ in each set $\{p_j\}_j^{(n)}$ to plot $p_j^{(n)}$ vs. $A'_i(n)$ and see if the resulting graphs allows us to recover the true $A'_i$ by extrapolation to $p = 0$? We tested $p_j^{(n)}$ as the mean value and the minimum and maximum values of set $\{p_j\}_j^{(n)}$. A comparison of these graphs with the graphs $n$ vs. $A'_i(n)$ shows that the latter are the better for estimating extrapolated values. This result is not a surprise if we consider the following facts:

(i) For exact data $f_j^{p=0}$ and $p_j$ in the region where the series (6) is valid, the first three data yield the exact coefficients $A'_i = A'_i(n = 3)$ since in this case least-squares fit coincides with the results given finite difference schemes. The remaining values $A'_i(n)$ coincide with the true ones $A'_i$. In the case of
data with errors $f'_j$, least-squares fit filters the errors and, consequently, yields $A'_j(n)$ almost constant and whose extrapolation to $n=3$ yields an estimation of $A'_j(n)$.

(ii) For perturbed data $f'_j$ out of the validity region of model (6), we will see a variation of $A'_j(n)$ as $n$ increases. This is the case of all the graphs $n$ vs. $A'_j(n)$ with the Argon data [6] studied in this work. The values $A'_j(n)$ change almost monotonically. The monotonicity and smoothness of $A'_j(n)$ is better as $n$ increases since the error data are better distributed between the fitted values. This is a valuable property to define the range of values of $n$ with which the extrapolation of $A'_j(n)$ at $n=3$ is estimated. In the case of Figure 1 the smoothness the graph of $A'_j(n)$ implies that the value $A'_j(n=3)$ is a suitable extrapolation of the remaining ones $A'_j(n)$.

![Figure 3. Argon second acoustic virial coefficient $A_2(7)$.](image)

4. Results

Following Wiebke [4], we report the acoustic coefficients $A_2$, $A_3$, $A_4$, in density-temperature domain given by the corresponding coefficients $A'_j(n)$ in pressure-temperature domain via equations (7)-(9). Let $A^{[5]}_j$ and $A^{\omega}_{j}$ denote coefficients from [5], [6], and this work. Coefficients $B_i$ of [8], were used. Figure 3 shows the differences $A^{[5]}_2 - A^{[8]}_2$ and $A^{\omega}_{2} - A^{[8]}_2$, the agreement between $A^{\omega}_{2}$ and $A^{[8]}_2$ is better than that of $A^{[5]}_2$. Figure 2 shows a very good agreement between $A^{[8]}_3$ and $A^{\omega}_{3}$ in contrast with the disagreement between $A^{[8]}_3$ and $A^{[5]}_3$. This can be explained in part by the fact that the factor $RT$ in equation (8) is of order $10^3$ so that small errors in $A'_3$ produce large errors in $A_3$. The iterative method described in [6] and used in [5] yields the fourth acoustic coefficient $A'_4$, but it was not reported in [5]. In this work we report the acoustic coefficient $A^{\omega}_{4}$ given by equation (9) and to compare it with the *ab initio* calculation of [8]. This comparison is not trivial since the factor $(RT)^2$ is of order $10^6$, so that $A^{\omega}_{4}$ is more sensitive to the errors in $A'_4$. Figure 4 shows a very good agreement between our $A^{\omega}_{4}$ and the *ab initio* $A^{[8]}_4$ for $T$ from 150 to 450 K, for $T$ below 150 the agreement becomes poor but the differences are consistent with the estimated errors.
5. Conclusions

The results of this work show that reliable third and fourth acoustic virial coefficients can indeed be obtained by data analysis pressure-temperature domain. The corresponding coefficients in density-temperature domain are in agreement with ab initio and other experimental results for Argon.

6. References

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