



Intermolecular Model Potentials and Virial Coefficients from Acoustic Data

^{1*}MONAGO, KO; ²DAWODU, OT

¹Department of Pure and Industrial Chemistry, ²School of Science Laboratory Technology, University of Port Harcourt, PMB 5323, Port Harcourt, Nigeria

*Corresponding author Email: ken.monago@uniport.edu.ng

ABSTRACT: A simple method is presented for the determination of model two- and three-body intermolecular potentials from acoustic data. The method is applied to argon, nitrogen, methane, ethane and propane. For argon, the second, third and fourth volumetric virial coefficients from the model potentials are compared with values determined in direct experiments. Second virial coefficients are shown to be in very good agreement with experiment. For the third volumetric virial coefficients, significant discrepancies are noted in the region of the maximum in the function. There are no experimental data for a direct comparison of the fourth volumetric virial coefficients presented here; however, because in a previous work, it was shown that fourth acoustic virial coefficients calculated from a similar method agreed with values determined in direct experiment, we argue that the values presented here are accurate.

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The virial equation of state (EOS) is based on rigorous theory because it can be derived from either the canonical or grand canonical ensemble using the method of cluster expansion. Its merit is that, although limited in scope to the gas phase, it is capable of very high accuracy and it is the only general equation of state method that can predict volumetric and caloric thermodynamic properties to better than 0.05 and 0.1 percent, respectively, for both pure gases and mixtures (Wiebke, *et al.*, 2011; Monago, 2013). The density virial equation can be represented by

$$Z = \frac{p}{\rho_n RT} = 1 + \sum_{k=2}^{\infty} B_k \rho_n^{k-1} \dots 1$$

In eq. (1), p is pressure, Z is the compressibility factor, ρ_n is the amount-of-substance density, R is the molar gas constant and T is the thermodynamic temperature. B_k is the k -th volumetric, or ordinary, virial coefficient; it is a function only of temperature and can be related to the interactions of an isolated k -molecule cluster. It is known that when eq. (1) is

$$\left. \begin{aligned} B_2 &= x_1^2 B_{11} + 2x_1 x_2 B_{12} + x_2^2 B_{22} \\ B_3 &= x_1^3 B_{111} + 3x_1^2 x_2 B_{112} + 3x_1 x_2^2 B_{122} + x_2^3 B_{222} \\ B_4 &= x_1^4 B_{1111} + 4x_1^3 x_2 B_{1112} + 6x_1^2 x_2^2 B_{1122} + 4x_1 x_2^3 B_{1222} + x_2^4 B_{2222} \end{aligned} \right\} 3$$

One of the failings of the virial EOS is that, as a power series, its radius of convergence is unknown, although it is known to be inapplicable at liquid-like

truncated after the fourth virial coefficient, it is capable of very high accuracy at least up to one-half the critical density, or at pressures up to at least 12 MPa (Monago, 2013). Another merit of eq. (1) is that there is a clear theoretical guide as to how it may be extended to mixtures. For a c -component mixture, the volumetric virial coefficients are given by the relations:

$$\left. \begin{aligned} B_2 &= \sum_{i=1}^c \sum_{j=1}^c x_i x_j B_{ij} \\ B_3 &= \sum_{i=1}^c \sum_{j=1}^c \sum_{k=1}^c x_i x_j x_k B_{ijk} \\ B_4 &= \sum_{i=1}^c \sum_{j=1}^c \sum_{k=1}^c \sum_{l=1}^c x_i x_j x_k x_l B_{ijkl} \end{aligned} \right\} \dots 2$$

Where, x_i is the mole fraction of component i and the coefficients with mixed indices B_{ij} , B_{ijk} , B_{ijkl} , in which $i \neq j \neq k \neq l$, are known as the interaction virial coefficients. The coefficients for which the indices are alike; that is, $i = j = k = l$, are the virial coefficients of the pure components. For a binary mixture, the above relations reduce to:

densities. The virial EOS has many applications in diverse areas of technology and commerce, which exploit its theoretical foundations and the quality of

the results it can give. In carbon dioxide capture and sequestration, mixtures of CO₂ and H₂O, possibly containing other contaminants, are transported in a cost effective manner through pipelines of mild steel construction at pressures between 8 and 20 MPa. To prevent corrosion of the pipeline, the gas mixtures must be dehydrated to the point where water cannot precipitate at high pressures while the gases are being transported. This task requires the knowledge of p - ρ - T - y properties of mixtures containing CO₂ and H₂O. The virial EOS is especially suited for the correlation and prediction of the vapor-liquid equilibrium, on the vapor side, in such mixtures.

Transport of natural gas in the gas-phase along pipelines is one of the oldest and well-known applications of the virial EOS. A particularly important feature of this mode of natural-gas transportation is the enormous amount of gas that can be exchanged, in a unit time, between the buyer and seller. Consequently, the accuracy with which gas rate of flow is determined becomes crucially important, as a small error in measurement or calculation can add up fast, leading to the loss of a substantial amount of money by one of the parties involved. For example, one of the joint venture partners in the Nigeria liquefied natural gas (NLNG) venture supplies a total of 1.2 billion standard cubic foot of gas per day to the plant from both on-shore and off-shore gas facilities (NLNG, 2014). Assuming an accuracy of 0.1 percent in measurement, this level of uncertainty translates to a loss of some 1.2 million standard cubic foot of gas per day and at the current price of \$ 3.3 per 1000 cubic foot set by the Federal Government, the 0.1 percent inaccuracy translates to a loss of about \$ 1 420 000 per year to the partner or NLNG.

Virial coefficients are experimentally accessible thermodynamic properties; the traditional route to their determination is by the analyses of isothermal p - ρ - y data by the limiting slope method. An alternative route to the virial coefficients is to postulate model intermolecular potential functions and to fit parameters in the models to some accurate and precise experimental property data.

Experimental acoustic data in the gas-phase is especially suitable for such analyses on account of its exceptionally high accuracy; this path has been exploited to determine virial coefficients, up to the fourth order (Monago, 2013). This method has the advantage that it leads directly to an EOS for the gas from which, in addition to the virial coefficients, all other thermodynamic properties of interest may be calculated. A recent development is the use of Monte

Carlo simulation method to calculate volumetric virial coefficients for real, non-spherical molecules and their mixtures. Benjamin *et al.* (2009) and Shaul *et al.* (2011) have calculated ordinary virial coefficients up to the fifth order and Shultz *et al.* (2015) have calculated volumetric second and third virial coefficients of CO₂/H₂O mixtures. However, the accuracy of the volumetric virial coefficients, which are higher than the third, calculated by simulation cannot be verified because no experimental data on these higher volumetric virial coefficients exist; the fourth volumetric virial coefficients calculated by Monago (2013) were believed to be accurate because the method also furnished acoustic fourth virial coefficients for which experimental data did exist (Monago, 2013; Estrada-Alexanders and Trusler, 1995). There is some evidence that higher volumetric virial coefficients calculated by simulation are, as yet, not very accurate; the second and third virial coefficients calculated by Kim *et al.* (2013) for mixtures of methane and ethane disagreed with experiment by up to 30 percent; also, water pressures calculated by Benjamin *et al.* (2009) using a fifth order virial EOS were deemed accurate only up to $\rho_c/2$!

The objective of this paper is to show that volumetric virial coefficients that are calculated by simple quadrature methods and based on pair- and triplet potentials can predict interesting thermodynamic properties of fluids at densities up to $\rho_c/2$ with accuracies that are better than 0.05 %.

MATERIALS AND METHODS

Numerical Methods: The analysis we present in this paper is based on published experimental values of speeds of sound as a function of temperature and pressure, $w(p,T)$ and involves the fit of parameters in model potential functions to experimental acoustic data.

The basic physical equations that relate equilibrium speed of sound to other thermodynamic properties may be set out as in eqn 4-11 (Monago, 2007). In Eq. (4) – (11), C_p and C_v are, respectively, isobaric and isochoric heat capacity functions, β_r is dimensionless inverse of the coefficient of isothermal bulk compressibility, R , is the molar gas constant and M is molar mass; other quantities in the equations have their usual meanings. The virial coefficients are related to the potentials of interaction by integral expressions which, in the language of linear graph, may be expressed by the eqn 12.

The Fit to speeds of Sound: Our analyses are based on published values of speeds of sound as a function of pressure and temperature for each of the systems studied (Estrada-Alexanders and Trusler, 1995; Trusler and Zarari, 1992; Ewing *et al.*, 1992; Estrada-Alexanders and Trusler, 1997; Ewing and Trusler, 1992; Estela-Uribe and Trusler, 2000). In each case, the number of acoustic data actually used in the fits were limited in two ways: because of limitations in available computer resources, only 9 – 12 isotherms

were actually used in the analysis of each system and for the systems we treated, only data that extended in density to no more than about $0.25\rho_c$ were included on each isotherm. The uncertainties in the experimental acoustic data were assumed to lie in the range 0.002 – 0.003 percent. The potential parameters that were obtained for the systems studied here are displayed in table 1.

Table 1: The intermolecular potential parameters for the systems studied in this work

System	r_m [nm]	ϵ/k [K]	M	κ	ν_{123} [K.nm ³]
Ar	0.37626	144.136	13.996	13.527	0.000533
N ₂	0.38676	139.037	19.422	13.0	0.001135
CH ₄	0.40179	203.284	17.199	12.0	0.002053
C ₂ H ₆	0.45050	393.335	32.510	12.604	0.013901
C ₃ H ₈	0.48657	560.810	67.655	12.0	0.044340

RESULTS AND DISCUSSION

In this section we present some additional results for argon, because it is prototypical of the spherically symmetric molecule for which the assumptions that underpin the present method are most fulfilled.

Figure 1 compares experimental second volumetric virial coefficients of argon (Estrada-Alexanders and Trusler, 1995; Michels *et al.*, 1958; Gilgen *et al.*, 1994) with the results obtained in this work and from which one can see that the molecular model used in this work agreed with experiment over the whole temperature range on that figure. In Fig. 2, we

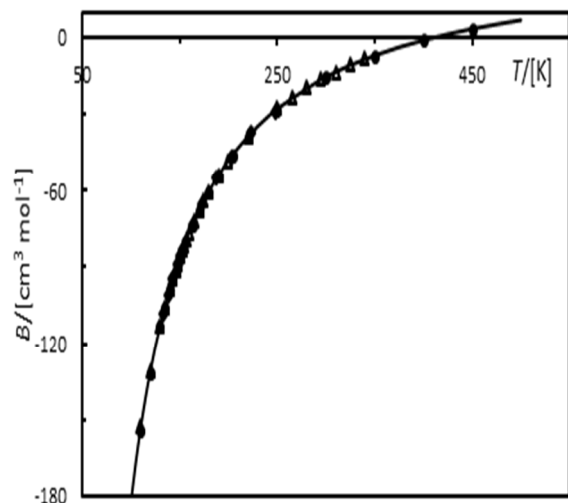


Fig. 1: Second volumetric virial coefficient, B , of argon as a function of temperature. • Estrada-Alexanders and Trusler (1995); ♦ Michels *et al.* (1958); Δ Gilgen *et al.* (1994); — this work

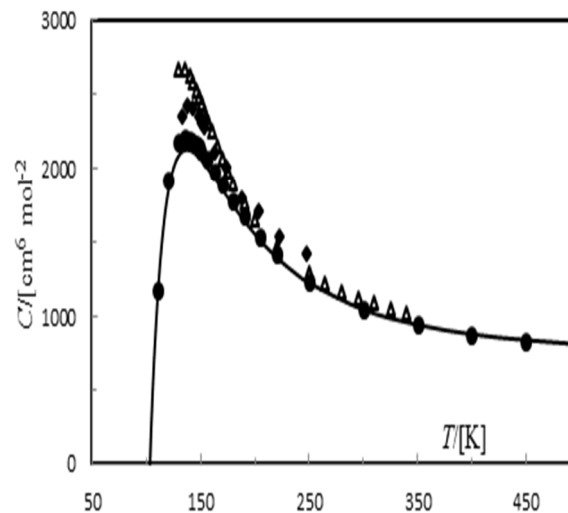


Fig. 2: Third volumetric virial coefficient, C , of argon as a function of temperature. • Estrada-Alexanders and Trusler (1995); ♦ Michels *et al.* (1958); Δ Gilgen *et al.* (1994); — this work

compare experimental (Estrada-Alexanders and Trusler, 1995; Michels *et al.*, 1958; Gilgen *et al.*, 1994) third volumetric virial coefficients of argon with the results calculated in the present work. The evidence of this plot seems to suggest that third volumetric virial coefficients are predicted accurately above a temperature of about 200 K; however, below this temperature, especially in region of the maximum in C , there are significant discrepancies, not only between experimental and calculated C , but among the experimental data themselves. However Fig.3, which compares experimental (Estrada-Alexanders and Trusler, 1995; Ewing and Trusler, 1992) third acoustic virial coefficients from two

sources with calculated values, shows excellent agreement.

The contradictory evidence presented in plots such as Fig. 2 and Fig. 3 has made others (Trusler *et al.*, 1997) to question the accuracy of experimental third volumetric virial coefficients of argon in the region of the maximum in C . Fourth Volumetric virial coefficients of argon calculated from the present model are shown in Fig. 4.

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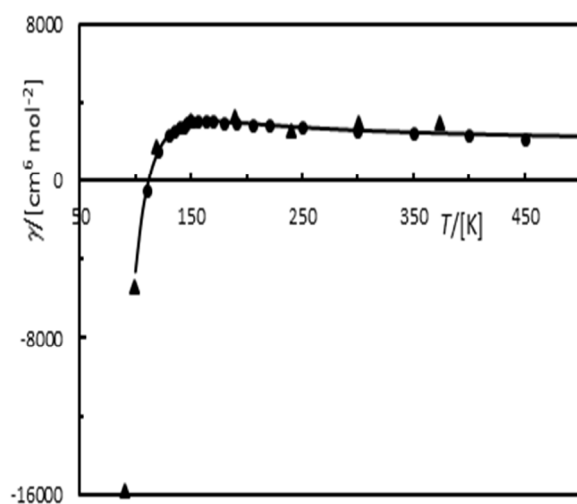


Fig. 3: Third acoustic virial coefficient of argon as a function of temperature. • Estrada-Alexanders and Trusler (1995); ▲ Ewing and Trusler (1992); — this work

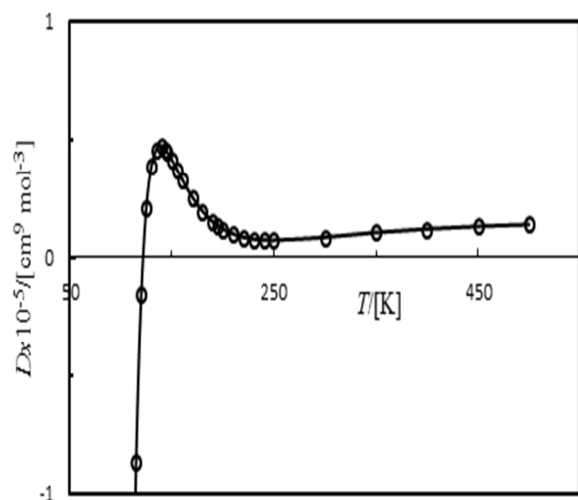


Fig. 4: Fourth volumetric virial coefficient of argon, D , calculated in this work as a function of temperature.

Fourth Volumetric virial coefficients of argon calculated from the present model are shown in Fig. 4. There are no experimental data with which these results can be compared with; however, in a previous work (Monago, 2013; 2005) we have compared calculated fourth acoustic virial coefficients obtained from a procedure similar to the present method with the experimental data of Estrada-Alexanders and Trusler (1997) and obtained excellent agreement. Fig. 5 compares the experimental p - ρ - T data of Gilgen *et al.* (1994) with the results obtained in this work; it is seen that compression factors are predicted with accuracies that are better than 0.05 percent at densities up to 5 mol/dm³.

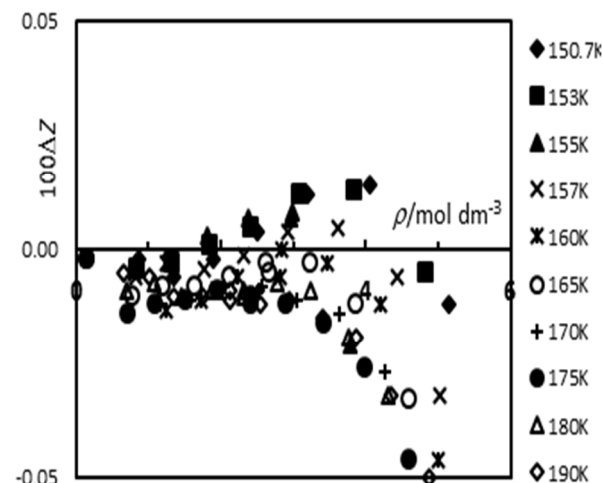


Fig. 5: Deviations $\Delta Z = Z_{\text{expt}} - Z_{\text{cal}}$ of calculated compression factors of argon from the experimental data of Gilgen *et al.* (1994) in the expanded critical region.

Conclusions: We have found that when parameters in a pair- and triplet potential functions are determined in a fit to acoustic data, the procedure is able to, not only correlate second and third volumetric virial coefficients in the temperature range of the input data, but permitted considerable extrapolation in temperature. We believe that the fourth volumetric virial coefficients presented in this paper are accurate. We have used the calculated volumetric virial coefficients to calculate compressibility factors for argon and found them to be in agreement with experiment to within accuracies of 0.05 % at densities up to 5 mol/dm³.

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