THERMODYNAMIC PROPERTIES OF SIMPLE GASES FROM MIE (N-6) POTENTIAL FUNCTION

K O Monago
Department of Pure and Industrial Chemistry, University of Port Harcourt, P M B 5323 Choba, Port Harcourt, Nigeria
Accepted: 27/03/2015
Corresponding author: ken.monago@uniport.edu.ng

Abstract
A fourth order virial equation of state was combined with the Mie (n-6) potential function and the triple-dipole term to determine the volumetric and caloric thermodynamic properties of argon in the gas phase. The parameters in the molecular model were determined in a fit to speed of sound data. The equation of state predicted second and third volumetric and acoustic virial coefficients of argon with good accuracy, but failed to predict fourth virial coefficients quantitatively. The equation of state predicted the P-V-T properties of argon with reasonable accuracy up to about six-tenth of the critical density ($\rho_c$). The (n-6) potential is, therefore, not only superior to the Lennard-Jones (12-6) potential, but can be used to perform exploratory calculations in practical problems.

Key words: Argon, Mie (n-6) potential fourth virial coefficients, equation of state

Introduction
It was already known by the early 1970s that a reasonable pair-potential when combined with the Axilrod-Teller triple-dipole term (of the multipole expansion) could correlate second and third virial coefficients of closed shell atoms with good accuracy [1,2,3]. Subsequent works in this direction only served to further develop and refine the above result [4-7]. The pair potentials that have been employed for this purpose varied from the Barker-Fisher-Watts potential [3] to the (ab initio) Tang-Toennies potential [6] and from the Maitland-Smith potential [5] to the Hartree-Fock dispersion (HFD) and exchange-coulomb (XC) type potentials [4,7]. The range and nature of these functional forms already make it clear that the pair-potential does not have to be “accurate” to correlate the virial coefficients of closed shell atomic species.

Recently, the Maitland-Smith (MS) potential was combined with the Axilrod-Teller term to determine a fourth order virial equation of state for argon in the gas phase [8]. The resulting equation of state was able to correlate all volumetric and acoustic virial coefficients of argon up to the fourth order. In the case of the fourth volumetric virial coefficient, its accuracy was adjudged by its agreement with the results of ref. 6; the later method was based on a completely different pair-potential function. In addition, the equation of state of ref. 8 predicted the PpT properties of argon to within 0.05 percent up to a density of one-half the critical density ($\rho_c$). The Maitland-Smith potential is a simple, analytic function with continuous first and second derivatives with respect to inter-nuclear separation and it has at most four adjustable parameters.

The MS potential has also been used to correlate virial coefficients for molecular fluids; to correlate volumetric second virial coefficient, $B$, by Estela-Urbe and Trusler [9]; to correlate $B$ and volumetric third virial coefficient, $C$, by Monago [10]. However for a symmetric linear molecule, calculation of $C$ with the MS potential takes about 14 hours on one temperature with a 2.83 GHz PC; this may be compared with the 8 hours it takes on the same machine for a Lennard-Jones (LJ) (12-6) potential function. Unfortunately, whereas the 12-6 potential correlated $B$ and $\beta$ (acoustic second virial coefficient), it failed to correlate $C$ and $\gamma$ (acoustic third virial coefficient); it also failed to correlate $D$, although it predicted $\delta$ (acoustic fourth virial coefficient) fairly accurately.

At the level of the third virial coefficient if one isothermal calculation of $C$ with anisotropic potential takes some 14 hours, there is little hope of extending this procedure to the fourth order. The purpose of this work is to use the Mie (n-6) potential to construct a fourth order virial equation of state for gaseous argon and to investigate what improvement over the (12-6) functional form is provided by the additional third parameter.

Theory
The Mie n-6 potential contains three parameters: the well-depth parameter, $\varepsilon$, the inter-nuclear separation at the potential minimum, $r_m$, and the repulsive exponent, $n$. In this work, the three parameters were determined by a fit to the speed-of-sound data of Estrada-Alexanders and Trusler [12]. The basic physical equations that relate equilibrium speed of sound, $w$, to other thermodynamic properties may be set out as follows [13]:
\[ V = \frac{ZRT}{P} \quad \ldots (1) \]
\[ Z = 1 + \frac{B}{V} + \frac{C}{V^2} + \frac{D}{V^3} \quad \ldots (2) \]
\[ \frac{1}{\beta T} = -\frac{\gamma}{RT} \left( \frac{\partial P}{\partial V} \right)_T \quad \ldots (3) \]
\[ \frac{1}{\beta T} = 1 + \frac{2B}{V} + \frac{3C}{V^2} + \frac{4D}{V^3} \quad \ldots (4) \]

In Eq. (1) – (8), \( Z \) is the compressibility factor and \( B, C, D \) are volumetric virial coefficients, which are functions only of temperature. Also, \( C_v \) is the isochoric heat capacity of the equivalent perfect gas. The other quantities have their usual meanings.

The volumetric virial coefficients are related to the potentials of interaction by integral expressions; in the language of linear graph

\[ \Delta \phi = C_v^\text{PG} - \left( \frac{P}{V^3} \right) \left( \frac{2T(dB/dT) + T^2(d^2B/dT^2)}{V^2} + \frac{2T(dC/dT)}{V} + \frac{2T(dD/dT)}{V^2} \right) \]

In Eq. (9), an unbroken line represents the two-body Mayer function, a dashed line represents the Boltzmann factor and a shaded triangular plate represents the three-body Mayer function. Explicit expressions for all the graphs have been given elsewhere [13,14].

In Eq. (2), the expansion of compressibility factor in powers of density assumes that the total intermolecular potential energy \( \phi(r^N) \) is the sum of pair and triplet interactions

\[ \phi(r^N) = \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} \phi_{ij} + \sum_{i=1}^{N-1} \sum_{j=i+1}^{N-2} \sum_{k=j+1}^{N} \Delta \phi_{ijk} \quad \ldots (10) \]

Where, \( \phi_{ij} \) is the pair-potential energy and \( \Delta \phi_{ijk} \) is the non-additive three-body potential energy of interaction. Furthermore, in Eq. (9) whereas the graph prescriptions for \( B \) and \( C \) are exact, the prescription for \( D \) is exact only at the level of graphs with no more than three triplet potentials; the graph with four triplet potentials and the non-additive four-body potential have been neglected.

Non-additive three-body forces are modeled by the Axilrod-Teller triple dipole term, Eq. (11)

\[ \Delta \phi(r_123) = \frac{3 \phi_{123}}{8(r_{12}r_{13}r_{23})^3} \left( \frac{2}{3} + \frac{r_{12}^2}{r_{13}^2} + \frac{r_{13}^2}{r_{23}^2} + \frac{r_{23}^2}{r_{12}^2} + \frac{r_{12}^2 + r_{13}^2 + r_{23}^2}{r_{12}^2 r_{13}^2 r_{23}^2} \right) \quad \ldots (11) \]

Eq. (11) adds the fourth parameter to the molecular model namely, \( \phi_{123} \), the three-body strength coefficient.
When researchers in experimental thermodynamics analyse speed-of-sound isotherms of gaseous substances, the preferred methodology is not the procedure outlined above, rather acoustic data along an isotherm are expanded in powers of density as in Eq. (12)

$$\frac{\omega_2}{A_0} = 1 + \beta \rho_n + \gamma \rho_n^2 + \delta \rho_n^3 + \cdots \tag{12}$$

Where, $\rho_n$ is the amount-of-substance density. Acoustic virial coefficients, like their volumetric counterparts, are functions only of temperature. The quantity $A_0$ is defined by Eq. (13)

$$A_0 = \frac{T R y_E}{M} \tag{13}$$

In Eq. (13), $R$ is the molar gas constant, $M$ is the molar mass and $y_E = c_p^E / c_v^E$ ; where, $c_p^E$ is the isobaric heat capacity of the hypothetical perfect-gas.

Volumetric and acoustic virial coefficients are not independent, but are related as set out in Eq. (14) – (16) below [14, 15]:

$$\beta = 2B + 2(y_{p_2} - 1)TB\{1\left[ \frac{TT(y_{p_2} - 1)}{y_{p_2}} \right]^{2B}\{2\right\} \tag{14}$$

$$\gamma = \frac{y_{p_2} - 1}{y_{p_2}} \left[ B + 2(y_{p_2} - 1)TB\{1\left[ (y_{p_2} - 1)T^2B\{2\right] \right] + \frac{2(2y_{p_2} + 1)C + 2(y_{p_2} - 1)TC\{1\left[ (y_{p_2} - 1)T^2C\{2\right]}{2y_{p_2}} \right] \tag{15}$$

$$\delta = \frac{(1/3y_{p_2})(6(y_{p_2} + 1)D + 2(y_{p_2} - 1)(y_{p_2} + 2)TD\{1\left[ (y_{p_2} - 1)T^2D\{2\right]} + \frac{(1/3y_{p_2})(6(y_{p_2} + 1)D + 2(y_{p_2} - 1)(y_{p_2} + 2)TD\{1\left[ (y_{p_2} - 1)T^2D\{2\right]} + (y_{p_2} - 1)T^2D\{2\} \right]}{2y_{p_2}} \right] \tag{16}$$

In Eq. (14) – (16), $X^{(1)}$ represents $dX/dT$ and $X^{(2)}$ represents $d^2X/dT^2$; where, $X$ is one of the volumetric virial coefficients, $B, C$ or $D$.

**Numerical Methods**

The four parameters in the molecular model were determined by solving the non-linear least square problem

$$\chi^2 = \mathbf{r}^T \mathbf{r} \tag{17}$$

as explained in a previous publication [14]. In Eq. (17),

$$R_i(x) = \left( w_{i,cal} - w_{i,expt} \right) / s_i \sqrt{N - N_p} \tag{18}$$

and $x$ is the parameter vector, $w_{i,expt}$ is the $i$-th experimental speed of sound value, $w_{i,cal}$ is the calculated value for the speed of sound at the $i$-th data point, $N$ is the total number of acoustic data points, $N_p$ is the number of adjustable parameters in the model and $s_i$ is the estimated standard deviation of $w_{i,expt}$.

Parameter optimisation using the systems of equations (1)-(8) and (17) was performed as described in previous works [13,14]. The second virial coefficient, $B$, and its two temperature derivatives were calculated as in ref. 14. Numerical integration of $C$ and its temperature derivatives were truncated beyond $r=20 \sigma_m$, the range of integration was divided into 40 equal panels each of which was evaluated by an eleven-point Gaussian quadrature. The graphs in $D$ (including $D_g$) and their temperature derivatives were calculated as in ref. 14, except that each graph was assumed to be zero beyond $r=8 \sigma_m$ and for each integral the range was divided into 16 equal panels each of which was evaluated by an eleven-point Gaussian quadrature.

**The Fit to the Speed of Sound**

The experimental speed-of-sound data on argon performed by Estrada-Alexanders [15] were given on 17 isotherms in the region $0.72 \leq T/T_c \leq 1.47$ and $\rho \leq \rho_c/2$; all the experimental isotherms were used in the parameter fitting. However, on each isotherm acoustic data employed in the fit were limited to those at densities that were no higher than $1.03 \text{ mol dm}^{-3}$ and each datum was assigned an uncertainty of 0.003 percent. The following set of parameters minimized Eq. (17):

$$r_m = 0.357071 \text{ nm}$$

$$\varepsilon / k = 157.440 \text{ K}$$

$$n = 17.6865$$

$$\nu_{123} / k = 0.000677821 \text{ K nm}^9$$

**Potential Parameters**

The potential parameters obtained in this work (Eq. 19) are compared with current best theoretical estimates of these quantities in table 1; also shown in the table are the parameters obtained with the MS and LJ (12-6) potential from ref. 8 and 11.
Table 1: Potential parameters from different molecular models: LJP, LJ potential; (n-6), this work; MSP, MS potential. The references in the table refer to theoretical estimates.

<table>
<thead>
<tr>
<th>potential</th>
<th>percentage error</th>
<th>ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>( r_m )</td>
<td>5</td>
<td>2</td>
</tr>
<tr>
<td>( \sigma/k )</td>
<td>10</td>
<td>-15</td>
</tr>
<tr>
<td>( C_6/k )</td>
<td>27</td>
<td>76</td>
</tr>
<tr>
<td>( \theta_{123}/k )</td>
<td>33</td>
<td>-4</td>
</tr>
</tbody>
</table>

Fig. 1: Second volumetric virial coefficient of argon as a function of temperature: ● experimental data [17]; ———, this work.

Fig. 2: Second acoustic virial coefficient of argon as a function of temperature: ■ Estrada-Alexanders and Trusler [12]; ———, this work.

The Virial Coefficients of Argon

Fig. 1 compares experimental second volumetric virial coefficients of argon of Gilgen et al [17] with the result obtained from this work; in spite of the wide temperature range of the data, the agreement is apparently good. However, with the n-6 potential one can expect deviations of up to 2 cm³/mol in calculate second virial coefficients. Furthermore, there are also clear signs of systematic deviations which seem to suggest that the n-6 potential is only able to provide a superficial fit of the thermodynamic surface. Fig. 2 compares the experimental second acoustic virial coefficient data of Estrada-Alexanders and Trusler [12] with results from this work; the agreement is seemingly good.

Fig. 3: Third volumetric virial coefficient of argon as a function of temperature: ● experimental data [17]; ———, this work.

Fig. 4: Third acoustic virial coefficient of argon as a function of temperature: ▲ experimental data [12]; ———, this work.
No experimental data exist for the fourth volumetric virial coefficients of argon with which to compare with the present theoretical results. However, Monago [8] has calculated the fourth volumetric virial coefficients for argon with the MS potential which are in agreement with those obtained by Wiebke et al [6]; the latter workers used a completely different method and potential models. In fig. 5 fourth volumetric virial coefficients of argon obtained from this work are compared with results of ref. 8. The values predicted by the $n$-6 potential are too low at all temperatures considered in that plot (when compared with the calculated data of ref. 8) and a reasonable tentative conclusion can be made to the effect that the $n$-6 potential is unable to correlate the fourth volumetric virial coefficient of argon.

Fourth acoustic virial coefficients of argon are compared with the experimental data of Estrada-Alexanders [14] in fig. 6 and it would seem that the $n$-6 potential was able to correlate the data. How can one explain the fact that the $n$-6 potential correlated $\delta$ while it apparently failed in the case of $D$? From Eq. (16), $\delta$ depends on $B$, $C$ and $D$ as well as on their first two temperature derivatives; therefore, given the erroneous values of $D$ predicted by the $n$-6 potential, the agreement observed in fig. 6 could only have come about at the expense of $dD/dT$ and $d^2D/dT^2$. A reasonable conclusion, then, is that the agreement in fig. 6 is the result of a fortuitous cancellation of errors in $dD/dT$ and $d^2D/dT^2$ and that the $n$-6 potential failed at the level of the fourth virial coefficient (both volumetric and acoustic).

Comparison with other Experimental Data
It is the aim of applied statistical thermodynamics to generate molecular models that relate macroscopic properties to their underlying causes in intermolecular interactions [18]. Although the virial equation of state, because it is inapplicable at liquid densities, is not suitable for vapour-liquid equilibrium calculations, given experimental vapour pressure data, it can be used to calculate vapour densities at saturation. Fig 7 shows such calculations for the experimental vapour pressure data of argon [19]; it shows that the $n$-6 potential can predict saturated vapour volume with good accuracy at densities greater than 0.6$\rho_c$. Another area of process thermodynamics in which the virial equation has found use is in the field of supercritical fluids extraction. Fig. 10 shows the performance of the current equation of state model when it is used to calculate fluid densities along the critical isotherm (150.69 K). The plot shows that the current equation of state can provide useful volumetric data on argon up to a density of about 0.8$\rho_c$. Of course the present model being analytic cannot be expected to reproduce the actual vapour-liquid critical point itself; for argon, or for any other fluid [20].

