Abstract
This work describes a method for the numerical calculation of second and third virial coefficients of simple linear molecules. The method is applied to nitrogen using a two-centre Lennard-Jones pair-potential and the Axilrod-teller term. Values of volumetric and acoustic second and third virial coefficients of nitrogen are reported from 95 – 500 K and compared with the experimental data of several authors. It is argued that the Lennard-Jones potential failed to correlate third virial coefficients because the model neglected dipole-quadrupole and higher dispersion contributions to the pair potential.

Keywords: Nitrogen; two-centre Lennard-Jones potential; volumetric virial coefficients, acoustic virial coefficients.

Introduction
The virial equation of state (EOS) belongs to the class of fluid theories that are based on cluster expansion of the configuration integral; therefore, it is firmly based on theory. The expansion itself is most elegantly derived within the framework of the grand canonical ensemble, although one may still derive it from the canonical ensemble [1,2]. Its merits are that:
(a) it can predict, as opposed to correlate, all accessible and interesting thermodynamic properties to their experimental uncertainties;
(b) few parameters are required to apply the method to pure fluids and these can usually be given physical meanings;
(c) the resulting intermolecular potential function, a by-product of the method, can find use in other areas of molecular thermodynamics and chemical physics;
(d) there is a clear theoretical guide as to how the method can be extended to mixtures.
Conversely, the virial equation of state, as a theory of the fluid phase, is defective in some respects:
(i) the method is capable of high accuracy only in the gas-phase region of the thermodynamic surface, and although, as a power series, its radius of convergence is uncertain, it is known to be inapplicable at liquid densities and, therefore, not useful for vapour-liquid equilibrium (VLE) calculations. VLE calculation is of considerable importance in process and chemical engineering thermodynamics.
(ii) Rigorous extensions of the virial EOS to non-spherical molecules using anisotropic potential models require the investment of considerable computational resources.
In theory, virial coefficients are experimentally accessible thermodynamic properties; in practice, only the first two non-trivial coefficients can be determined experimentally from isothermal $P$-$V$-$T$ data, using the limiting slope analysis. Volumetric fourth and higher virial coefficients are not accessible by the limiting slope analysis because of deleterious effects of experimental errors.
An alternative to direct experimental determination is to first fit parameters in a model intermolecular potential function to some accurate and precise thermophysical property data, then to use the resulting potential function to calculate virial coefficients. This method has been used to determine the virial coefficients of argon (the prototype for isotropic interactions) up to the fourth order and the resulting fourth acoustic virial coefficients were shown to be in very good agreement with values determined experimentally [3,4]. In addition, the fourth-order virial EOS obtained from the procedure predicted experimental $P$-$V$-$T$ data of argon to better than 0.05 percent at densities up to $\rho_c/2$ or about 12 MPa in pressure [3].
Although theoretically inexact, model isotropic potential functions have been used in the manner outlined above to determine virial coefficients of non-spherical molecules with some success, especially at supercritical temperatures. However, at low reduced temperatures second and third virial coefficients of non-spherical molecules determined by the above method tend to exhibit clear signs of systematic deviations from experimental values [5-8]. These deviations are probably due, in part, to errors in the experimental virial coefficients, but also due to inaccuracies in the molecular models which only became apparent at low temperatures. In the case of the volumetric second virial coefficients of nitrogen, the prototypical for axially symmetric molecules, it was shown that agreement between calculated and experimental values improved markedly when the isotropic potential in the model was...
replaced with an anisotropic pair potential function [5, 6].

Until recently, calculation of virial coefficients for real molecular fluids using anisotropic potential models had been limited to the second order level [7]. However, Lucas and his co-workers used an anisotropic model potential to calculate volumetric third virial coefficients for some linear molecules [9,10]; also, Kusalik et al. have calculated volumetric third virial coefficients of certain water models [11].

A more recent development is the use of Monte Carlo simulation techniques to calculate volumetric virial coefficients of real non-spherical molecules. Benjamin et al. [12] and Shaul et al. [13] have calculated volumetric virial coefficients up to the fifth order. However, the accuracy of calculated volumetric virial coefficients higher than the third cannot be verified because no experimental data on the higher volumetric virials exist; the volumetric fourth virial coefficients calculated in ref. 3 was adjudged accurate by reference to experimental acoustic virial coefficients and the EOS derived from the volumetric virials. There is some evidence to suppose that higher virials calculated by simulation are as yet not sufficiently accurate. For example, second and third virial coefficients calculated by Kim et al. [14] for mixtures of methane and ethane disagreed with experiment by between 5 – 10 and 20 – 30 percent, respectively. Also, the pressures of water calculated by Benjamin et al. [12] using a fifth-order model 

\[ \int \frac{1}{r^2} dr_1 dr_2 \int_1^\infty d(cos \theta_1) \int_1^\infty d(cos \theta_2) \int_0^{2\pi} f_{12} d\phi_1 \]

\[ B = -\frac{N^2}{4} \int_0^\infty r_1^2 dr_1 \int_0^1 d(cos \theta) \int_0^{2\pi} f_{12} d\phi_1 \]

For the volumetric third virial coefficient of a linear, rigid molecule, \( C \), the appropriate expression is

\[ C = -\frac{N^2}{24\pi} \int_0^\infty r_1^2 dr_1 \int_0^\infty r_2^2 dr_2 \int_0^\infty r_3^2 dr_3 \int_1^\infty d(cos \alpha) \int_1^\infty d(cos \beta) \int_0^{2\pi} d\phi_1 \int_0^{2\pi} d\phi_2 \int_0^{2\pi} d\phi_3 \]

\[ f_{123} = f_{12} + f_{13} + f_{23} \]

Eq. (1) and (2) are written in the space-fixed reference frame and the notations here follow those of Lucas [15]. The systems considered in this article are composed of symmetric linear molecules between which there exist additive and non-additive three-body forces. These forces can be specified by a pair potential, \( \phi(r, \omega_1, \omega_2) \), and a triplet potential, \( \Delta \phi(r_{12}) \), functions. The pair potential used in this work is the two-centre Lennard-Jones pair-potential.

\[ \phi(r_{12}, \omega_1, \omega_2) = \frac{1}{2} \sum_{j=1}^2 \sigma_{ij} \left( \frac{\sigma_{ij}}{r_{ij}} \right)^6 - \frac{1}{2} \sum_{j=1}^2 \sigma_{ij} \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{12} \]

In the above scheme, \( \omega_i \) denotes the Eulerian angles of molecule i, \( r_{ij} \) is the distance between site i and site j on two different molecules and \( r_{12} \) is the distance between the molecular centres of 1 and 2; also, \( \sigma \) and \( \epsilon \) are adjustable parameters.

For the systems under consideration, \( r_{12} \) and \( r_{ij} \) are related by [15].
\[ r_{ij}^2 = r_{12}^2 + l_1^2 + l_2^2 - 2r_{12}[(\pm l_1)c_1 - (\pm l_2)c_2] - 2(\pm l_1)(\pm l_2)[c_1c_2 + s_1s_2c_{12}] \] (4)

Where, \( l_i \) is the distance of site \( i \) from the centre of mass of the molecule, \( c_i = \cos \theta_i, s_i = \sin \theta_i \) and \( c_{12} \) denotes \( \cos \phi_{12} (= \cos \theta_2 \cos \theta_1) \). Eq. (3) and (4) are written in the so-called intermolecular reference frame.

For interactions between two molecules, one can choose the directed distance between the molecular centres to lie along the z-axis in the space-fixed reference frame; therefore, Eq. (3) and (4) can be used without modification. For interactions between three molecules, one must relate the angles in the space-fixed reference frame (\( \theta, \phi \)) to the angles in the intermolecular reference frame (\( \theta', \phi' \)). Details of this transformation are given in ref. 12 and 15; ref. 15 in particular gives the pertinent relationships to reduce the range of integration in Eq. (2); the result is (see, for example, Sherwood and Prausnitz [16] and, also, Trusler [17]):

\[ \Delta \Phi(r_{123}) = \frac{3\theta_{123}}{8(r_{12}r_{13}r_{23})^3} \left( \frac{2 + \frac{r_{12}^2 + r_{13}^2}{r_{23}^2} + \frac{r_{12}^2 + r_{23}^2}{r_{13}^2} + \frac{r_{13}^2 + r_{23}^2}{r_{12}^2}}{(r_{12}r_{13}r_{23})^2} \right) \] (5)

The first two temperature derivatives of \( B \) and \( C \) were obtained by ordinary differentiation of Eq. (1) and (6), [2].

**Numerical Methods**

The virial coefficients were calculated according to Eq. (1) and (6), using multi-panel Gaussian quadrature. In the case of \( B \), the semi-infinite integration over \( r_{12} \) was performed as follows: first, the interval \( (0, r_{\text{max}}) \) was divided into three panels jointed at \( r_{12} = 2\sigma \) and \( r_{\text{max}} = 20\sigma \). The first and second panels were further sub-divided into 6 and 12 equal partitions, respectively, and each partition was integrated over by a 5 point Gaussian quadrature. The last panel was integrated over analytically. In the case of \( C \), integration over \( r_{12} \) was performed as for \( B \), except that the interval \( (0, r_{\text{max}}) \) was divided into two panels jointed at \( r_{12} = 2\sigma \). The range in this case was to a maximum distance (\( r_{\text{max}} \)) of 8\( \sigma \). The first panel was sub-divided into 6 equal partitions, while the second was sub-divided into 5 partitions; in both cases each partition was integrated over by a 3 point Gaussian quadrature.

In Eq. (6), the lower limit of integration over \( r_{13} \) depends on \( r_{12} \), whereas the limits over \( r_{23} \) depend on both \( r_{12} \) and \( r_{13} \). Integration over \( r_{13} \) and \( r_{23} \) were performed such that if the limits \( (0, r_{12} - r_{\text{max}}) \) and \( r_{12} - r_{13} \) - \( r_{13} \), for integration over \( r_{13} \) and \( r_{23} \), respectively, lay in the range \( (0, 2\sigma) \), it was divided into \( N_1 \) equal partitions such that \( 2\sigma/N_1 \approx \sigma/3 \). Conversely, when the limits lay in the range \( (2\sigma, r_{\text{max}}) \), it was divided into \( N_2 \) partitions such that \( (r_{\text{max}} - 2\sigma)/N_2 \approx \sigma \). Each partition was then integrated over by a three-point Gaussian quadrature.

For both \( B \) and \( C \), angle integration over \( \cos \theta_i \) was performed with the interval \( (0, \pi) \) divided into two equal partitions and each partition was integrated over by a three-point Gaussian quadrature. The reduction in the range of integration was possible because of the symmetry in \( \cos \theta_i \). Similarly, for integration over \( \phi_i \) and \( \phi_i' \) (where \( \phi_i' = \phi_i - \phi_i' \)), use was made of the symmetry about \( \pi \) and the interval \( (0, \pi) \) was divided into four equal partitions, thereafter, each partition was integrated over with a three-point Gaussian quadrature. The first two temperature derivatives of \( B \) and \( C \) were calculated by quadrature, as the virial coefficients themselves. Second, \( B \), and third, \( C \), acoustic virial coefficients were calculated from \( B \), \( C \), their two temperature derivatives and the heat capacity of nitrogen in the hypothetical perfect-gas state according to standard formulae [6,18]
Potential Parameters
The Lennard-Jones pair potential function has two parameters (σ, ε) and the values for nitrogen were determined in a fit to the experimental second acoustic virial coefficients of Ewing and Trusler [5] and Estela-Uribe and Trusler [6]; no other data were used in the fit. The parameters were determined by solving the nonlinear least-squares problem:

\[ \chi^2 = R^T R \]  

(7)

Where,

\[ R_i(X) = (\beta_{i,\text{cal}} - \beta_{i,\text{expt}})/s_i\sqrt{N - N_p} \]

Here, x is the parameter vector, \( \beta_{i,\text{expt}} \) is the value of the i-th experimental second acoustic virial coefficient, \( \beta_{i,\text{cal}} \) is the corresponding value of the calculated acoustic second virial coefficient, N is the number of acoustic second virial coefficient data, \( N_p \) is the total number of adjustable parameters and \( s_i \) is the estimated standard deviation of \( \beta_{i,\text{expt}} \). The following values minimized Eq. (7): \( \varepsilon/k = 148.527 \) K, \( \sigma = 0.332772 \) nm, Third virial coefficient data were not employed in the parameter optimization because of the excessive amount of computation that would have been required. Instead the value for the three-body strength coefficient of Eq. (5) was set equal to the value obtained in ref. 19; namely, \( \varepsilon_{123}/k = 0.001 \) K nm\(^9\). Also, the distance between the centres of mass was set equal to the N—N bond length in nitrogen (0.109 nm).

Results and Discussion

Fig. 1: Volumetric second virial coefficient of nitrogen as a function of \( T \): ● ref. 20; ———, calculated with a two-centre LJ potential model.

Fig. 1 compares experimental volumetric second virial coefficients of Nowak et al [20] with results from this work and it is clear that a good correlation has been achieved. In Fig. 2, experimental acoustic second virial data of Ewing and Trusler [5] and Estela-Uribe and Trusler are compared with values calculated in this work. This comparison shows that the LJ 12-6 potential can also correlate acoustic second virial coefficient data with good accuracy over a wide temperature range.

Fig. 2: Acoustic second virial coefficient of nitrogen as a function of \( T \): ● ref. 5; ■ ref. 6; ———, calculated with a two-centre LJ potential model.

Experimental and calculated volumetric third virial coefficients are compared in Fig. 4; Fig. 5 is a similar plot for the acoustic third virial coefficients of nitrogen. In both plots we see that there is a clear tendency for the LJ 12 potential to over-predict the third virial coefficients of nitrogen. The question immediately arises as to which model is to be blamed for the apparent failure of the LJ 12-6 function to correlate the third virial coefficients of a linear molecule; the site-site model that incorporates the effects of molecular shape, or the LJ 12-6 potential function, which interrelates microscopic and macroscopic properties?

Fig. 3: Volumetric third virial coefficient of nitrogen as a function of \( T \): ● ref. 20; ———, calculated with a two-centre LJ potential model.

Fig. 4: Acoustic third virial coefficient of nitrogen as a function of \( T \): ● ref. 5; ■ ref. 6; ———, calculated with a two-centre LJ potential model.
Although the LJ 12-6 potential is known to be inaccurate in both the short- and long-range regions of pair interactions, it is most deficient in its representation of long-range dispersion interactions. The dispersion pair-potential, $\varphi_{\text{dis}}$, of an isotropic fluid is given in the long-range by:

$$\varphi_{\text{dis}} = -\frac{C_6}{r_{12}^6} - \frac{C_8}{r_{12}^8} - \frac{C_{10}}{r_{12}^{10}} - \ldots$$

Where, $C_6$, $C_8$, and $C_{10}$ represent, respectively, the dipole-dipole, dipole-quadrupole, and quadrupole-quadrupole dispersion coefficients. The dipole-quadrupole and quadrupole-quadrupole interactions, which are neglected in the LJ 12-6 potential, significantly affect the shape of the well-region of a true pair potential. Ref. [21] compared the values of LJ 12-6 potential parameters for argon determined in a fit to acoustic data against their current best theoretical estimates and found that the well-depth parameter, $\epsilon$, was in error by about 15 percent. This error in turn propagates to some 76 percent error in the estimate of the $C_6$ coefficient. The Maitland-Smith potential is defined by

$$\varphi(r_{12}) = \frac{\epsilon}{n - 6} \left\{ 6 \left( \frac{r_m}{r_{12}} \right)^n - n \left( \frac{r_m}{r_{12}} \right)^6 \right\}$$

with

$$n = m + \tau \left( \frac{r_{12}}{r_m} - 1 \right)$$

Where, $r_m = \sigma \left( \frac{n - 6}{n} \right)$ is the distance at the potential minimum; $m$ and $\tau$ are shape parameters. In the Maitland-Smith potential, by making $n$ a linear function of distance, the shape parameters are able to modify the shape of the well-depth region, which the LJ 12-6 potential completely neglected. Fig. 5 compares experimental volumetric third virial coefficients of nitrogen with values calculated with the site-site model and the Maitland-Smith potential. Fig. 6 is the corresponding plot for the acoustic third virial coefficient. Fig. 5 and 6 suggest that, by being more flexible in the well-depth region, the Maitland-Smith potential became more successful in correlating the third virial coefficients of linear molecules.

**Conclusion**

Parameters in a two-centre pair-potential function determined from acoustic second virial coefficient alone were combined with a three-body strength coefficient determined from isotropic pair and triplet potentials and were used to predict the third volumetric and acoustic virial coefficients of nitrogen. Calculated virial coefficients when compared with experimental data gave mixed results. On the one hand, calculated $B$ and $\beta$ in good agreement with experimental data; on the other hand, the two-centre LJ model failed to predict volumetric and acoustic third virial coefficients of nitrogen quantitatively. It was argued that this failure can be explained by the complete neglect of dipole-quadrupole and higher dispersion interactions by the LJ model.

**References**