

EMPIRICAL VIRIAL EQUATION: USE OF THEORETICAL TEMPERATURE DEPENDENCE

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Expansions in reciprocal temperature, which have recently been shown to be valid theoretically for the virial coefficients of simple fluids, are used for real fluids in tests of the empirical virial equation of state. It is shown that the second and third virial coefficients for a Lennard-Jones 6-12 fluid may be described within 0.01% for $0.85 < T^* < 4.0$ by eight terms in these expansions. Tests of the adequacy of reciprocal temperature expansions for real fluids were made by empirically determining coefficients using volumetric data for methane including densities approaching twice the critical density. It was found that a fifth order expression in density with truncated coefficient expansions could be used to describe methane compressibility factors at 508 points with an average deviation of 0.082%.

It is well known that the density and composition dependence of the virial equation of state may be derived theoretically. However, until quite recently, the temperature dependence of the virial equation was considered to be directly dependent upon the analytical form of the intermolecular potential function used in evaluating the virial coefficients. It, therefore, was not possible to develop an empirical virial equation of state having general and yet theoretically correct dependence on temperature. This restriction has now been removed for the case of fluids for which the intermolecular potential energy is a sum of pair potentials. For such fluids, it has been shown (1) that the virial coefficients can be expressed as expansions in reciprocal temperature, with coefficients which are dependent upon the intermolecular potential. Thus, the virial equation of state can be written in the form

$$P/P^0kT = 1 + \sum_{n=2}^{\infty} \left[\sum_{s=0}^{\infty} A_{ns}/T^s \right] \rho^{n-1} \quad \text{Eq. 1}$$

The sum in brackets is the n^{th} virial coefficient,

$$B_n = \sum_{s=0}^{\infty} A_{ns}/T^s \quad \text{Eq. 2}$$

and the A_{ns} are coefficients which are dependent upon the intermolecular potential but are independent of temperature.

The major purpose of this paper was to test empirically the applicability of truncated

reciprocal temperature expansions of virial coefficients. Initial calculations were made to determine the number of terms required in truncated expansions for accurate representation of the second and third virial coefficients of a hypothetical Lennard-Jones 6-12 fluid. Subsequent calculations were made to determine the coefficients A_{ns} empirically from PVT data for a real fluid, methane. Methane was chosen for this purpose because of the availability of accurate PVT data for wide temperature and density ranges. Also, since the low density behavior of methane is adequately described by use of the Lennard-Jones 6-12 potential, it was possible to use lower order virial coefficients generated by the 6-12 potential, while treating higher order coefficients empirically.

LENNARD-JONES 6-12 FLUID

The objective of considering a simple fluid model was to determine the truncation parameters S_n which will allow accurate representation of the virial coefficients by the relation given in Equation 2, with s ranging from zero to S_n , rather than from zero to infinity.

Determination of these truncation parameters is a simple matter for the case of a hypothetical Lennard-Jones 6-12 fluid because discrete values of the reduced virial coefficients have been tabulated by Hirschfelder, Curtiss and Bird (2) for wide reduced temperature ranges. Thus, appropriate

ate values for S_n can be determined merely by performing regression calculations for various values of S_n to determine the dimensionless coefficients A_{ns} in the equation

$$B_n^* = \sum_{s=0}^{S_n} A_{ns}^* / (T^*)^s \quad \text{Eq. 3}$$

In this relation, $T^* = kT/\epsilon$ is reduced temperature and $B_n^* = B_n/b^{n-1}$ is the reduced n^{th} virial coefficient, where $b = 2/3 \pi \sigma^3$ is the molecular covolume. In the present calculations, ϵ and σ are the parameters in the Lennard-Jones 6-12 potential (2),

$$\phi(R) = 4\epsilon \left[(\sigma/R)^{12} - (\sigma/R)^6 \right] \quad \text{Eq. 4}$$

For the reduced temperature range $0.85 < T^* < 4.0$, it was found that the average deviations of reduced second and third virial coefficients calculated by Equation 3 were less than 0.01% when the expansions were truncated at eight terms. The resultant relations for the reduced second and third virial coefficients are

$$B_2^* = 0.64097 - 1.32146/T^* - 4.43825/(T^*)^2 + 7.10149/(T^*)^3 - 8.83675/(T^*)^4 + 6.57100/(T^*)^5 - 2.74277/(T^*)^6 + 0.48770/(T^*)^7 \quad \text{Eq. 5}$$

$$B_3^* = 0.25819 + 0.56973/T^* - 2.70337/(T^*)^2 + 8.11300/(T^*)^3 - 9.44159/(T^*)^4 + 5.78783/(T^*)^5 - 2.32601/(T^*)^6 + 0.17188/(T^*)^7 \quad \text{Eq. 6}$$

Higher order virial coefficients calculated on the assumption of pairwise additivity of intermolecular potential energy may be expected to deviate widely from real virial coefficients. For this reason, reciprocal temperature expansions of higher order virial coefficients for a hypothetical Lennard-Jones 6-12 fluid were not developed. However, the question of the adequacy of representation of real virial coefficients by such expansions was pursued because of the potential practical value of such a study to the development of empirical equations of state having theoretically correct analytical forms.

REAL FLUIDS

To determine the adequacy of reciprocal

temperature expansions of virial coefficients for representation of the PVT behavior of methane, the following truncated expansion was used,

$$P/\rho kT = 1 + \sum_{n=2}^N \left[\frac{S_n}{\rho} A_{ns}^* / (T^*)^s \right] (\rho b)^{n-1} \quad \text{Eq. 7}$$

Values of the potential parameters ϵ and σ for use in this expression were determined by nonlinear regression utilizing PVT data for methane in the temperature range 131.93°K to 623.16°K and density range 0.0225 g-mole/liter to 3.0 g-mole/liter. The results of this procedure, which have been discussed by Vernick (3), were $\epsilon/k = 147.67^\circ\text{K}$ and $\sigma = 3.8117 \text{ \AA}$. These parameter values yield a good fit of methane second virial coefficients, as shown in Figure 1. An adequate fit of methane third

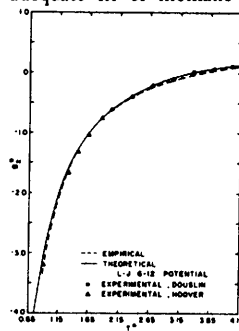


FIGURE 1. Comparison of empirical, theoretical and experimental reduced second virial coefficients for methane.

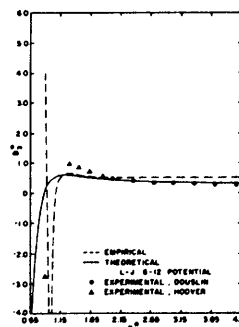


FIGURE 2. Comparison of empirical, theoretical and experimental reduced third virial coefficients for methane.

virial coefficients was obtained for temperatures above $T^* = 2.0$, as shown in Figure 2. Empirical estimates of higher order virial coefficients were then obtained using these theoretical second and third virial coefficients and the above values of ϵ and σ .

Linear regression calculations using higher density methane PVT data to determine estimates of the A_{ns}^* in Equation 7 were made for the levels of density truncation $N = 4, 5$, and 6 using $S_4 = 4, S_5 = 3, S_6 = 2$ in all cases. Methane PVT data from four sources were employed in these calculations (4-7). The temperature and density ranges of the 508 data points utilized were 131.93°K to 623.16°K and 0.0225 g-mole/liter to 18.5 g-mole/liter. Resultant average deviations of the 508 calculated compressibility factors, $Z = P/pkT$, from experimental values were 1.971% , 1.066% and 0.199% for density truncations $N = 4, 5$, and 6 , respectively. The resultant empirical reduced virial coefficients for the density truncation $N = 6$ were

$$b_4^* = -0.4365 + 2.0583/T^* - 1.2923/(T^*)^2 + 5.3791/(T^*)^3, \quad \text{Eq. 8}$$

$$b_5^* = 0.4993 + 0.5720/T^* - 3.9625/(T^*)^2, \quad \text{Eq. 9}$$

$$b_6^* = -0.6278 + 1.5634/T^*. \quad \text{Eq. 10}$$

NONADDITIVITY AND INTERMOLECULAR POTENTIAL EFFECTS

The theoretical second and third virial coefficients used in the above regression calculations to determine empirical estimates of higher order virial coefficients obviously are not exact for methane. Two factors contribute to the inexactness of these lower order virial coefficients. Either coefficient may be inexact because the parameters ϵ and σ or the 6-12 potential itself are inappropriate. In addition, the theoretical

third virial coefficient relation may be inexact because the potential energy of molecular triplets was ignored in its development (8). This is a possible reason for the discrepancies between theoretical and experimental third virial coefficients for methane shown in Figure 2 for $T^* < 2.0$.

Of course, the discrepancies in Figure 2 also may be due to errors in the experimental values. For example, Hoover (5) assigned a maximum probable error of 90% to the reported third virial coefficient at the lowest temperature of his data, 131.93°K . If nonadditivity effects alone contributed to the discrepancies in Figure 2, and if the theoretical second virial coefficients were exact, then a regression calculation treating the third and higher virial coefficients empirically should fit the experimental third virial coefficients more closely. When this calculation was carried out, it was found that only at the lowest temperature of the data does the resultant empirical coefficient curve fit experimental behavior much better than the theoretical third virial coefficient curve. However, the average deviation of the 508 calculated compressibility factors from experimental values was reduced from 0.199% to 0.130% .

EMPIRICAL VIRIAL EQUATION

To remove completely effects of the intermolecular potential, a final regression calculation was carried out to determine a totally empirical virial equation by treating the second and third as well as higher order coefficients empirically. Eight terms were used in the reciprocal temperature expansions for B_2^* and B_3^* , that is $S_2 = 8, S_3 = 8$. The density truncation $N = 6$ was used and the remaining temperature truncations were $S_4 = 4, S_5 = 3, S_6 = 2$, as in previous calculations. Thus, the number of pa-

TABLE 1. Coefficients in empirical virial equation.

s	A_{ns}^*				
	n=2	n=3	n=4	n=5	n=6
1	1.89412	-1.39016	-0.53754	1.76204	-1.02987
2	-21.4930	29.0922	-2.13740	-1.63607	2.18507
3	124.936	-188.499	7.23454	-3.53338	
4	-433.378	663.866	-2.12062		
5	852.944	-1355.11			
6	-959.156	1591.40			
7	569.871	-994.050			
8	-138.252	256.225			

parameters determined empirically was $n \stackrel{6}{\leq} 2$

$S_n = 25$. The resultant empirical virial equation is represented by Equation 7, with values of the parameters given in Table I. The empirical second and third virial coefficients obtained from this calculation are shown in Figures 1 and 2. At low temperatures the empirical second virial coefficients are in better agreement with the experimental values than are the theoretical values based on the Lennard-Jones 6-12 potential. At all temperatures, the empirical virial coefficients are smaller than the theoretical values. On the other hand, the empirical third virial coefficients generally are greater than the theoretical values, which might be expected because of their negative statistical correlation with second virial coefficients. The behavior of the empirical third virial coefficient curve in the low temperature region most likely is due to the uncertainty in the experimental data at the lowest temperature. Use of the empirical virial equation for predictions of volumetric behavior at high densities therefore should be limited to $T^* > 1.2$.

The average deviation of the 508 calculated compressibility factors from experimental values in this final calculation was 0.082%. This average deviation is significantly lower than the 0.199% average deviation obtained when theoretical second and third virial coefficients calculated using the 6-12 potential were employed. It might be possible to obtain even lower deviations by using only the Douslin (4) and Vennix (7) data. Vennix (7) obtained an average deviation of 0.02% with a 25 parameter equation by this approach. In the present cal-

culations, we have used a greater number of data points, including data with uncertainty near 0.082%. It, therefore, can be concluded that although the coefficients of the various powers of density in Equation 7 from this calculation are not true virial coefficients, this empirical virial equation provides an accurate representation of the volumetric behavior of methane with a theoretically correct dependence on temperature as well as density.

DISCUSSION

The calculations presented in this paper show that the theoretical virial equation expressed as an infinite series expansion in both reciprocal temperature and density can be truncated successfully for empirical use. For a hypothetical Lennard-Jones 6-12 fluid, eight terms in the reciprocal temperature expansions of the second and third virial coefficients are sufficient for the temperature range $0.85 < T^* < 4.0$. For a real fluid, methane, simultaneous truncation of the density and temperature series yields an accurate representation of volumetric behavior when expansion coefficients are determined empirically. These calculations indicate that, although the theoretical reciprocal temperature expansions of the virial coefficients were derived for a hypothetical fluid having pairwise additive intermolecular potential energy, this temperature dependence also is appropriate for real fluids, such as methane.

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NOMENCLATURE

A_{ns} = Coefficients in expansions of virial coefficients.

B_n = n^{th} virial coefficient, liter/g-mole.

b = Molecular covolume.

k = Boltzman constant.

P = Pressure, atmospheres.

R = Distance between molecule pairs.

S_n = Truncation parameter.

T = Absolute temperature, °K.

Greek Letters:

ϵ = Minimum intermolecular potential energy.

ρ = Molecule number density, molecules/liter.

$\phi(R)$ = Intermolecular pair potential.

σ = Intermolecular separation for which ϕ

$\phi = 0$.

Superscript:

* = Dimensionless coefficient.

Subscript:

n = n^{th} virial coefficient.

s = s^{th} power of reciprocal temperature.

REFERENCES

1. G. A. MANSOORI, Expansion of Virial Coefficients with Respect to Temperature, Ph.D. General Examination problem, University of Oklahoma, 1967.
2. J. O. HIRSCHFELDER, C. F. CURTISS, and R. B. BIRD, Molecular Theory of Gases and Liquids, John Wiley & Sons, New York, 1964.
3. B. H. VERNICK, M.S. Thesis, The University of Oklahoma, 1968.
4. D. R. DOUSLIN, Progress in International Research on Thermodynamic and Transport Properties, Academic Press, New York, 1962.
5. A. E. HOOVER, Ph.D. Dissertation, Rice University, 1965.
6. B. H. SAGE and W. N. LACEY, Thermodynamic Properties of Hydrocarbons, American Petroleum Institute, New York, 1950.
7. A. J. VENNIX, Ph.D. Dissertation, Rice University, 1966.
8. A. E. SHERWOOD, A. G. DeROCCO, and E. A. MASON, J. Chem. Phys. 44: 2984 (1966).