

On the virial coefficients of the equation of state of a system of non-axial molecules

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Abstract. A thermodynamic perturbation theory in which all angle-dependent interactions are considered as a perturbation of the central potential is applied to calculate the second and third virial coefficients of a fluid composed of non-axial molecules. The influence of a large number of anisotropic pair- and three-body non-additive interactions has been considered. Experimental values have been used for the dipole moment, quadrupole tensor and for anisotropic polarizability. The parameters for the central Lennard-Jones (12-6) potential have been determined from the viscosity data. The relative contribution of each branch of pair and triplet interactions has been evaluated as a function of temperature for molecules possessing both the axial- and non-axial symmetries. It has been shown that the non-axial approximation is an improvement over the axial one. Theoretical results have been compared with the experimental data of CH_3OH .

Keywords. Second and third virial coefficients; electric multipole moments; induction, dispersion and repulsive interactions; Pade approximant.

1. Introduction

In earlier studies, Singh and Singh (1976, 1977a) hereafter the two papers in combination are referred to as I, have devised a perturbation scheme to study the effects of anisotropic pair- and three-body non-additive interactions on the virial coefficients of the equation of state of a gas composed of rigid molecules of arbitrary symmetry. In this method the angle-dependant part of the pair- and all branches of three-body non-additive interactions were treated as a perturbation of pair central potential which characterizes the reference potential. Using the set of central force parameters as determined from the gaseous viscosity data the theory of I was applied to calculate the second and third virial coefficients for a gas of (i) one-component axially symmetric nonpolar molecules (Singh and Singh 1976, 1977 b) and their binary mixtures (Singh and Shukla 1978), (ii) one-component polar molecules of axial symmetry (Singh and Singh 1977a; Singh 1977a, b, 1980), and (iii) binary mixtures of polar-quadrupolar molecules having axial symmetry (Singh 1979a, b).

The present work is an application of the theory of I to asymmetric top polar molecular fluids. Three different empirical approaches have so far been used in statistical mechanics to study the molecular properties of polar fluids. The one often quoted is the Stockmayer 12-6-3 potential augmented by dipole-dipole interaction. Another approach used occasionally in the treatment of transport properties is that of Mon-chick and Mason (1961) (unaveraged potential model) in which the relative orientation of the molecules is taken to be fixed during a collision. Yet another

more successful and computationally easy approach is that of Singh and Singh (1971, 1972), the 'preaveraged potential model' in which the angle-dependant parts of the interaction are represented by an averaged potential. Using the latter two approaches we report here the calculation of second and third virial coefficients of a gas of polar molecules having non-axial symmetry. The results are then compared with the values obtained by using axial approximation and with the experimental values. The details of the theory and procedure adopted in the calculation are available in I. For those readers not familiar with this work we give here a brief account of it.

2. Second and third virial coefficients

The pair- and three-body interactions which are required for the calculation of second and third virial coefficients can be written as

$$u(1, 2) = \phi_{12}(r_{12}) + V_{12}^{\text{perm}}(r_{12}, \omega_1, \omega_2) + V_{12}^{\text{in}}(r_{12}, \omega_1, \omega_2) \\ + V_{12}^{\text{dis}}(r_{12}, \omega_1, \omega_2) + V_{12}^{\text{sh}}(r_{12}, \omega_1, \omega_2), \quad (1)$$

$$u(1, 2, 3) = \sum_{j>i=1}^3 u(i, j) + V_{123}^{\text{in}} + V_{123}^{\text{dis}} + V_{123}^{\text{rep}}, \quad (2)$$

where ω_i represents the Euler angles ($=\theta_i \phi_i \psi_i$ for non-axial, and $=\theta_i \phi_i$ for axial molecules) which specify the orientation of molecule i . ϕ_{12} is the central pair potential which is represented by the Lennard-Jones (12-6) model. V_{12}^{perm} is the interaction between the permanent multipole moments of the molecules, V_{12}^{in} the interaction of induced multipole moments in one molecule with the permanent moments in the other molecules, V_{12}^{dis} the interaction between anisotropic dispersion forces of the molecules, and V_{12}^{sh} the angle-dependent overlap interaction. V_{123}^{in} , V_{123}^{dis} and V_{123}^{rep} are, respectively, three-body nonadditive interactions arising from the classical electric induction, dispersion and short range three-body exchange forces. The functional form and other details of these interactions are given in I and elsewhere (Stogryn 1969, 1970). However, it is pertinent to mention here that very little is known about V_{12}^{sh} and V_{123}^{rep} . The only expression available for V_{12}^{sh} is due to Pople (1954) derived for molecules of axial symmetry. Consequently this term has not been considered here in the treatment of non-axial fluids. For V_{ijk}^{rep} Sherwood *et al* (1966) have derived an expression for molecules having spherical symmetry from an electrostatic distortion model. The contribution of this term, however, is included in the study of third virial coefficient.

For a pure gas the pressure second and third virial coefficients, as defined by

$$p = \rho kT [1 + B(T)\rho + C(T)\rho^2 + \dots],$$

$$\text{are given by } B(T) = -2\pi N \int \int \int \omega_1 \int \omega_2 \{ \exp[-\beta u(1, 2)] - 1 \} r_{12}^2 dr_{12} d\omega_1 d\omega_2 \quad (3)$$

$$\text{and } C(T) = -2 N^2 b_3(T) + 4 B^2(T), \quad (4)$$

where $b_3(T)$ represents a reducible cluster integral involving a three vertex:

$$\begin{aligned}
 b_3(T) = & \frac{4}{3} \pi^2 \iiint \omega_1 \int \omega_2 \int \omega_3 \{ \exp [-\beta u(1, 2, 3)] \\
 & - \exp [-\beta u(1, 2)] - \exp [-\beta u(1, 3)] - \exp [-\beta u(2, 3)] \\
 & + 2 \} r_{12} r_{13} r_{23} dr_{12} dr_{13} dr_{23} d\omega_1 d\omega_2 d\omega_3, \quad (5)
 \end{aligned}$$

$$\beta = 1/kT.$$

The contributions of different branches of the interaction to virial coefficients have been evaluated by adopting a perturbation method in which tensor forces are taken as perturbation of the pair central potential. For the second virial coefficient the perturbation series can be written as

$$\begin{aligned}
 B^*(T^*) = & B_0^*(T^*) + B^*(\text{perm}) + B^*(\text{in}) + B^*(\text{dis}) \\
 & + B^*(\text{perm} \times \text{in}) + B^*(\text{perm} \times \text{dis}) + B^*(\text{in} \times \text{dis}), \quad (6)
 \end{aligned}$$

where $B_0^*(T^*) = t^{-2} [H_{12}(t) - \frac{1}{2} H_6(t)]$ (6.1)

$$\begin{aligned}
 B^*(\text{perm}) = & -\frac{1}{192} \left(\frac{\bar{\mu} \cdot \bar{\mu}}{\epsilon \sigma^3} \right)^2 H_6(t) - \frac{1}{96} \left(\frac{\bar{\mu} \cdot \bar{\mu}}{\epsilon \sigma^3} \right) \left(\frac{\Theta : \Theta}{\epsilon \sigma^5} \right) H_8(t) \\
 & - \frac{7}{720} \left(\frac{\Theta : \Theta}{\epsilon \sigma^5} \right)^2 H_{10}(t) + \frac{1}{320} t^2 \left(\frac{\bar{\mu} \cdot \Theta \cdot \bar{\mu}}{\epsilon^{3/2} \sigma^{11/2}} \right) H_{11}(t) \\
 & + \frac{1}{280} t^2 \left(\frac{(\bar{\mu} \cdot \Theta \cdot \bar{\mu})(\Theta : \Theta \cdot \Theta)}{\epsilon^3 \sigma^{13}} \right) H_{13}(t) \\
 & + \frac{1}{490} t^2 \left(\frac{\Theta : \Theta \cdot \Theta}{\epsilon^3 \sigma^{15}} \right) H_{15}(t) + \dots \quad (6.2)
 \end{aligned}$$

$$B^*(\text{in}) = -\frac{1}{8} \alpha^* T^{-2} \left[\left(\frac{\bar{\mu} \cdot \bar{\mu}}{\epsilon \sigma^3} \right) H_6(t) + \left(\frac{\Theta : \Theta}{\epsilon \sigma^5} \right) H_8(t) \right] \quad (6.3)$$

$$\begin{aligned}
 B^*(\text{dis}) = & -\frac{1}{7200} \frac{1}{\alpha^4} [19 (\hat{\alpha} : \hat{\alpha})^2 \\
 & - 54 \bar{\alpha}^2 (\hat{\alpha} : \hat{\alpha}) - 9 \bar{\alpha}^4 H_{12}(t) + \dots] \quad (6.4)
 \end{aligned}$$

$$\begin{aligned}
 B^*(\text{perm} \times \text{in}) = & \frac{1}{40} \left(\frac{(\hat{\alpha} : \Theta)(\bar{\mu} \cdot \Theta \cdot \bar{\mu})}{\epsilon^2 \sigma^{11}} \right) H_{11}(t) \\
 & + \frac{1}{70} \left(\frac{(\hat{\alpha} : \Theta)(\Theta : \Theta \cdot \Theta)}{\epsilon^2 \sigma^{13}} \right) H_{13}(t) + \dots \quad (6.5)
 \end{aligned}$$

$$B^* (\text{perm} \times \text{dis}) = \frac{1}{100} \frac{(\hat{\alpha} : \Theta)^2}{\bar{\alpha}^2 \epsilon \sigma^5} H_{11}(t) + \dots \quad (6.6)$$

$$B^* (\text{in} \times \text{dis}) = \frac{1}{2400} \left(\frac{1}{\bar{\alpha}^2 \epsilon \sigma^6} \right) [3 \bar{\alpha} (\bar{\alpha}^2 + 3 \hat{\alpha} : \hat{\alpha}) (\mu \cdot \mu) \\ + (27 \bar{\alpha}^2 - 19 \hat{\alpha} : \hat{\alpha}) (\bar{\mu} \cdot \Theta \cdot \bar{\mu})] H_{12}(t) + \dots \quad (6.7)$$

The function $H_n(t)$, which is defined as

$$H_n(t) = 12 t^4 \sigma^{n-3} \int_0^\infty r^{-n} \exp(-\phi_{12}/kT) r^2 dr$$

is tabulated by Buckingham and Pople (1955) for several values of n and t ($= 2(\epsilon/kT)^{1/2}$). Other symbols have their usual meaning.

In addition to terms given in (6), the following terms appear in the expansion for a fluid of axially symmetric molecules:

$$B^* (\text{sh}) + B^* (\text{perm} \times \text{sh}) + B^* (\text{dis} \times \text{sh})$$

where $B^* (\text{sh}) = -\frac{1}{5} D^2 H_{24}(t)$ (6.8)

$$B^* (\text{perm} \times \text{sh}) = \frac{1}{240} \left(\frac{\bar{\mu} \cdot \bar{\mu}}{\epsilon \sigma^3} \right) D t^2 \left[\left(\frac{\bar{\mu} \cdot \bar{\mu}}{\epsilon \sigma^3} \right) H_{18}(t) \right. \\ \left. - 16.875 D H_{27}(t) + \dots \right] \\ + \frac{2}{3} \left(\frac{\Theta : \Theta}{\epsilon \sigma^5} \right) t^2 D \left[\frac{3}{50} D H_{29}(t) + \frac{1}{84} \left(\frac{\Theta : \Theta}{\epsilon \sigma^5} \right) H_{22}(t) + \dots \right] \quad (6.9)$$

$$B^* (\text{dis} \times \text{sh}) = \frac{1}{5} K D H_{18}(t) + \dots \quad (6.10)$$

In terms of the quantities as defined by

$$\bar{\mu} \cdot \bar{\mu} = \mu^2,$$

$$\Theta : \Theta = \Theta_{xx}^2 + \Theta_{yy}^2 + \Theta_{zz}^2,$$

$$\bar{\mu} \cdot \Theta \cdot \bar{\mu} = \mu^2 \Theta_{zz},$$

$$\Theta : \Theta \cdot \Theta = \Theta_{xx}^3 + \Theta_{yy}^3 + \Theta_{zz}^3,$$

$$\hat{\alpha} : \Theta = \Theta_{xx} \alpha_{xx} + \Theta_{yy} \alpha_{yy} + \Theta_{zz} \alpha_{zz},$$

$$\hat{\alpha} : \hat{\alpha} = \alpha_{xx}^2 + \alpha_{yy}^2 + \alpha_{zz}^2,$$

$$\bar{\alpha} = \frac{1}{3} (\alpha_{xx} + \alpha_{yy} + \alpha_{zz}),$$

for non-axial molecules and

$$\bar{\mu} \cdot \bar{\mu} = \mu^2,$$

$$\Theta : \Theta = \frac{3}{2} \Theta_{zz}^2,$$

$$\bar{\mu} \cdot \Theta \cdot \bar{\mu} = \mu^2 \Theta_{zz},$$

$$\Theta : \Theta \cdot \Theta = \frac{3}{4} \Theta_{zz}^3,$$

$$\hat{\alpha} \Theta = 3 \bar{\alpha} K \Theta_{zz},$$

$$\hat{\alpha} : \hat{\alpha} = 3 \bar{\alpha}^2 (1 + 2K^2),$$

for axial molecular symmetry, numerical evaluation is done for CH_3OH . In the calculation the values of quadrupole moment and anisotropic polarizability components available from the independent measurements have been used. The values of central force parameters ϵ and σ (and D for axial symmetry) are determined from the gas viscosity data in conjunction with the second virial coefficient data. This is an iterative procedure which converges quickly. Table 1 reports these parameters as obtained from the Monchick and Mason (1961) method (unaveraged potential) and preaveraged model (for axial symmetry only) together with other parameters, used in the calculation. From the calculation we find that all branches of pair interaction contribute significantly at all the temperatures investigated here. The calculated values are compared with the experimental values in table 2. The agreement

Table 1. Potential parameters for methanol used in the virial coefficients calculation.

$\mu \times 10^{-18}$ (esu cm)	$\theta_{xx}, \theta_{yy}, \theta_{zz}$ 10^{26}	$\bar{\alpha} (A^3)$	K^+	Potential model	$\sigma (A^3)$	$\epsilon/k(k)$	D
1.70	0.45	3.23	0.1186	Preaveraged axial	4.209	130	-0.20
	0.62						
	-1.07			Unaveraged axial	3.690	417	-0.23
				non-axial	3.965	340	

*Here $K = (\alpha_{||} - \alpha_{\perp})/3 \bar{\alpha}$ for axial molecules and $K^2 = (\alpha_{xx}^2 + \alpha_{yy}^2 + \alpha_{zz}^2 - 3 \bar{\alpha}^2)/6 \bar{\alpha}^3$ for non-axial molecules.

Table 2. Comparison of calculated and experimental second virial coefficient.

T(K)	-B(T) (cm ³ /mole)			
	Exptl	Calc.		
		Preaveraged	Unaveraged non-axial	axial
423	320	310	290	250
448	258	251	245	230
473	219	213	212	198
498	181	183	182	184
523	156	159	164	170
573	113	116	120	139

Experimental data: Kell and McLauring (1969).

between theory and experiment is very satisfactory over the entire temperature range for the preaveraged potential model. Further, the non-axial approximation yields values which are more close to the experiment as compared to the values obtained using the axial approximation.

For the third virial coefficient the perturbation series can be written as

$$\begin{aligned}
 C^*(T^*) &= C^{*(0)}(T^*) + C^{*(1,a)}(T^*) + C^{*(2,a)}(T^*) + \\
 &C^{*(3,a)}(T^*) + \dots + C^{*(1,\text{non})}(T^*) + C^{*(2,\text{non})}(T^*) \\
 &+ \dots + \sum_{p=4} C^{*(\text{perm},a)}(T^*). \quad (7)
 \end{aligned}$$

In this equation the number in superscript indicates the order of perturbation and letters 'a' and 'non', respectively, the contribution arising from pair and three-body nonadditive interactions.

$$C^{*(0)}(T^*) = T^{*-1/2} \sum_{p=0}^{\infty} C_p(0) T^{*-p/2}, \quad (8)$$

$$C^{*(1,a)}(T^*) = C^{*(1,a)}(\text{in}), \quad (9)$$

$$\begin{aligned}
 C^{*(2,a)}(T^*) &= C^{*(2,a)}(\text{dip}) + C^{*(2,a)}(\text{dip-quad}) + C^{*(2,a)}(\text{quad}) \\
 &+ C^{*(2,a)}(\text{dis}) + C^{*(2,a)}(\text{dip} \times \text{in}) + C^{*(2,a)}(\text{quad} \times \text{in}) \\
 &+ C^{*(2,a)}(\text{quad} \times \text{dis}) + C^{*(2,a)}(\text{in} \times \text{dis}) + C^{*(2,a)}(\text{dis} \times \text{dis}) \quad (10)
 \end{aligned}$$

$$\begin{aligned}
 C^{*(3,a)}(T^*) &= C^{*(3,a)}(\text{dip} \times \text{quad}) + C^{*(3,a)}(\text{quad}) \\
 &+ C^{*(3,a)}(\text{dip, dip} \times \text{quad}) + C^{*(3,a)}(\text{quad} \times \text{quad}) \quad (11)
 \end{aligned}$$

$$C^{*(1, \text{non})}(T^*) = C^{*(1, \text{non})}(\text{dis}) + C^{*(1, \text{non})}(\text{rep}) \quad (12)$$

and

$$\begin{aligned} C^{*(2, \text{non})}(T^*) &= C^{*(2, \text{non})}(\text{dis} \times \text{in}) + C^{*(2, \text{non})}(\text{quad} \times \text{in}) \\ &+ C^{*(2, \text{non})}(\text{dis} \times \text{in}) + C^{*(2, \text{non})}(\text{dis}) + C^{*(2, \text{non})}(\text{quad} \times \text{dis}) \\ &+ C^{*(2, \text{non})}(\text{dis} \times \text{dis}) \end{aligned} \quad (13)$$

where

$$\begin{aligned} C^{*(1, a)}(\text{in}) &= 6 \alpha^* \left[\left(\frac{\bar{\mu} \cdot \bar{\mu}}{\epsilon \sigma^3} \right) T^{*-1} \sum_{p=0}^{\infty} C_p(6) T^{*-p/2} \right. \\ &\left. + \left(\frac{\Theta : \Theta}{\epsilon \sigma^5} \right) T^{*-5/6} \sum_{p=0}^{\infty} C_p(8) T^{*-p/2} \right] \end{aligned} \quad (9.1)$$

$$C^{*(2, a)}(\text{dip}) = \left(\frac{\bar{\mu} \cdot \bar{\mu}}{\epsilon \sigma^3} \right) T^{*-2} \sum_{p=0}^{\infty} C_p(6) T^{*-p/2} \quad (10.1)$$

$$C^{*(2, a)}(\text{dip-quad}) = 2 \left(\frac{\bar{\mu} \cdot \bar{\mu}}{\epsilon \sigma^3} \right) \left(\frac{\Theta : \Theta}{\epsilon \sigma^5} \right) T^{*-11/6} \sum_{p=0}^{\infty} C_p(8) T^{*-p/2} \quad (10.2)$$

$$C^{*(2, a)}(\text{quad}) = \frac{28}{15} \left(\frac{\Theta : \Theta}{\epsilon \sigma^5} \right) T^{*-5/3} \sum_{p=0}^{\infty} C_p(10) T^{*-p/2} \quad (10.3)$$

$$C^{*(2, a)}(\text{dis}) = \frac{24}{5} K^2 (2 + 3.8K^2) T^{*-3/2} \sum_{p=0}^{\infty} C_p(12) T^{*-p/2} \quad (10.4)$$

$$C^{*(2, a)}(\text{dip} \times \text{in}) = -\frac{24 (\hat{\alpha} : \Theta) (\bar{\mu} \cdot \Theta \cdot \bar{\mu})}{5 \epsilon^2 \sigma^{11}} T^{*-19/12} \sum_{p=0}^{\infty} C_p(11) T^{*-p/2} \quad (10.5)$$

$$\begin{aligned} C^{*(2, a)}(\text{quad} \times \text{in}) &= -\frac{96 (\hat{\alpha} : \Theta) (\Theta : \Theta \cdot \Theta)}{35 \epsilon^2 \sigma^{13}} T^{*-17/12} \\ &\times \sum_{p=0}^{\infty} C_p(13) T^{*-p/2} \end{aligned} \quad (10.6)$$

$$C^{*(2,a)}(\text{quad} \times \text{dis}) = -\frac{48}{25} \frac{(\hat{\alpha} : \Theta)^2}{\bar{\alpha}^2 \epsilon \sigma^5} T^{*-19/12} \sum_{p=0}^{\infty} C_p(11) T^{*-p/2} \quad (10.7)$$

$$C^{*(2,a)}(\text{in} \times \text{dis}) = \frac{24}{5} \frac{\alpha^* \bar{\mu} \cdot \bar{\mu}}{\epsilon \sigma^3} K^2 T^{*-3/2} \left[\sum_{p=0}^{\infty} (C_p(12) + \bar{C}_p(12)) T^{*-p/2} \right] \quad (10.8)$$

$$C^{*(2,a)}(\text{dis} \times \text{dis}) = \frac{48}{5} K^2 T^{*-3/2} \sum_{p=0}^{\infty} \bar{C}_p(12) T^{*-p/2} \quad (10.9)$$

$$C^{*(3,a)}(\text{dip} \times \text{quad}) = -\frac{12}{5} \frac{\bar{\mu} \cdot \Theta \cdot \bar{\mu}}{\epsilon^{3/2} \sigma^{11/2}} T^{*-31/12} \sum_{p=0}^{\infty} C_p(11) T^{*-p/2} \\ - \frac{96}{35} \frac{(\bar{\mu} \cdot \Theta \cdot \bar{\mu})(\Theta : \Theta \cdot \Theta)}{\epsilon^3 \sigma^{13}} T^{*-29/12} \sum_{p=0}^{\infty} C_p(13) T^{*-p/2} \quad (11.1)$$

$$C^{*(3,a)}(\text{quad}) = -\frac{384}{245} \frac{(\Theta : \Theta \cdot \Theta)^2}{\epsilon^3 \sigma^{15}} T^{*-9/4} \sum_{p=0}^{\infty} C_p(15) T^{*-p/2} \quad (11.2)$$

$$C^{*(3,a)}(\text{dip}, \text{dip} \times \text{quad}) = -\frac{1}{9} \left(\frac{\bar{\mu} \cdot \bar{\mu}}{\epsilon \sigma^3} \right) T^{*-11/4} \sum_{p=0}^{\infty} \bar{C}_p(9) T^{*-p/2} \\ - \frac{1}{15} \left(\frac{\bar{\mu} \cdot \bar{\mu}}{\epsilon \sigma^3} \right)^3 \left(\frac{\Theta : \Theta}{\epsilon \sigma^5} \right) T^{*-31/12} \sum_{p=0}^{\infty} \bar{C}_p(11) T^{*-p/2} \\ - \frac{1}{15} \left(\frac{\bar{\mu} \cdot \bar{\mu}}{\epsilon \sigma^3} \right) \left(\frac{\Theta : \Theta}{\epsilon \sigma^5} \right)^2 T^{*-29/12} \sum_{p=0}^{\infty} \bar{C}_p(13) T^{*-p/2} \quad (11.3)$$

$$C^{*(3,a)}(\text{quad} \times \text{quad}) = -\frac{1}{225} \left(\frac{\Theta : \Theta}{\epsilon \sigma^5} \right)^3 T^{*-9/4} \sum_{p=0}^{\infty} \bar{C}_p(15) T^{*-p/2} \quad (11.4)$$

$$C^{*(\text{perm}, a)}(T^*) = C^{*(2,a)}(\text{perm}) \left(1 - \left| \frac{C^{*(2,a)}(\text{perm})}{C^{*(3,a)}(\text{perm})} \right| \right)^{-1} \quad (11.5)$$

$$C^*(1, \text{non}) (\text{dis}) = \alpha^* T^{*-3/4} \sum_{p=0}^{\infty} C_p^{\text{non}}(0) T^{*-p/2} \quad (12.1)$$

$$C^*(1, \text{non}) (\text{rep}) = \frac{6}{T^*} \int_0^{\infty} \int_{1/2}^1 \int_{1-y}^y \exp \left(- \sum_{i,j=1}^3 u_0^*(i, j)/T^* \right)$$

$$(xy)^{-6} R^{*-16} [y^{-6} \cos 2\theta_x + x^{-6} \cos 2\theta_y + (xy)^{-6} \cos 2\theta] dx dy dR^* \quad (12.2)$$

$$C^*(2, \text{non}) (\text{dip} \times \text{in}) = - \alpha^* \left(\frac{\bar{\mu} \cdot \bar{\mu}}{\epsilon \sigma^3} \right) T^{*-7/4} \sum_{p=0}^{\infty} \bar{C}_p(9) T^{*-p/2}$$

$$- \frac{2}{5} \alpha^* \left(\frac{\bar{\mu} \cdot \bar{\mu}}{\epsilon \sigma^3} \right) \left(\frac{\Theta : \Theta}{\epsilon \sigma^5} \right) T^{*-19/12} \sum_{p=0}^{\infty} \bar{C}_p(11) T^{*-p/2} \quad (13.1)$$

$$C^*(2, \text{non}) (\text{quad} \times \text{in}) = - \frac{1}{5} \alpha^* \left(\frac{\Theta : \Theta}{\epsilon \sigma^5} \right) T^{*-17/12} \sum_{p=0}^{\infty} \bar{C}_p(13) T^{*-p/2} \quad (13.2)$$

$$C^*(2, \text{non}) (\text{dis} \times \text{in}) = \frac{2}{25} \frac{(\hat{\alpha} : \Theta)^2}{\alpha \epsilon \sigma^8} T^{*-4/3} \sum_{p=0}^{\infty} \bar{C}_p(14) T^{*-p/2} \quad (13.3)$$

$$C^*(2, \text{non}) (\text{dis}) = \frac{9}{2} \alpha^{*2} T^{*-1} \sum_{p=0}^{\infty} C'_p(18) T^{*-p/2} \quad (13.4)$$

$$C^*(2, \text{non}) (\text{quad} \times \text{dis}) = \frac{36}{25} \frac{(\hat{\alpha} : \Theta)^2}{\alpha \epsilon \sigma^8} T^{*-4/12} \sum_{p=0}^{\infty} C'_p(14) T^{*-p/2} \quad (13.5)$$

$$C^*(2, \text{non}) (\text{dis} \times \text{dis}) = - \frac{36}{25} \alpha^* K^2 (10 + 19K^2) T^{*-5/4} \sum_{p=0}^{\infty} C'_p(15) T^{*-p/2}$$

$$+ \frac{144}{25} \alpha^* K^2 (10 - K^2) T^{*-5/4} \sum_{p=0}^{\infty} \bar{C}'_p(15) T^{*-p/2} \quad (13.6)$$

The expansion coefficients $C_p(u)$, $\bar{C}_p(u)$, $C'_p(u)$ and $\bar{C}'_p(u)$ which appear in the above equations are triplet integrals over positions and orientations of three particles form-

ing a triangle. These functions are tabulated by Stogryn (1969, 1970) for many values of p and u .

For the potential parameters as given in table 1 we evaluate the additive and non-additive contributions to the third virial coefficient for methanol at several temperatures. It is found that at low temperatures the contribution of all branches of pair and triplet interactions are substantial. The contribution of first-order additive induction interaction, $C^{(1, a)}$ (in), and second order nonadditive dispersion interaction, $C^{(2, \text{non})}$ (dis) are small at high temperatures. The induction and dispersion non-additive contributions are always positive whereas that of nonadditive repulsive interaction is always negative. This simply demonstrates that three-body induction and dispersion nonadditive energy is repulsive for most of the orientations while that of repulsive three-body interaction is attractive for most orientations. The overall effect of the nonadditive contribution to the third virial coefficient is that it shifts the maximum in the additive contribution to a lower temperature and increases the value of maximum. It has, further, been found that a proper convergence of the perturbation series for all branches of pair and triplet potential except the multiple-interaction branch of the pair potential is achieved, through the second order term. For the quadrupole-quadrupole pair interaction the proper convergence is achieved through the third order perturbation term. The higher order terms in the additive contribution arising from the dipole-dipole and dipole-quadrupole interactions have been evaluated by using simple [1,0] Pade approximant.

Figure 1 compares the calculated and experimental third virial coefficient of CH_3OH . The experimental data which are given in the figure by dotted lines are due to Bottomley and Spurling (1967). It can be seen from the figure that the agreement between theory and experiment is not satisfactory for any method. However, the preaveraged values are more close to the experiment as compared to unaveraged (axial as well as nonaxial) values. It can also be seen that the molecular non-axial approximation is an improvement over the axial approximation. Unfortunately, the experimental data available for the third virial coefficient in the literature are very scanty and at the same time most inaccurate. The experimental values are derived from gas compressibility measurements by fitting an isotherm with a polynomial in density, the values

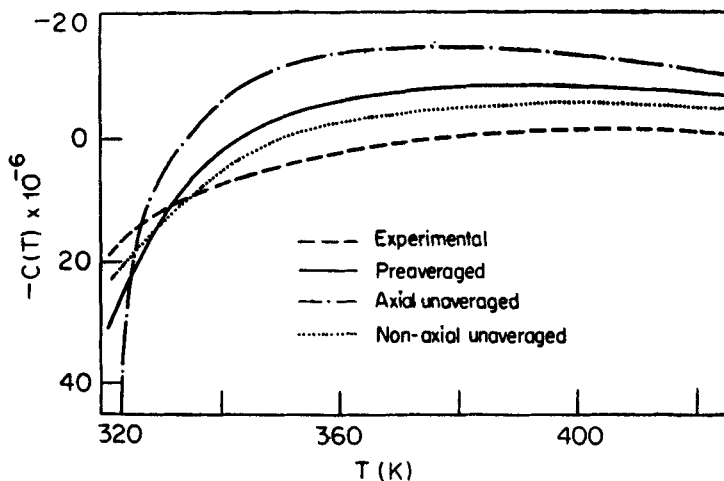


Figure 1. Comparison of the calculated and experimental third virial coefficients.

are subject to uncertainties in the isotherm and the degree of polynomial used, in addition to the experimental inaccuracies. Due to these reasons the agreement found here can be taken as satisfactory. The calculation reported here provides a check on the suitability of the above approaches for treating polar fluids. More significantly the calculation demonstrates explicitly the effects of the various branches of non-spherical interactions on the second and third virial coefficients of methanol. The importance of molecular non-axiality has been shown and found to be significant.

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