Calculation of the second virial coefficient of nonspherical molecules: Revisited

Hossein Eslami a,*, Farkhondeh Mozaffarib, Ali Boushehri b

a Department of Chemistry, College of Sciences, Persian Gulf University, Boushehr 75168, Iran
b Department of Chemistry, College of Sciences, Shiraz University, Shiraz 71454, Iran

(Received 9 September 2000, accepted 12 January 2001)

Abstract — An accurate Hartree–Fock dispersion individually damped (HFD-ID) potential type improved by Boyes for argon has been used as a core potential to calculate both the spherical and nonspherical contributions to the second virial coefficient of simple molecules. The auxiliary functions that occur in the perturbation terms for calculating the nonspherical contributions, have been calculated numerically and are tabulated over a wide range of temperatures from \( T^* = 0.5 \) to \( T^* = 10 \), where \( T^* = kT/\varepsilon \) and \( \varepsilon \) is the potential well-depth. By fitting the well-depth and the position of the minimum in the core potential, we have calculated the second virial coefficient of \( \text{N}_2 \), \( \text{O}_2 \), \( \text{CO} \), \( \text{NO} \), and \( \text{CO}_2 \) over the whole temperature range reported in the literature. The calculated results are compared with the large body of experimental data in the literature, and with the previous calculations by Boushehri et al. (1987). The agreement with both experimental data and theoretical calculations is quite good.

Nomenclature

\[ B \] second virial coefficient \( \text{m}^3\cdot\text{mol}^{-1} \)
\[ C_6-C_{14} \] dispersion coefficients \( \text{J} \cdot \text{m}^6 - \text{J} \cdot \text{m}^{14} \)
\[ I \] unit vector
\[ J_n \] auxiliary function defined by equation (6)
\[ k \] Boltzmann constant \( \text{J} \cdot \text{K}^{-1} \)
\[ N \] Avogadro’s number \( \text{mol}^{-1} \)
\[ \rho \] interparticle distance \( \text{nm} \)
\[ r \] vector separating molecular centers \( \text{nm} \)
\[ T \] absolute temperature \( \text{K} \)
\[ T \] dipole–dipole interaction tensor \( \text{nm}^{-2} \)
\[ u \] potential energy function \( \text{J} \)

\[ \mu \] dipole moment vector \( \text{J}^{1/2} \cdot \text{m}^{3/2} \)
\[ \kappa \] anisotropy of dipole polarizability

Subscripts

0 spherical contribution
ns nonspherical contribution
ind induced
d dipole

Superscripts

* reduced quantity
\( \perp \) vertical component
\( \parallel \) parallel component

1. INTRODUCTION

A realistic potential for neutral atoms can be constructed theoretically by a detailed quantum-mechanical calculation. At large separations, the dominant contribution to the potential comes from the multipole dispersion interactions between the instantaneous electric moments in one atom and those induced in the other one. Although the atoms are neutral, these moments arise due to spontaneous fluctuations in the electronic charge distributions.
The most important term varies as $r^{-6}$ and describes the dipole-induced dipole interaction. Higher-order terms represent dipole-quadrupole interaction (varies as $r^{-8}$), quadrupole-quadrupole interaction (varies as $r^{-10}$), and so on. All these terms represent attractive contributions to the potential. A rigorous calculation of the short-range interaction is more difficult. In practice, it is more usual to represent the short-range repulsion by an inverse power law, i.e., $r^{-n}$, with $n$ lying typically between 9 and 15. Many potential functions of this form are presented so far; as an example, we may address to the Lennard-Jones [1] potential, which provides a fair description of interaction between pairs of rare gases and also of quasispherical molecules. Recently, a great advance has been made in this field with the development of the Hartree–Fock–Dispersion (HFD) type potentials by Aziz et al. [2–6], which are in more coincidence with experimental and theoretical results than the others.

The description of the interaction between two molecules poses greater problems than for spherical particles, because the intermolecular potential is a function both of the separation of the molecules and of their mutual orientations. A general model potential for describing polar molecules in which a point-dipole interaction is superimposed on a spherically symmetric potential is of the form:

$$u = u_0(r) + \mu_1 \cdot T(r) \cdot \mu_2$$

(1)

where $r$ is the vector separating the molecular centers, $u_0(r)$ is the spherically symmetric term, $\mu_i$ is the dipole moment vector of the $i$th molecule, $T(r)$ is the dipole–dipole interaction tensor given by

$$T(r) = \frac{3rr}{r^5} - \frac{1}{r^3}$$

and $I$ is a unit tensor. Two examples of the above potential that are of particular interest are those of dipolar hard-spheres, where $u_0(r)$ is the hard-sphere interaction and the Stockmayer [7] potential, where $u_0(r)$ is the Lennard-Jones function. Both these models together with generalizations that include, for example, dipole–quadrupole and quadrupole–quadrupole interactions, have received much attention from theoreticians. In this work we have used a Hartree–Fock dispersion individually damped (HFD-ID) potential developed by Boyes [8] as the core potential to calculate the second virial coefficient of molecular gases.

2. THEORY

The pertinent statistical–mechanical expression for the second virial coefficient reads as [9]:

$$B(T) = \frac{N}{8\pi} \int_0^\infty \int_0^\pi \int_0^{2\pi} \int_0^{2\pi} [1 - \exp(-u/kT)] r^2$$

$$\times dr \sin \theta_1 d\theta_1 \sin \theta_2 d\theta_2 d\varphi_1 d\varphi_2$$

(3)

where $N$ is the Avogadro’s number, $k$ is the Boltzmann’s constant, $T$ is the absolute temperature, and $\theta$ and $\varphi$ are the usual Eulerian angles. The intermolecular potential, $u(r, \theta, \varphi)$, can be written as a spherical part, $u_0(r)$, and a nonspherical contribution, $u_{ns}(\theta, \varphi)$, i.e.,

$$u = u_0(r) + u_{ns}(\theta, \varphi)$$

(4)

The spherical part depends on the distance $r$ between the molecular centers of mass and the nonspherical part depends on the relative orientation of molecules.

The contributions to the nonspherical potential can be regarded as the contributions from electrostatic, induction, dispersion, and shape effects. The former one arise from the interaction between permanent dipole moment, $\mu$, quadrupole moment, $\Theta$, and higher-order moments. The electrostatic interaction between axially symmetric molecules possessing dipole and quadrupole moments have been discussed by Morgenau [10]. The presence of permanent quadrupoles will lead to further induced moments. These interactions involve the molecular dipole polarizability, $\alpha_d$, the molecular quadrupole polarizability, $\alpha_q$, the quantum-mechanical fluctuations in the distribution of charge in an atom or molecule give rise to transient multipole moments. These transient multipole moments induce a corresponding transient multipole moment in another molecule. The dispersion energy contribution to the second virial coefficient is due to the electrostatic interaction between these two sets of moments. The average dispersion energy contributes only to $u_0(r)$, but nonspherical contributions arise from the anisotropies of the molecular polarizabilities and their angular dependencies can be calculated by classical electrostatic, although the average coefficients require quantum mechanics for the determination. In the simplest scheme, the nonspherical dispersion interaction which varies as $r^{-6}$ depends on the dispersion coefficient, $C_6$, and the anisotropy of the dipole polarizability, $\kappa$. Molecular shape is another factor that may play an important role in determining the interactions of polar molecules. A nonspherical shape implies that the short-range overlap repulsive forces depend on orientation. The complete mathematical expressions for the above contributions to the nonspherical part of potential energy are complicated and we avoid presenting them here; they can be found in the literature [11].

Knowing the form of $u$, the second virial coefficient will be calculated by solving equation (3). As we mentioned earlier, the potential energy is then separated into.
Calculation of the second virial coefficient of nonspherical molecules: Revisited

a spherical part and a nonspherical part. The nonspherical part is expanded as a following series [11]:

\[ \exp(-u_{ns}/kT) = 1 + \sum_{j=1}^{n} (-1)^{j} \frac{(u_{ns})^{j}}{j!} \]

(5)

The first term in the expansion gives the spherical contribution to the second virial coefficient and the others give the nonspherical contributions. A similar method was first achieved by Stockmayer [7] for evaluating the second virial coefficient of molecules with permanent dipoles, and by Harris and Alder [12] for dealing with polarizable molecules. Buckingham and Pople [13] have also developed a method similar to that of Stockmayer [7], but different in the details of mathematics and final form. Their method is claimed [14] to be preferable from the viewpoint of computational conveniences. Buckingham and Pople [13] had expressed the final form derived for \( B(T) \) in terms of a set of dimensionless functions.

Putting the series expansion (5) into equation (3) for \( B(T) \), we have shown previously [15] that the results for radial part are expressible as a set of dimensionless integrals, \( J_{n}(T^{*}) \), which are simply related to the proposed functions by Buckingham and Pople [13] and are defined as:

\[ J_{n}(T^{*}) = \frac{n - 3}{2} \int_{0}^{\infty} (r^{*})^{2-n} \exp(-u_{ns}^{*}/kT) dr \]

(6)

where \( T^{*} = kT/\varepsilon, r^{*} = r/\sigma, u_{ns}^{*} = u_{ns}/\varepsilon, \) and \( \varepsilon, \sigma \) are the potential well-depth and the interparticle distance at which \( u_{ns} = 0 \), respectively. For the sake of clarification, we have explained the integration method for dipole–dipole electrostatic interaction energy, as a typical contributing term to \( u_{ns} \), in Appendix I. The new auxiliary functions, \( J_{n}(T^{*}) \), vary in a much smoother manner than the proposed functions by Buckingham and Pople [13]. Here, \( J_{n}(T^{*}) \) values have been calculated using a HFD-ID type core potential [8] and are employed to calculate the nonspherical contribution to the second virial coefficient of gases.

3. RESULTS AND DISCUSSION

The core potential used in this work is of the HFD-ID type, developed by Aziz [6] for Ar–Ar interaction. Recently, this potential has been improved by Boyes [8] to reproduce both the acoustic and volumetric virial coefficients as well as the best available transport and spectroscopic data. The complete form of this potential is given in Appendix II.

Although this potential has been developed for Ar, it is regarded as a realistic general model for \( u_{0}(r) \) in this work. We have adopted only its shape and the scale parameters \( \varepsilon \) and \( \sigma \) remain adjustable. The values of \( J_{n}(T^{*}) \) for this potential model are calculated by numerical integration for \( 0.5 \leq T^{*} \leq 10 \) and \( 6 \leq n \leq 30 \) and are tabulated in Appendix III. Below \( T^{*} = 0.5 \) the convergence of series expansion (5) is poor, and above \( T^{*} = 10 \) the nonspherical contributions to the second virial coefficient are usually negligible.

The nonspherical contributions to the second virial coefficient are classified as five groups: electrostatic, induction, dispersion, shape effects, and cross terms. The effects of former four groups on the potential energy are discussed briefly, earlier. The cross terms result from multiplying the terms \( u_{0}(r)/kT \) in the expansion equation (5). Inclusion of the shape effects on the potential energy, and hence, on the second virials requires the specification of shape factor. Here, we have neglected the effect of this factor on the second virial coefficients. The complete mathematical expressions for the contribution of the above mentioned effects to the second virial coefficient are given in Appendix IV.

Previously, we have critically evaluated and divided the second virial coefficients into two classes called primary data and secondary data [16]. The division into two classes was based on several objective and subjective criteria. These were:

(a) a subjective assessment of the reliability of the data, guided by an examination of internal consistency of error analysis and reproducibility,

(b) the authors’ statement of precision and accuracy,

(c) a direct intercomparison of results from different laboratories and of results obtained by different methods, and

(d) an evaluation of the capability of the method used and the theory of the instrument.

In this work, the primary data were exclusively used in adjusting \( \varepsilon \) and \( \sigma \). The parameters \( \varepsilon/k \) and \( \sigma \) so determined are listed in table I together with the molecular properties [17–24] used to determine the nonspherical contributions to the second virial coefficients. The secondary data are also used for the sake of comparison.

Employing the values of \( J_{n}(T^{*}) \), listed in Appendix III, and the molecular properties, listed in table I, we have calculated the second virial coefficient for the technologically and industrially important linear molecular gases \( \text{N}_2, \text{O}_2, \text{CO}, \text{NO}, \text{and CO}_2 \). The results for
TABLE I

The parameters used for calculation of the second virial coefficients.

<table>
<thead>
<tr>
<th>Gas</th>
<th>$\varepsilon/k$ (K)</th>
<th>$\sigma$ (nm)</th>
<th>$\mu^*$ [17]</th>
<th>$\Theta^*$ [18]</th>
<th>$\alpha^*$ [20]</th>
<th>$\kappa$ [21]</th>
<th>$C_6^*$ [22]</th>
</tr>
</thead>
<tbody>
<tr>
<td>N₂</td>
<td>113.13</td>
<td>0.3669</td>
<td>0</td>
<td>0.433$^a$</td>
<td>0.03521</td>
<td>0.131</td>
<td>1.845</td>
</tr>
<tr>
<td>O₂</td>
<td>142.60</td>
<td>0.3395</td>
<td>0</td>
<td>0.131</td>
<td>0.0401</td>
<td>0.229</td>
<td>1.970</td>
</tr>
<tr>
<td>CO</td>
<td>113.13</td>
<td>0.3669</td>
<td>0.128</td>
<td>0.774</td>
<td>0.0398</td>
<td>0.090</td>
<td>2.226$^b$</td>
</tr>
<tr>
<td>NO</td>
<td>130.50</td>
<td>0.3884</td>
<td>0.142</td>
<td>0.411</td>
<td>0.0251</td>
<td>0.162</td>
<td>0.848$^c$</td>
</tr>
<tr>
<td>CO₂</td>
<td>225.01</td>
<td>0.4357</td>
<td>0</td>
<td>0.618</td>
<td>0.0354</td>
<td>0.268</td>
<td>0.863</td>
</tr>
</tbody>
</table>

$^a$ This value is taken from Ref. [19].
$^b$ This value is taken from Ref. [23].
$^c$ This value is taken from Ref. [24].

Figure 1. Comparison of the calculated second virial coefficients of N₂ in the present work with experiment [25, 26] and with the previous calculations by Boushehri et al. [16].

Figure 2. The same as figure 1 for O₂.

Figure 3. The same as figure 1 for CO₂.

Figure 4. Comparison of the calculated second virial coefficients with the experimental data [27–29] and with the previous calculations [16] for CO.
Calculation of the second virial coefficient of nonspherical molecules: Revisited

Figure 5. The same as figure 4 for NO.

Figure 6. Deviation ($B_{\text{cal}} - B_{\text{expt}}$) plot for the calculated second virial coefficient of N$_2$ compared with primary data.

Figure 7. Deviation plot for the second virial coefficient of N$_2$ compared with secondary data.

Figure 8. The same as figure 6 for O$_2$.

Figure 9. The same as figure 7 for O$_2$.

N$_2$, O$_2$, and CO$_2$ are compared both with the smoothed values reported by Dymond and Smith [25] and with the previous method by Boushehri et al. [16] in figures 1–3, respectively. The results for N$_2$ are also compared with the recent publications by Ewing and Trusler [26]. Figure 4 shows the calculated second virial coefficients for CO, compared with the primary data [27–29] and with those given in Ref. [16]. There are only three reports in the literature [30–32] on the second virial coefficient of NO, which are considered as secondary data. Our calculations for NO are compared with these data [30–32] and...
with the calculated values by Boushehri et al. [16] in figure 5. Figures 6–14 show the extent of deviation between our calculated values and experimental primary and secondary data for the aforementioned gases.

Analysis of the results in figures 1–14 shows that our calculations are in good agreement with experimental data [25–70]. The calculated values reported in figures 1–5 show that the results are within the range of experimental uncertainties. Our calculations are nearly of the same accuracy or better than those performed by Boushehri et al. [16], furthermore, the present method extends the predictive range to much lower temperatures than those reported by Boushehri et al. [16].

In order to compare the orders of magnitude of the spherical and nonspherical contributions to the second virial coefficients, we have shown the results for CO as a typical example in table II at two temperatures, a much low temperature and a relatively high temperature, at which the experimental data do exist [27, 29]. The results show that the dominant contribution to the nonspherical part is due to electrostatic (quadrupole–quadrupole) interaction.

In this work, the effects of nonspherical molecular shapes and asymmetric charge distributions are taken into account to well reproduce the experimental second virial coefficient data. Although this approach has been used earlier with such potentials as Lennard-Jones [13–15], here, a more realistic potential energy function proposed for Ar has been used as the core potential. Following
Calculation of the second virial coefficient of nonspherical molecules: Revisited

Table II
The contribution of different terms to the second virial coefficient of CO at 90.67 K and 423.20 K.

<table>
<thead>
<tr>
<th>Type of interaction</th>
<th>Contributing term</th>
<th>$B_m$ (cm$^3$·mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>90.67 K</td>
</tr>
<tr>
<td>Electrostatic</td>
<td>$B_m(\mu \mu)$</td>
<td>-1.864 × 10$^{-2}$</td>
</tr>
<tr>
<td></td>
<td>$B_m(\mu \Theta)$</td>
<td>-1.420</td>
</tr>
<tr>
<td></td>
<td>$B_m(\Theta \Theta)$</td>
<td>50.056</td>
</tr>
<tr>
<td>Induction</td>
<td>$B_m(\mu \mu_{ind})$</td>
<td>-7.528 × 10$^{-6}$</td>
</tr>
<tr>
<td></td>
<td>$B_m(\mu \Theta_{ind})$</td>
<td>-2.369 × 10$^{-2}$</td>
</tr>
<tr>
<td></td>
<td>$B_m(\Theta \mu_{ind})$</td>
<td>-2.800 × 10$^{-2}$</td>
</tr>
<tr>
<td>Dispersion</td>
<td>$B_m(C_6 \text{ anis})$</td>
<td>0.722</td>
</tr>
<tr>
<td>Cross effects</td>
<td>$B_m(\mu \times \Theta)$</td>
<td>0.422</td>
</tr>
<tr>
<td></td>
<td>$B_m(\mu \mu_{ind} \times \Theta \mu_{ind})$</td>
<td>-1.229 × 10$^{-3}$</td>
</tr>
<tr>
<td></td>
<td>$B_m(\mu \mu_{ind} \times \mu \mu_{ind})$</td>
<td>-7.772 × 10$^{-5}$</td>
</tr>
<tr>
<td></td>
<td>$B_m(\mu \mu_{ind} \times \Theta \mu_{ind})$</td>
<td>-1.347 × 10$^{-4}$</td>
</tr>
<tr>
<td></td>
<td>$B_m(\Theta \Theta \times C_6 \text{ anis})$</td>
<td>1.530</td>
</tr>
<tr>
<td></td>
<td>$B_m(\mu \mu_{ind} \times C_6 \text{ anis})$</td>
<td>-4.625 × 10$^{-3}$</td>
</tr>
<tr>
<td></td>
<td>$B_m(\Theta \mu_{ind} \times C_6 \text{ anis})$</td>
<td>-0.243</td>
</tr>
<tr>
<td>$B_m$ (total)</td>
<td></td>
<td>-50.57</td>
</tr>
<tr>
<td>$B_0$</td>
<td></td>
<td>-186.77</td>
</tr>
<tr>
<td>$B$</td>
<td></td>
<td>-237.34</td>
</tr>
<tr>
<td>Experimental value</td>
<td></td>
<td>-233.00</td>
</tr>
</tbody>
</table>

*The explicit formulas for each type of interaction are given in Appendix IV.*

Figure 14. The same as figure 7 for NO.

Figure 15. Angular coordinates for two interacting axially symmetric molecules.

the above mentioned procedure, we have tabulated the auxiliary functions, $J_n(T^*)$, in a wide range of temperatures. The tabulations have been employed to well reproduce the second virial coefficient of five gases over a wide range of temperatures. Comparison of the calculated results with the previous work [16] shows that the present calculations are in better agreement with experimental data. It is worth mentioning that the tables can be used for all molecules because the same functions appear in the perturbation expansion. Once the $J_n(T^*)$ values are known, the second virial coefficient can be calculated from the procedure explained above.

Acknowledgements

We acknowledge the research committee of Shiraz University. Dr. H. Eslami thanks the research committee and the computer facilities of Persian Gulf University.

REFERENCES


[38] Michels A., Lunbeck R.J., Wolkers G.J., Thermodynamic properties of nitrogen as functions of density and temperature between −125°C and +150°C and densities up to 760 amagat, Phys. 17 (1951) 801–816.


Calculation of the second virial coefficient of nonspherical molecules: Revisited


[50] Michels A., Schamp H.W., de Graaff W., Compressibility isotherms of oxygen at 0, 25, and 50° and at pressures up to 135 atmospheres, Phys. 20 (1954) 1209-1214.


APPENDIX I

To describe the method of integration, we will describe the dipole-dipole electrostatic interaction as an example.

\[ u_{dB}(\mu\mu) = -\mu \int_0^\pi \int_0^\pi \int_0^{2\pi} \int_0^{2\pi} \left\{ \frac{1}{kT} \left[ 2 \cos \theta_1 \cos \theta_2 - \sin \theta_1 \sin \theta_2 \cos(\phi_2 - \phi_1) \right] \right\} \, \frac{d\theta_1 d\theta_2 d\phi_1 d\phi_2}{4\pi} \]

where \( u_{dB}(\mu\mu) \) is the dipole-dipole interaction energy, \( \mu \) is the dipole moment, \( k \) is the Boltzmann constant, and \( T \) is the temperature. The integral is taken over the solid angle, with \( \theta_1, \theta_2, \phi_1, \phi_2 \) representing the polar and azimuthal angles, respectively. Details of the calculation can be found in reference [15]. The first term in the expansion equation (5) gives the spherical contribution. According to equations (3)–(5), the nonspherical contributions are expressed as:

\[ B_{ns}(\mu\mu) = \frac{N}{8\pi} \sum_{j=1}^\infty (-1)^j \int_0^{2\pi} \int_0^{2\pi} \int_0^{2\pi} \int_0^{2\pi} \left\{ \frac{1}{kT} \left[ 2 \cos \theta_1 \cos \theta_2 - \sin \theta_1 \sin \theta_2 \cos(\phi_2 - \phi_1) \right] \right\} \, d\theta_1 d\theta_2 d\phi_1 d\phi_2 \]
The integration over angular part is carried out straightforwardly. According to the convention adopted in the previous work [15], integration over angle of the first term \((j = 1)\) yields zero, because any nonzero average parts of \(u_{ns}\) have been assigned to \(u_0\). The radial part in the above equation is written in terms of a set of dimensionless integrals defined in equation (6) of the text.

**APPENDIX II**

The HFD-ID potential for Ar has the following form [8]:

\[
u = A \exp(-\alpha r + \beta r^2) - f(\rho r) \left[ \sum_n C_n \rho^{-n} g_n(\rho r) \right] + u_A(r)
\]

\[n = 6, 8, 10, 12, 14\]

in which

\[f(\rho r) = 1 - (\rho r)^{1.68} \exp(-0.78 \rho r)\]

\[#^{\text{APPENDIX III}}\]

The dimensionless parameters of the dimensionless \(u_0^* = u_0/\varepsilon\) are of the following values

\[
\begin{align*}
A^* &= 92163.2432 & \beta^* &= -2.33375162 \\
\alpha^* &= 9.08372872 & \rho &= 1.12315660 \\
C^*_6 &= 1.08473169 & \epsilon/\kappa &= 143.22262\text{ K} \\
C^*_8 &= 0.51339682 & \rho_m &= 3.76445\text{ Å} \\
C^*_0 &= 0.32666130 & A_4 &= -11.7412234 \\
C^*_2 &= 0.28351216 & r_1/r_m &= 0.40329052 \\
C^*_4 &= 0.32354602 & r_2/r_m &= 0.703015165
\end{align*}
\]

**TABLE III**

The values of \(J_0(T^*)\) as a function of \(T^* = kT/\varepsilon\) for \(6 \leq n \leq 30\).

<table>
<thead>
<tr>
<th>(T^*)</th>
<th>(J_0)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>1.7869</td>
</tr>
<tr>
<td>0.6</td>
<td>1.4163</td>
</tr>
<tr>
<td>0.7</td>
<td>1.2103</td>
</tr>
<tr>
<td>0.8</td>
<td>1.0819</td>
</tr>
<tr>
<td>0.9</td>
<td>0.9555</td>
</tr>
<tr>
<td>1.0</td>
<td>0.9341</td>
</tr>
<tr>
<td>1.2</td>
<td>0.8540</td>
</tr>
<tr>
<td>1.4</td>
<td>0.8052</td>
</tr>
<tr>
<td>1.6</td>
<td>0.7733</td>
</tr>
<tr>
<td>1.8</td>
<td>0.7515</td>
</tr>
<tr>
<td>2.0</td>
<td>0.7362</td>
</tr>
<tr>
<td>2.5</td>
<td>0.7140</td>
</tr>
<tr>
<td>3.0</td>
<td>0.7043</td>
</tr>
<tr>
<td>3.5</td>
<td>0.7009</td>
</tr>
<tr>
<td>4.0</td>
<td>0.7010</td>
</tr>
<tr>
<td>4.5</td>
<td>0.7031</td>
</tr>
<tr>
<td>5.0</td>
<td>0.7066</td>
</tr>
<tr>
<td>6.0</td>
<td>0.7157</td>
</tr>
<tr>
<td>7.0</td>
<td>0.7263</td>
</tr>
<tr>
<td>8.0</td>
<td>0.7376</td>
</tr>
<tr>
<td>9.0</td>
<td>0.7491</td>
</tr>
<tr>
<td>10.0</td>
<td>0.7605</td>
</tr>
</tbody>
</table>

\[\sum_{n=0}^{\infty} \exp(-u_0/kT)r^2 dr\]
Calculation of the second virial coefficient of nonspherical molecules: Revisited

APPENDIX IV

Contribution of different terms to the nonspherical second virial coefficients is as follow:

(a) Electrostatic contributions:

\[ B_{ns}^*(\mu \mu) = -\frac{2}{3} \left( \frac{\mu^2}{T^*} \right)^2 J_6 + \frac{1}{25} \left( \frac{\mu^2}{T^*} \right)^2 J_{12} + \cdots \]  

(IV.1)

\[ B_{ns}^*(\mu \Theta) = -\frac{6}{5} \left( \frac{\mu^* \Theta^*}{T^*} \right)^2 \times \left[ J_8 + \frac{726}{3185} \left( \frac{\mu^* \Theta^*}{T^*} \right)^2 J_{16} + \cdots \right] \]  

(IV.2)

\[ B_{ns}^*(\Theta \mu) = -\frac{6}{5} \left( \frac{\Theta^*}{T^*} \right)^2 \left[ J_{10} - \frac{6}{49} \left( \frac{\Theta^*}{T^*} \right)^2 J_{15} + \cdots \right] \]  

(IV.3)

(b) Induction contributions:

\[ B_{ns}^*(\mu \mu)_{ind} = -\frac{2}{15} \left( \frac{\mu^2 \alpha_d^4}{T^*} \right)^2 \left( J_{12} + 11 \alpha_d^2 J_{18} + \cdots \right) \]  

(IV.4)

\[ B_{ns}^*(\mu \Theta)_{ind} = -\frac{864}{77} \left( \frac{\mu^* \Theta^* \alpha_d^4}{T^*} \right)^2 J_{14} + \cdots \]  

(IV.5)

\[ B_{ns}^*(\Theta \mu)_{ind} = \frac{162}{455} \left( \frac{\Theta^* \alpha_d^4}{T^*} \right)^2 J_{16} + \cdots \]  

(IV.6)

(c) Dispersion contribution:

\[ B_{ns}^*(C_6 \text{C}_6)_{ind} = -\frac{2}{15} \left( \frac{k C_6^*}{T^*} \right) \left( 1 + 1.9 k^2 \right) J_{12} + \cdots \]  

(IV.7)

(d) Cross terms:

\[ B_{ns}^*(\mu \times \Theta) = \frac{3}{5} \left( \frac{\mu^* \Theta^*}{T^*} \right)^2 \left[ \left( \frac{\mu^2}{T^*} \right) J_{11} + \frac{24}{35} \left( \Theta^2 \right) J_{13} + \cdots \right] \]  

(IV.8)

\[ B_{ns}^*(\mu \mu \mu \times \Theta \mu \mu \mu) = -\frac{144}{385} \left( \frac{\mu^* \Theta^* \alpha_d^4}{T^*} \right)^2 J_{14} + \cdots \]  

(IV.9)

\[ B_{ns}^*(\mu \mu \mu \times \mu \mu \mu) = -\frac{4}{3} \left( \frac{\mu^2}{T^*} \right) \alpha_d^4 J_{12} \left[ \alpha_d^4 + \frac{1}{15} \left( \frac{\mu^2}{T^*} \right) + \cdots \right] \]  

(IV.10)
\( B^*_{\mu\mu} (\mu \times \Theta \mu_{\text{ind}}) = -\frac{48}{385} \left( \frac{\mu^*}{T^*} \right)^2 \left( \frac{\Theta^*}{T^*} \right) \alpha_d^* J_{14} + \ldots \) \hspace{1cm} (IV.11)

\( B^*_{\Theta\Theta} (\Theta \Theta \times C_6 \text{ anis}) = \frac{27}{25} \left( \frac{\Theta^*}{T^*} \right) \left( \frac{C_6^*}{T^*} \right) \kappa^* J_{11} + \ldots \) \hspace{1cm} (IV.12)

\( B^*_{\mu\mu} (\mu \mu_{\text{ind}} \times C_6 \text{ anis}) = -\frac{4}{15} \left( \frac{\mu^*}{T^*} \right) \left( \frac{C_6^*}{T^*} \right) \alpha_d^* \kappa J_{12} + \ldots \) \hspace{1cm} (IV.13)

\( B^*_{\Theta\mu} (\Theta \mu_{\text{ind}} \times C_6 \text{ anis}) = -\frac{144}{385} \left( \frac{\Theta^*}{T^*} \right) \left( \frac{C_6^*}{T^*} \right) \alpha_d^* \kappa J_{14} + \ldots \) \hspace{1cm} (IV.14)

where,

\( B^* = \frac{B}{2\pi/3N\sigma^3} \) \hspace{1cm} (IV.15)

\( \mu^* = \mu / (\varepsilon \sigma^3)^{1/2} \) \hspace{1cm} (IV.16)

\( \Theta^* = \Theta / (\varepsilon \sigma^5)^{1/2} \) \hspace{1cm} (IV.17)

\( \alpha^* = \alpha_d / \sigma \) \hspace{1cm} (IV.18)

\( \alpha_d = 1/3 (\alpha_d^1 + 2\alpha_d^2) \) \hspace{1cm} (IV.19)

\( C_6^* = C_6 / \varepsilon \sigma^6 \) \hspace{1cm} (IV.20)

\( \kappa = (\alpha_d^1 - \alpha_d^2) / 3\alpha_d \) \hspace{1cm} (IV.21)