

Improved Tables for the Calculation of Nonspherical Contributions to Second Virial Coefficients

A. Boushehri,^{1,2} E. A. Mason,¹ and J. Kestin¹

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A set of improved numerical tables is given for use in calculating the effects of nonspherical molecular interactions on the second virial coefficients of simple molecular gases. The second virial coefficients are given as a spherical-core contribution (not discussed in this paper) plus a series of nonspherical perturbation terms. The tables give easy-to-interpolate auxiliary functions that occur in the perturbation terms. These functions depend on the form assumed for the spherical-core part of the interaction potential, but only in a relatively insensitive way, so that the tables should be adequate for almost all calculations that are likely to occur in this connection. The auxiliary functions $J_n(T^*)$ are tabulated for n from 6 to 30 and T^* from 0.5 to 10, where $T^* = kT/\varepsilon_0$ and ε_0 is the well depth of the spherical-core potential. Explicit formulas are given for the simple cases of axially symmetric molecules, but the tabulated functions can also be used for more complex cases.

KEY WORDS: equation of state; molecular gases; nonspherical interactions; second virial coefficients.

1. INTRODUCTION

The purpose of this paper is to present improved tables for the calculation of the nonspherical contributions to the second virial coefficients of simple molecular gases. The calculation method is the perturbation procedure developed by Pople [1] and by Buckingham and Pople [2], who represented the intermolecular potential as a spherically symmetric core plus terms representing various nonspherical interactions, such as dipole-dipole and

¹ Brown University, Providence, Rhode Island 02912, U.S.A.

² Permanent address: Department of Chemistry, Shiraz University, Shiraz, Iran.

quadrupole–quadrupole interactions. There are two reasons why such improved tables are needed. The primary reason is that the magnitudes of the nonspherical contributions depend on the form assumed for the dominant spherical core, and existing tabulations are based on Lennard–Jones (12–6) [2] or (18–6) [3] models for the core. These models are now considered too crude for use in accurate calculations of gas properties. The secondary reason is that the existing tabulations are rather scanty and involve functions that change rapidly with temperature, making interpolation difficult.

This paper replaces the (12–6) or (18–6) spherical cores with a more realistic (and hence elaborate) potential. The results are presented as tables of convenient auxiliary functions from which the desired nonspherical contributions to second virial coefficients can be easily calculated. It turns out that the nonspherical contributions are not overly sensitive to the details of the spherical-core potential, so that the present tables are likely to be adequate for any foreseeable applications.

Although the present tables are expected to be useful for calculations involving most molecular gases, the motivation for preparing them arises from a more specialized application. A successful simultaneous correlation of the equilibrium and transport properties of the noble gases and their mixtures at low densities has recently been achieved [4] on the basis of a combination of a principle of corresponding states and a knowledge of the interaction potentials [5, 6]. In its final form, the correlation can be used in a predictive mode, because the use of proven theory has ensured complete internal consistency among the different properties of a particular system as well as among the different systems of the set.

It is natural to attempt to develop a similar synthesis for the more complicated case of molecular gases. It is clear, however, that this task is more difficult, because the intermolecular potentials cease to be spherically symmetric, the theoretical formulas that must be used are more complicated, and reliable experimentally determined property data become scarcer with increasing molecular complexity. Furthermore, no principle of corresponding states of comparable accuracy has been discovered even for groups of molecular gases. To be successful, such an extension must begin by taking into account the lack of spherical symmetry of the intermolecular potentials. A common procedure is to picture the potential as a spherically symmetrical core plus terms representing various individual nonspherical interactions. The effects of such nonspherical terms on second virial coefficients can then be evaluated by the Pople–Buckingham perturbation procedure [1, 2], and the present tables were prepared with this application in mind. The effects of the nonspherical terms on the transport properties are believed to be much smaller than on the second virial coef-

ficients, largely on the basis of approximate numerical calculations using simplified potential models [7]. The hope is then that an extended principle of corresponding states can be developed for the spherical core of the potential, at least for some of the simpler molecular gases. It should be emphasized, however, that the applicability of the present tables in no way hinges on the success or failure of any principle of corresponding states. The tables can stand on their own.

2. POTENTIAL MODEL

We write the intermolecular pair potential as the sum of a spherical portion V_0 and a nonspherical portion V_{ns} ,

$$V = V_0(r) + V_{\text{ns}}(\omega_i) \quad (1)$$

in which V_0 depends only on the distance r between the molecular centers of mass, and V_{ns} depends also on the angles ω_i that specify the relative orientation of the molecular pair. This means that the molecules are treated as rigid rotating bodies and that the effects of the vibrational degrees of freedom are left unaccounted for. The effects of vibration on second virial coefficients are usually negligible for simple molecular gases except near the dissociation limit, which means at very high temperatures [8]. The unweighted average of V_{ns} over all relative orientations is forced to be zero by assigning any nonvanishing average terms to V_0 . The usual approximation for V_{ns} , following the pioneering work of Stockmayer [9] on dipolar gases, is to represent it as a sum of terms that describe the long-range interactions; an additional term to describe the molecular shape, or the dependence of the short-range steric repulsions on orientation, was suggested by Pople [1] and Buckingham and Pople [2], so that V_{ns} is represented as

$$V_{\text{ns}} = V_{\text{ns}}(\text{long-range}) + V_{\text{ns}}(\text{shape}) \quad (2)$$

The long-range contributions are customarily taken to be the asymptotic forms given by theory as series in r^{-n} , and $V_{\text{ns}}(\text{shape})$ is often empirically represented by the first term in an expansion in spherical harmonics.

The fact that asymptotic long-range forms are used for V_{ns} suggests that the results for the second virial coefficient are valid only at higher temperatures, where such terms are significant but not dominant. This is consistent with the use of a perturbation calculation to find the effects of V_{ns} , and the results appear as series that converge only for high temperatures. Roughly speaking, the results are usually limited to temperatures greater than about $kT/\varepsilon_0 \simeq 1$, where ε_0 is the well depth of $V_0(r)$, although the

details depend on the individual molecular parameters. The criteria for convergence are made more precise in the following sections.

The contributions to $V(\text{long-range})$ can be conveniently divided into three parts,

$$V_{\text{ns}}(\text{long-range}) = V_{\text{ns}}(\text{electrostatic}) + V_{\text{ns}}(\text{induction}) \\ + V_{\text{ns}}(\text{dispersion}) \quad (3)$$

The electrostatic contributions arise from the interactions between permanent multipole moments of the molecules, which are symbolized by

- μ , dipole;
- Θ , quadrupole;
- Ω , octopole;
- Φ , hexadecapole;
- etc.

These interactions are entirely classical and do not involve quantum effects. Even quite symmetrical molecules have nonzero multipole moments: homonuclear diatomic molecules such as N_2 and O_2 have quadrupole (and higher) moments, tetrahedral molecules such as CH_4 and CF_4 have octopole (and higher) moments, and octahedral molecules such as SF_6 have hexadecapole (and higher) moments.

The induction contributions are also entirely classical and arise from the interactions between the permanent multipole moments of one molecule and the moment that they induce in a second molecule. These interactions involve the molecular polarizabilities:

- α_d , dipole polarizability;
- α_q , quadrupole polarizability;
- etc.

The dispersion contributions, first clearly recognized by London [10, 11], are fundamentally quantum-mechanical in nature but have a simple semiclassical interpretation. The electron distribution of an atom or molecule undergoes quantum-mechanical fluctuations that give rise to transient multipole moments, which induce corresponding transient moments in a second molecule. The electrostatic interactions between these

two sets of moments give rise to the attractive dispersion energy. The average dispersion energy contributes only to $V_0(r)$, but nonspherical contributions arise from the anisotropies of the molecular polarizabilities. Their angular dependence can be calculated by classical electrostatics, although the average coefficients require quantum mechanics for their determination.

In general, the foregoing multipoles and multipole polarizabilities are tensors, but in most cases the symmetry of the molecules reduces the complexity of the interaction expressions considerably. The most important asymptotic long-range interactions are collected in Table I and arranged according to their dependence on separation distance. The only entries whose meanings are not physically obvious are the term $(\mu\Theta, \text{ind}\mu)$, which varies as r^{-7} , and the term $(\mu^2\alpha_d^2)$, which varies as r^{-9} .

The term $(\mu\Theta, \text{ind}\mu)$ arises when the molecules have both permanent dipole and permanent quadrupole moments. The dipole of molecule 1 induces a dipole in molecule 2 that interacts back with the quadrupole of molecule 1. In addition, the quadrupole of molecule 1 induces a dipole in molecule 2 that interacts back with the dipole of molecule 1. Both of these interactions fall off as r^{-7} .

The term $(\mu^2\alpha_d^2)$ is really one of higher order in the expansion of $(\mu, \text{ind}\mu)$; it corresponds physically to the interaction of the induced dipole of molecule 2 with the dipole that it in turn induces in molecule 1. There are, of course, hosts of such higher-order terms, but $(\mu^2\alpha_d^2)$ is believed to be the most important [2].

General formulas for the full tensorial interactions are too complex to be presented here; they can be found in the literature [12, 13]. Here we give explicit expressions only for what are believed to be the most important terms in the simple case of the interaction of two axially symmetric

Table I. Long-Range Nonspherical Molecular Interactions According to Their Asymptotic Dependence on Separation

Separation dependence	Electrostatic	Induction	Dispersion
r^{-3}	$\mu\mu$	—	—
r^{-4}	$\mu\Theta$	—	—
r^{-5}	$\Theta\Theta; \mu\Omega$	—	—
r^{-6}	$\Theta\Omega; \mu\Phi$	$\mu, \text{ind}\mu$	$C_6(\alpha_d)$ anis
r^{-7}	$\Omega\Omega; \Theta\Phi; \dots$	$\mu\Theta, \text{ind}\mu$	—
r^{-8}	$\Omega\Phi; \dots$	$\Theta, \text{ind}\mu; \mu, \text{ind}\Theta$	$C_8(\alpha_d, \alpha_q)$ anis
r^{-9}	$\Phi\Phi; \dots$	$\mu^2\alpha_d^2; \dots$	—

molecules. The coordinate system used is shown in Fig. 1, and the following abbreviations are used:

$$\begin{aligned} c_1 &= \cos \theta_1, & s_1 &= \sin \theta_1 \\ c_2 &= \cos \theta_2, & s_2 &= \sin \theta_2 \\ c &= \cos(\phi_2 - \phi_1) \end{aligned} \quad (4)$$

The dominant electrostatic interactions are

$$V_{\text{ns}}(\mu\mu) = -\frac{\mu^2}{r^3} (2c_1 c_2 - s_1 s_2 c) \quad (5)$$

$$V_{\text{ns}}(\mu\Theta) = \frac{3\mu\Theta}{2r^4} (c_2 - c_1)(3c_1 c_2 - 2s_1 s_2 c + 1) \quad (6)$$

$$V_{\text{ns}}(\Theta\Theta) = \frac{3\Theta^2}{4r^5} [1 - 5c_1^2 - 5c_2^2 - 15c_1^2 c_2^2 + 2(4c_1 c_2 - s_1 s_2 c)^2] \quad (7)$$

These interactions vanish when averaged over all angles.

The dominant nonspherical induction interactions are

$$V_{\text{ns}}(\mu, \text{ind}\mu) = -\frac{\mu^2 \alpha_d}{2r^6} (3c_1^2 + 3c_2^2 - 2) - \frac{\mu^2 \alpha_d^2}{r^9} (8c_1 c_2 - s_1 s_2 c) \quad (8)$$

which includes the higher-order term ($\mu^2 \alpha_d^2$) in Table I, plus

$$V_{\text{ns}}(\mu\Theta, \text{ind}\mu) = -\frac{12\mu\Theta\alpha_d}{r^7} (c_1^3 + c_2^3) \quad (9)$$

and

$$V_{\text{ns}}(\Theta, \text{ind}\mu) = -\frac{9\Theta^2 \alpha_d}{8r^8} \left(4c_1^4 + 4c_2^4 + s_1^4 + s_2^4 - \frac{8}{3} \right) \quad (10)$$

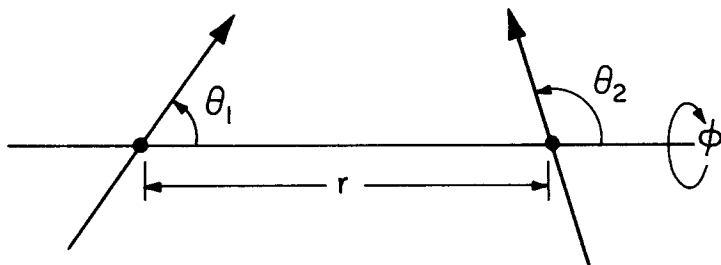


Fig. 1. Coordinate system for the relative orientation of two axially symmetric molecules.

There is an analogous term for $V_{\text{ns}}(\mu, \text{ind}\Theta)$ that varies as $\mu^2\alpha_q/r^8$; it is customarily neglected, in part because almost no information is available on the quadrupole polarizabilities of molecules. The above expressions can also contain an additional implicit dependence on orientation due to the anisotropy of α_d (and α_q). These interactions all vanish when averaged over all angles, because we have assigned any nonzero parts to $V_0(r)$. The nonzero parts are

$$V_0(\mu, \text{ind}\mu) = -\frac{2\mu^2\bar{\alpha}_d}{r^6} \quad (11)$$

$$V_0(\Theta, \text{ind}\mu) = -\frac{3\Theta^2\bar{\alpha}_d}{r^8} \quad (12)$$

where $\bar{\alpha}_d$ is the orientation-averaged polarizability. The term $V_0(\Theta, \text{ind}\mu)$ is sometimes included in the nonspherical contribution [7, 12], especially when the model adopted for $V_0(r)$ contains no r^{-8} term, as is the case for Lennard-Jones ($n-6$) potentials.

The dominant nonspherical dispersion interaction is

$$V_{\text{ns}}(C_6 \text{anis}) = \frac{\kappa\bar{C}_6}{r^6} \left[1 - \frac{3}{2}(1-\kappa)(c_1^2 + c_2^2) - \frac{3}{2}\kappa(2c_1c_2 - s_1s_2c)^2 \right] \quad (13)$$

where \bar{C}_6 is the mean dispersion coefficient and κ is the anisotropy of the dipole polarizability,

$$\kappa \equiv (\alpha_d^{\parallel} - \alpha_d^{\perp})/3\bar{\alpha}_d \quad (14)$$

α_d^{\parallel} being the polarizability along the molecular axis of symmetry and α_d^{\perp} being that perpendicular to it. The corresponding expression for $V_{\text{ns}}(C_8 \text{anis})$ is very complicated [14] and is always neglected in calculations of virial coefficients.

The foregoing discussion ignores the so-called eccentricity effects, which arise when the geometric center of a molecule does not coincide with the center of mass or the center of charge. These give rise to other terms in r^{-n} and should be included in any treatment of unsymmetrical molecules [13, 14]. The calculation of their effects on second virial coefficients involves the same auxiliary functions that are tabulated in this paper, and we do not bother to write down the detailed expressions here.

The corresponding expressions for V_{ns} for two unlike axially symmetric molecules are summarized in the monograph of Mason and Spurling [15].

Finally, the only calculations for the effect of the short-range

$V_{\text{ns}}(\text{shape})$ on second virial coefficients have been confined to an empirical representation as an inverse power,

$$V_{\text{ns}}(\text{shape}) = \frac{A}{r^n} (3c_1^2 + 3c_2^2 - 2) \quad (15)$$

where A is a constant and n is an integer (usually 12). The auxiliary functions tabulated here are also suitable for this form of $V_{\text{ns}}(\text{shape})$.

3. CALCULATIONS

The second virial coefficient for nonspherical interactions is

$$B(T) = \frac{N_A}{2\Omega_0^2} \iiint [1 - \exp(-V/kT)] dr d\omega_1 d\omega_2 \quad (16)$$

where N_A is Avogadro's number, Ω_0 is the normalization factor for the angular integration over $d\omega$, r is the separation between the molecular centers of mass, and the integrations extend over all of the relative configuration space. For a three-dimensional rigid rotator, for example,

$$d\omega = \sin \theta d\theta d\phi d\psi, \quad \Omega_0 = 8\pi^2 \quad (17a)$$

where θ , ϕ , and ψ are the usual Eulerian angles, and for an axially symmetric rigid rotator,

$$d\omega = \sin \theta d\theta d\phi, \quad \Omega_0 = 4\pi \quad (17b)$$

where θ and ϕ are the usual polar and azimuthal angles (see Fig. 1).

To carry out the integrations, the pair potential is divided into spherical and nonspherical parts as in Eq. (1), and the nonspherical part is considered as a perturbation; the exponential is then expanded in a series as follows:

$$\exp(-V_{\text{ns}}/kT) = 1 + \sum_{j=1}^n \frac{(-1)^j}{j!} (V_{\text{ns}}/kT)^j \quad (18)$$

The first term in the expansion gives the spherical contribution to $B(T)$ and the summation gives the nonspherical contribution,

$$B(T) = B_0(T) + B_{\text{ns}}(T) \quad (19)$$

where

$$B_0(T) = 2\pi N_A \int_0^\infty [1 - \exp(-V_0/kT)] r^2 dr \tag{20}$$

and

$$B_{ns}(T) = -\frac{N_A}{2\Omega_0^2} \sum_{j=1}^\infty \frac{(-1)^j}{j!} \iiint (V_{ns}/kT)^j \exp(-V_0/kT) d\mathbf{r} d\omega_1 d\omega_2 \tag{21}$$

It is the appearance of $\exp(-V_0/kT)$ in the integrals for B_{ns} that requires the new tabulations reported in the present work.

According to the convention adopted here, integration over angles of the first term ($j = 1$) of the series (21) for B_{ns} yields zero, because any non-zero average parts of V_{ns} have been assigned to V_0 at the beginning. We emphasize that this is only a convention and that the functions we tabulate are just as useful if a different convention is adopted. The explicit formulas for B_{ns} will, of course, depend on the convention adopted but will obviously always be expressible as linear combinations of the following integrals that remain after angular integrations have been performed [2, 12]:

$$\langle r^{-n} \rangle \equiv \int r^{-n} \exp(-V_0/kT) d\mathbf{r} = 4\pi \int_0^\infty r^{-n} \exp(-V_0/kT) r^2 dr \tag{22}$$

In this paper we do not tabulate the $\langle r^{-n} \rangle$ but, rather, a related set of dimensionless integrals,

$$J_n(T^*) \equiv \frac{n-3}{2} \int_0^\infty \frac{dr^*}{(r^*)^{n-2}} \exp(-V_0^*/T^*) = \frac{n-3}{8\pi} \sigma_0^{n-3} \langle r^{-n} \rangle \tag{23}$$

where

$$T^* \equiv kT/\epsilon_0 \tag{24a}$$

$$V_0^* \equiv V_0/\epsilon_0 \tag{24b}$$

$$r^* \equiv r/\sigma_0 \tag{24c}$$

and ϵ_0 and σ_0 are the energy and distance scaling parameters of V_0 . This definition of the $J_n(T^*)$ is chosen so that their dependence on n and T^* is

relatively weak; their relation to the functions $H_n(y)$ used by Buckingham and Pople [2] is

$$J_n(T^*) = \frac{n-3}{24y^4} H_n(y) \quad (25a)$$

$$T^* = 4/y^2 \quad (25b)$$

The values of the $J_n(T^*)$ are listed in Table AI in the Appendix for T^* from 0.5 to 10 and n from 6 to 30. Below $T^* = 0.5$ the model for V_{ns} and the convergence of the series expansion (21) are suspect, and above $T^* = 10$ the nonspherical corrections to $B(T)$ are usually negligible. The $J_n(T^*)$ were calculated by numerical integration; comparison with the $H_n(y)$ of Buckingham and Pople for a Lennard-Jones (12-6) model, which were calculated by an analytical method [2], leads us to believe that the accuracy of the entries in Table AI is not worse than about 1 part in 10^4 . The form chosen for V_0 was

$$V_0^* = Ax^2e^{-\alpha x} - \left(\frac{C_6}{x^6} + \frac{C_8}{x^8} + \frac{C_{10}}{x^{10}} \right) F(x) \quad (26a)$$

where

$$x \equiv r/r_m \quad (26b)$$

$$F(x) = \exp \left[- \left(\frac{1.4}{x} - 1 \right)^2 \right], \quad x < 1.4 \quad (26c)$$

$$F(x) = 1, \quad x \geq 1.4 \quad (26d)$$

and

$$A = 9.502720 \times 10^6$$

$$\alpha = 16.345655$$

$$C_6 = 1.0914254 \quad (26e)$$

$$C_8 = 0.6002595$$

$$C_{10} = 0.3700113$$

$$r_m/\sigma_0 = 1.119629$$

Here r_m is the position of the potential minimum, σ_0 is the value of r for which $V_0 = 0$, and ε_0 is the depth of the potential well. This potential has the same *shape* as the HFD-C potential of Aziz and Chen [16] for Ar-Ar interactions but should be regarded here simply as a realistic general model for $V_0(r)$. In particular, the C_6 , C_8 , and C_{10} coefficients in Eq. (26) are not

just the dispersion coefficients but contain spherical contributions from induced moments as well [such as those given by Eqs. (11) and (12), which contribute to C_6 and C_8 , respectively].

For concreteness, we give explicit formulas for some of the non-spherical contributions to $B(T)$ for axially symmetric molecules. These correspond to the formulas for V_{ns} given in Eqs. (5)–(13). Other cases involving more complicated tensorial interactions can be straightforwardly obtained by carrying out the angular integrations in Eq. (21). We use the following dimensionless notation:

$$B^* = B/(2\pi N_A \sigma_0^3/3) \quad (27a)$$

$$\mu^* = \mu/(\varepsilon_0 \sigma_0^3)^{1/2} \quad (27b)$$

$$\Theta^* = \Theta/(\varepsilon_0 \sigma_0^5)^{1/2} \quad (27c)$$

$$\alpha_d^* \equiv \bar{\alpha}_d/\sigma_0^3 \quad (27d)$$

$$\alpha_q^* \equiv \bar{\alpha}_q/\sigma_0^5 \quad (27e)$$

$$C_6^* \equiv \bar{C}_6/\varepsilon_0 \sigma_0^6 \quad (27f)$$

$$A^* \equiv A/\varepsilon_0 \sigma_0^n \quad (27g)$$

The contributions to B_{ns} can be divided into five groups: three groups (electrostatic, induction, dispersion) corresponding to the division of V_{ns} (long-range) in Eq. (3), a pure shape contribution from V_{ns} (shape) of Eq. (15), and a large number of cross terms resulting from multiplying out the terms $(V_{\text{ns}}/kT)^j$ in Eq. (21),

$$\begin{aligned} B_{\text{ns}}^*(T^*) &= B_{\text{ns}}^*(\text{electrostatic}) + B_{\text{ns}}^*(\text{induction}) \\ &+ B_{\text{ns}}^*(\text{dispersion}) + B_{\text{ns}}^*(\text{shape}) \\ &+ B_{\text{ns}}^*(\text{cross terms}) \end{aligned} \quad (28)$$

The individual electrostatic contributions are as follows:

$$B_{\text{ns}}^*(\mu\mu) = -\frac{2}{3} \left(\frac{\mu^{*2}}{T^*} \right)^2 \left[J_6 + \frac{1}{25} \left(\frac{\mu^{*2}}{T^*} \right)^2 J_{12} + \dots \right] \quad (29)$$

$$B_{\text{ns}}^*(\mu\Theta) = -\frac{6}{5} \left(\frac{\mu^*\Theta^*}{T^*} \right)^2 \left[J_8 + \frac{726}{3185} \left(\frac{\mu^*\Theta^*}{T^*} \right)^2 J_{16} + \dots \right] \quad (30)$$

$$B_{\text{ns}}^*(\Theta\Theta) = -\frac{6}{5} \left(\frac{\Theta^{*2}}{T^*} \right)^2 \left[J_{10} - \frac{6}{49} \left(\frac{\Theta^{*2}}{T^*} \right) J_{15} + \dots \right] \quad (31)$$

The complete series for $B_{\text{ns}}^*(\mu\mu)$ is available [2].

The individual induction contributions are as follows:

$$B_{\text{ns}}^*(\mu, \text{ind}\mu) = -\frac{2}{15} \left(\frac{\mu^{*2} \alpha_d^*}{T^*} \right)^2 (J_{12} + 11\alpha_d^{*2} J_{18}) + \dots \quad (32)$$

$$B_{\text{ns}}^*(\mu\Theta, \text{ind}\mu) = -\frac{864}{77} \left(\frac{\mu^* \Theta^* \alpha_d^*}{T^*} \right)^2 J_{14} + \dots \quad (33)$$

$$B_{\text{ns}}^*(\Theta, \text{ind}\mu) = -\frac{162}{455} \left(\frac{\Theta^{*2} \alpha_d^*}{T^*} \right)^2 J_{16} + \dots \quad (34)$$

plus an analogous term for $B_{\text{ns}}^*(\mu, \text{ind}\Theta)$ that varies as $(\mu^{*2} \alpha_q^*/T^*)^2 J_{16}$.

The dispersion contribution is

$$B_{\text{ns}}^*(C_6 \text{anis}) = -\frac{2}{15} \left(\frac{\kappa C_6^*}{T^*} \right)^2 \left(1 + \frac{19}{10} \kappa^2 \right) J_{12} + \dots \quad (35)$$

and the shape contribution is

$$B_{\text{ns}}^*(\text{shape}) = -\frac{8}{5} \left(\frac{3}{2n-3} \right) \left(\frac{A^*}{T^*} \right)^2 J_{2n} + \dots \quad (36)$$

There are, of course, many cross terms, and the hope is that the convergence of the perturbation expansion is good enough so that not too many such terms are needed. The leading cross terms among just the electrostatic interactions are

$$B_{\text{ns}}^*(\mu \times \Theta) = \frac{3}{5} \left(\frac{\mu^* \Theta^*}{T^*} \right)^2 \left[\left(\frac{\mu^{*2}}{T^*} \right) J_{11} + \frac{24}{35} \left(\frac{\Theta^{*2}}{T^*} \right) J_{13} + \dots \right] \quad (37)$$

and the leading cross term among just the induction interactions is

$$B_{\text{ns}}^*(\mu, \text{ind}\mu \times \Theta, \text{ind}\mu) = -\frac{144}{385} \left(\frac{\mu^* \Theta^* \alpha_d^*}{T^{*2}} \right)^2 J_{14} + \dots \quad (38)$$

The leading cross terms between the electrostatic and the induction interactions are

$$B_{\text{ns}}^*(\mu\mu \times \mu, \text{ind}\mu) = -\frac{4}{3} \left(\frac{\mu^{*2}}{T^*} \right)^2 \alpha_d^* J_{12} \left[\alpha_d^* + \frac{1}{15} \left(\frac{\mu^{*2}}{T^*} \right) + \dots \right] \quad (39)$$

the first term of which is of the same form as the first term of $B_{\text{ns}}^*(\mu, \text{ind}\mu)$ of Eq. (32), and

$$B_{\text{ns}}^*(\mu\mu \times \Theta, \text{ind}\mu) = -\frac{48}{385} \left(\frac{\mu^{*2}}{T^*} \right)^2 \left(\frac{\Theta^{*2}}{T^*} \right) \alpha_d^* J_{14} + \dots \quad (40)$$

The leading cross terms involving the dispersion interaction are

$$B_{\text{ns}}^*(\Theta\Theta \times C_6 \text{anis}) = \frac{27}{25} \left(\frac{\Theta^{*2}}{T^*} \right) \left(\frac{C_6^*}{T^*} \right) \kappa^2 J_{11} + \dots \quad (41)$$

$$B_{\text{ns}}^*(\mu, \text{ind}\mu \times C_6 \text{anis}) = -\frac{4}{15} \left(\frac{\mu^{*2}}{T^*} \right) \left(\frac{C_6^*}{T^*} \right) \alpha_{\text{d}}^* \kappa J_{12} + \dots \quad (42)$$

$$B_{\text{ns}}^*(\Theta, \text{ind}\mu \times C_6 \text{anis}) = -\frac{144}{385} \left(\frac{\Theta^{*2}}{T^*} \right) \left(\frac{C_6^*}{T^*} \right) \alpha_{\text{d}}^* \kappa J_{14} + \dots \quad (43)$$

For simplicity we omit the cross terms involving $V_{\text{ns}}(\text{shape})$.

Except for the cross terms involving $V_{\text{ns}}(\text{shape})$, the foregoing formulas include all terms of order $(1/T^*)^2$ but only those terms of order $(1/T^*)^3$ that are generally believed to be the most important. There are other terms of order $(1/T^*)^3$. The only terms of order $(1/T^*)^4$ that appear are those involving dipole-dipole and dipole-quadrupole electrostatic interactions. In any event, the $J_n(T^*)$ given in Table AI are adequate for the calculation of any higher terms that might be thought significant, as well as for the calculation of terms involving octopoles, hexadecapoles, induced quadrupoles, eccentricity effects, and so on.

4. NUMERICAL EXAMPLE

Before discussing the use of the tables, we wish to illustrate the influence of the choice of the spherical-core potential $V_0(r)$ on the calculated nonspherical contributions to second virial coefficients. For this purpose we choose a hypothetical molecule having properties approximately corresponding to CO_2 , that is, a linear molecule with an appreciable quadrupole moment but no dipole moment. Two sets of results are shown in Table II, one set with $V_0(r)$ given by the (12-6) potential and the other set with $V_0(r)$ given by Eqs. (26a-e), each calculated at two reduced temperatures, $T^* = 1$ and 5. The major nonspherical contributions are $B_{\text{ns}}^*(\Theta\Theta)$ and $B_{\text{ns}}^*(\Theta\Theta \times C_6 \text{anis})$. It is clear that none of the contributions to B_{ns}^* is affected very much by the choice of $V_0(r)$ in this range of reduced temperatures. The convergence of the perturbation calculation for B_{ns}^* becomes questionable for $T^* < 1$, and the nonspherical corrections diminish rapidly in importance for $T^* > 5$.

The most important conclusion to be drawn from Table II is that the effects of changing $V_0(r)$ on B_{ns}^* are rather small in the temperature range where the perturbation calculation is appropriate. From this it follows that further efforts involving more refined forms for $V_0(r)$ would probably be pointless.

Table II. Numerical Example of the Effect of Different Forms of $V_0(r)$ on the Calculated Nonspherical Contributions to Second Virial Coefficients for CO_2^a

Contribution	$T^* = 1$		$T^* = 5$	
	(12,6)	Present	(12,6)	Present
$B_{ns}^*(\Theta\Theta)$	-0.6379	-0.6332	-0.0233	-0.0243
$B_{ns}^*(\Theta, \text{ind}\mu)$	-0.0006	-0.0006	-0.00003	-0.00003
$N_{ns}^*(C_6 \text{anis})$	-0.0689	-0.0688	-0.0027	-0.0029
$B_{ns}^*(\Theta\Theta \times C_6 \text{anis})$	+0.1491	+0.1486	+0.0054	+0.0057
$B_{ns}^*(\Theta, \text{ind}\mu \times C_6 \text{anis})$	-0.0100	-0.0100	-0.0005	-0.0005
B_0^*	-2.5381	-2.0369	+0.2430	+0.3226

^a $\Theta^* = 0.8473$; $\kappa = 0.2664$; $\alpha_d^* = 0.0491$; $C_6^* = 2.328$.

The most striking differences in Table II are the values of the spherical contributions B_0^* for the two forms of V_0 . We believe that these differences are largely artifacts resulting from the relative crudeness of the (12-6) potential. In particular, if the parameters ϵ_0 and σ_0 of this potential are correct, then the implied value of $C_6 = 4\epsilon_0\sigma_0^6$ is too large by nearly a factor of two [17]. In addition, there is no r^{-8} attraction term in the potential. In practice, in fitting data the values of ϵ_0 and σ_0 for the (12-6) potential would be adjusted to compensate for such inadequacy, and a comparison with real data for different forms of V_0 would involve different sets of parameters. Such a method of comparison would, however, distort the B_{ns}^* values, and we have therefore avoided it.

In short, the choice of the form of $V_0(r)$ has a marked effect on B_0^* but only a minor effect on the B_{ns}^* .

5. USE OF TABLES

Table AI lists values of the function $J_n(T^*)$, defined by Eq. (23), for T^* and n in the ranges

$$0.5 \leq T^* \leq 10 \quad (44)$$

$$6 \leq n \leq 30 \quad (45)$$

The convergence of the perturbation calculation of B_{ns} becomes

questionable for most systems when $T^* < 0.5$, and the spherical contribution B_0 usually dominates for $T^* > 10$. The numerical values of $J_n(T^*)$ were obtained with the form of the spherical-core potential $V_0(r)$ as given by Eqs. (26a–e). The example in the preceding section illustrates that the results, somewhat surprisingly, are not sensitive to the form chosen for $V_0(r)$. The tables allow the effects of the molecular rotational degrees of freedom on second virial coefficients to be calculated. They take no account of the vibrational degrees of freedom, whose effects are usually negligible, as already stated earlier.

To use the tables, the intermolecular potential must first be written as the sum of a spherical part V_0 and a nonspherical part V_{ns} , as in Eq. (1), and then V_{ns} must be expressed as a sum of terms, each of the form of r^{-n} multiplied by a function of the relative orientations of the two molecules. Any terms from V_{ns} that do not vanish on averaging over all orientations must be put into V_0 . Substitution of V_{ns} into Eq. (21) and evaluation of the angular integrations then lead to an expression for B_{ns} as a series in the functions J_n , each multiplied by an inverse power of T . We have given detailed formulas only for the case of two identical axially symmetric molecules, but the tables can be used with more complicated cases as well because the same functions J_n will appear.

For illustration let us consider the case of a polarizable molecule with a permanent quadrupole moment and include the nonspherical dispersion interaction but neglect the nonspherical steric repulsion (shape) interaction. The molecular parameters needed are then Θ , $\bar{\alpha}_d$, κ , and C_6 , which must be obtained from independent sources (usually dielectric and optical data). In addition, the spherical parameters ϵ_0 and σ_0 must be known. These might be obtained independently from analysis of viscosity data or possibly even from the second virial coefficients themselves (in which case an iteration procedure would be necessary). Then the explicit formula for calculating the second virial coefficient as a function of temperature is

$$\begin{aligned} \frac{B(T)}{(2\pi/3) N_A \sigma_0^3} &\equiv B^*(T^*) = B_0^*(T^*) + B_{ns}^*(\Theta\Theta) + B_{ns}^*(\Theta, \text{ind}\mu) \\ &+ B_{ns}^*(C_6 \text{anis}) + B_{ns}^*(\Theta\Theta \times C_6 \text{anis}) \\ &+ B_{ns}^*(\Theta, \text{ind}\mu \times C_6 \text{anis}) + \dots \end{aligned} \quad (46)$$

The determination of the spherical contribution B_0^* is entirely outside the scope of this paper. It can be obtained from some assumed form for $V_0(r)$, from a corresponding-states correlation, or from any other source. It

is to be emphasized that it does *not* have to be obtained from the same form of V_0 that we have used to evaluate the J_n functions in Table AI. Although this might seem desirable from the standpoint of consistency, it is unnecessary because of the relative insensitivity of the J_n to V_0 , as illustrated in the preceding section.

The calculation of $B(T)$ is completed by evaluation of the individual terms in Eq. (46) as follows: $B_{ns}^*(\Theta\Theta)$ from Eq. (31), $B_{ns}^*(\Theta, \text{ind}\mu)$ from Eq. (34), $B_{ns}^*(C_6\text{anis})$ from Eq. (35), $B_{ns}^*(\Theta\Theta \times C_6\text{anis})$ from Eq. (41), and $B_{ns}^*(\Theta, \text{ind}\mu \times C_6\text{anis})$ from Eq. (43). If slow convergence is suspected, say because Θ^* happens to be unusually large, then additional terms arising from the expansion of Eq. (21) can be calculated straightforwardly.

APPENDIX

Table AI. The Functions $J_n(T^*)$ for the Calculation of Nonspherical Contributions to Second Virial Coefficients

T^*	J_6	J_7	J_8	J_9	J_{10}
0.5	1.7818	1.9819	2.1198	2.2123	2.2715
0.6	1.4128	1.5553	1.6545	1.7225	1.7679
0.7	1.2075	1.3189	1.3977	1.4532	1.4919
0.8	1.0795	1.1721	1.2388	1.2872	1.3225
0.9	0.9932	1.0737	1.1328	1.1770	1.2107
1.0	0.9319	1.0040	1.0581	1.0998	1.1328
1.2	0.8517	0.9137	0.9622	1.0017	1.0351
1.4	0.8028	0.8593	0.9054	0.9447	0.9797
1.6	0.7708	0.8243	0.8697	0.9098	0.9470
1.8	0.7488	0.8009	0.8463	0.8880	0.9277
2.0	0.7333	0.7847	0.8309	0.8744	0.9168
2.5	0.7106	0.7627	0.8122	0.8611	0.9110
3.0	0.7004	0.7548	0.8086	0.8635	0.9211
3.5	0.6964	0.7540	0.8124	0.8736	0.9391
4.0	0.6960	0.7569	0.8203	0.8879	0.9612
4.5	0.6976	0.7622	0.8305	0.9045	0.9858
5.0	0.7005	0.7689	0.8422	0.9226	1.0118
6.0	0.7087	0.7845	0.8678	0.9608	1.0659
7.0	0.7183	0.8016	0.8947	1.0002	1.1210
8.0	0.7286	0.8192	0.9219	1.0398	1.1763
9.0	0.7391	0.8369	0.9491	1.0792	1.2312
10.0	0.7496	0.8544	0.9758	1.1180	1.2856

T^*	J_{11}	J_{12}	J_{13}	J_{14}	J_{15}
0.5	2.3061	2.3227	2.3258	2.3193	2.3058
0.6	1.7967	1.8135	1.8215	1.8233	1.8206
0.7	1.5185	1.5364	1.5481	1.5554	1.5598
0.8	1.3485	1.3680	1.3828	1.3946	1.4044
0.9	1.2370	1.2581	1.2759	1.2915	1.3058
1.0	1.1599	1.1830	1.2035	1.2225	1.2409
1.2	1.0646	1.0916	1.1174	1.1428	1.1685
1.4	1.0122	1.0434	1.0743	1.1058	1.1384
1.6	0.9827	1.0182	1.0542	1.0916	1.1310
1.8	0.9669	1.0066	1.0478	1.0911	1.1372
2.0	0.9596	1.0037	1.0500	1.0992	1.1521
2.5	0.9630	1.0182	1.0774	1.1417	1.2117
3.0	0.9826	1.0490	1.1215	1.2012	1.2891
3.5	1.0101	1.0879	1.1739	1.2694	1.3760
4.0	1.0419	1.1313	1.2310	1.3428	1.4687
4.5	1.0761	1.1772	1.2909	1.4195	1.5653
5.0	1.1118	1.2246	1.3526	1.4984	1.6649
6.0	1.1854	1.3221	1.4793	1.6607	1.8706
7.0	1.2601	1.4212	1.6086	1.8272	2.0831
8.0	1.3351	1.5210	1.7393	1.9966	2.3010
9.0	1.4099	1.6209	1.8710	2.1685	2.5237
10.0	1.4842	1.7207	2.0034	2.3426	2.7509

T^*	J_{16}	J_{17}	J_{18}	J_{19}	J_{20}
0.5	2.2873	2.2655	2.2417	2.2166	2.1912
0.6	1.8149	1.8074	1.7987	1.7896	1.7806
0.7	1.5624	1.5638	1.5649	1.5660	1.5675
0.8	1.4131	1.4213	1.4296	1.4384	1.4479
0.9	1.3196	1.3334	1.3478	1.3629	1.3793
1.0	1.2592	1.2780	1.2978	1.3187	1.3412
1.2	1.1951	1.2229	1.2525	1.2841	1.3181
1.4	1.1726	1.2090	1.2480	1.2898	1.3350
1.6	1.1728	1.2176	1.2659	1.3181	1.3746
1.8	1.1866	1.2399	1.2976	1.3604	1.4287
2.0	1.2091	1.2710	1.3385	1.4122	1.4928
2.5	1.2885	1.3729	1.4659	1.5686	1.6824
3.0	1.3866	1.4948	1.6155	1.7501	1.9007
3.5	1.4952	1.6289	1.7793	1.9487	2.1400
4.0	1.6107	1.7714	1.9537	2.1608	2.3967
4.5	1.7312	1.9204	2.1367	2.3845	2.6689
5.0	1.8557	2.0749	2.3273	2.6186	2.9555
6.0	2.1143	2.3979	2.7288	3.1158	3.5695
7.0	2.3835	2.7372	3.1548	3.6490	4.2354
8.0	2.6620	3.0914	3.6038	4.2167	4.9518
9.0	2.9489	3.4596	4.0748	4.8179	5.7181
10.0	3.2439	3.8413	4.5672	5.4521	6.5338

T^*	J_{21}	J_{22}	J_{23}	J_{24}	J_{25}
0.5	2.1659	2.1411	2.1172	2.0945	2.0731
0.6	1.7720	1.7642	1.7573	1.7516	1.7473
0.7	1.5698	1.5731	1.5775	1.5834	1.5907
0.8	1.4586	1.4705	1.4839	1.4989	1.5158
0.9	1.3971	1.4164	1.4377	1.4609	1.4863
1.0	1.3655	1.3918	1.4203	1.4513	1.4850
1.2	1.3547	1.3942	1.4370	1.4833	1.5335
1.4	1.3838	1.4367	1.4941	1.5563	1.6239
1.6	1.4361	1.5028	1.5755	1.6548	1.7411
1.8	1.5032	1.5847	1.6737	1.7712	1.8781
2.0	1.5811	1.6781	1.7846	1.9018	2.0309
2.5	1.8084	1.9484	2.1039	2.2771	2.4701
3.0	2.0694	2.2586	2.4713	2.7106	2.9803
3.5	2.3564	2.6015	2.8796	3.1958	3.5558
4.0	2.6659	2.9736	3.3259	3.7302	4.1948
4.5	2.9961	3.3733	3.8088	4.3128	4.8970
5.0	3.3460	3.7996	4.3275	4.9433	5.6629
6.0	4.1026	4.7306	5.4718	6.3489	7.3891
7.0	4.9329	5.7648	6.7592	7.9508	9.3823
8.0	5.8360	6.9023	8.1915	9.7542	11.6533
9.0	6.8117	8.1441	9.7716	11.7652	14.2138
10.0	7.8602	9.4913	11.5028	13.9905	17.0757

T^*	J_{26}	J_{27}	J_{28}	J_{29}	J_{30}
0.5	2.0532	2.0349	2.0183	2.0034	1.9903
0.6	1.7444	1.7430	1.7433	1.7453	1.7490
0.7	1.5997	1.6104	1.6229	1.6373	1.6538
0.8	1.5345	1.5554	1.5784	1.6038	1.6316
0.9	1.5141	1.5444	1.5773	1.6132	1.6521
1.0	1.5215	1.5611	1.6040	1.6504	1.7006
1.2	1.5878	1.6467	1.7104	1.7794	1.8541
1.4	1.6973	1.7771	1.8638	1.9581	2.0606
1.6	1.8354	1.9383	2.0507	2.1736	2.3081
1.8	1.9952	2.1237	2.2649	2.4202	2.5909
2.0	2.1731	2.3300	2.5032	2.6948	2.9067
2.5	2.6854	2.9260	3.1951	3.4965	3.8346
3.0	3.2846	3.6287	4.0181	4.4596	4.9609
3.5	3.9663	4.4353	4.9720	5.5870	6.2931
4.0	4.7298	5.3469	6.0599	6.8854	7.8426
4.5	5.5757	6.3656	7.2866	8.3626	9.6220
5.0	6.5056	7.4946	8.6575	10.0276	11.6451
6.0	8.6252	10.0977	11.8555	13.9584	16.4798
7.0	11.1060	13.1865	15.7035	18.7558	22.4657
8.0	13.9672	16.7934	20.2539	24.5016	29.7281
9.0	17.2291	20.9521	25.5608	31.2806	38.3973
10.0	20.9125	25.6972	31.6800	39.1807	48.6092

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