

**The statistical mechanics of  
non-spherical polyatomic molecules  
Application to the properties of carbon dioxide†**

by JAMES F. ELY‡ and H. J. M. HANLEY  
Cryogenics Division, National Bureau of Standards,  
Boulder, Colorado 80302

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Collision integrals and equilibrium pressure and dielectric second virial coefficients are calculated for a non-spherical  $m-6-8$  model potential energy function. The results are applied in a correlation of the physical properties of carbon dioxide. It is shown that the inclusion of non-spherical contributions in the calculation of the collision integrals has a small but significant effect with respect to the accurate representation of data. The Mason-Monchick approximation that non-spherical molecules collide with fixed relative orientations is briefly discussed. Agreement between calculated and experimental values for the viscosity coefficient, the thermal conductivity coefficient, the second virial coefficients and the isotopic thermal diffusion factor is generally satisfactory.

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1. INTRODUCTION

In previous publications [1, 2] the  $m-6-8$  model potential function [3] was shown to be of practical value in correlating various thermophysical properties of monatomic fluids. More recently [4, 5] the application of this potential has been extended to axially symmetric quadrupolar molecules, in particular, nitrogen, oxygen, carbon dioxide and fluorine. In this later work a potential of the form

$$\Phi = \phi(\text{spherical}) + \phi(\text{permanent}) + \phi(\text{induction}) \quad (1)$$

was used to calculate equilibrium properties (pressure and dielectric virial coefficients). Transport properties were calculated by using only the spherical term in equation (1) [the  $m-6-8$  potential function]. A feature of the work was that the  $m-6-8$  spherical potential parameters, determined by fitting wide temperature range viscosity data, were used in the calculation of both transport and equilibrium properties. Also, the molecular parameters appearing in the anisotropic terms (e.g. quadrupole moments and molecular polarizabilities) were not determined from a fit of the potential to data, but were taken from independent experimental sources. The results demonstrated that a satisfactory representation of the experimental data could be achieved, but it was apparent that systematic differences between experimental second virial coefficients and

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‡ National Research Council Postdoctoral Fellow. Present address: Department of Chemical Engineering, Rice University, Houston, Texas 77001.

those calculated using equation (1) existed. The preliminary conclusion drawn was that the effect of anisotropic interactions on the collision integrals should be re-investigated.

In this paper the application of the model potential of equation (1) to carbon dioxide is re-examined. In particular, the contribution of the non-spherical terms to the Chapman-Enskog collision integrals (and hence to the viscosity) is investigated. The results are demonstrated graphically by comparing the calculations with experimental data for several macroscopic properties: the pressure and dielectric second virial coefficients, the viscosity and thermal conductivity coefficients and the isotopic thermal diffusion factor. Carbon dioxide was chosen for this study owing to the relative size of its quadrupole moment and abundance of experimental data, but the results are qualitatively similar for other axially symmetric quadrupolar fluids.

## 2. KINETIC THEORY OF POLYATOMIC MOLECULES

For spherically symmetric molecules the calculation of transport properties is straightforward: the Chapman-Enskog solution of the Boltzmann equation provides a direct connection between the intermolecular potential and the dilute gas transport coefficients via the collision integrals,  $\Omega^{(l, s)}$  [6]. For non-spherical molecules, however, the theory is complicated by anisotropic forces associated with the internal structure of the molecules. In particular, the presence of internal structure introduces inelastic collisions (usually translational-rotational energy transfers) and the required scattering cross-section calculations become very complicated. To circumvent these difficulties, one of three possible approximations is normally used. The first of these is that used in our previous studies [4, 5] and is to simply neglect the anisotropic forces in the cross-section calculations in the hope that the effects are small. The second method which has been used extensively [7-10] is to 'pre-average' the anisotropic potential to obtain an effective spherically symmetric potential with temperature-dependent parameters. Although this approximation may be valid in the limit of large impact parameters or low relative velocities [9-12] it is difficult to draw any significant conclusions about the potential function thus derived or the results obtained from its use [7].

The collision integral calculations reported herein are based on the third approach to the problem which has been discussed extensively by Mason and Monchick and their co-workers [13-17]. The model proposed by these authors is based on the formal theory of Wang Chang and Uhlenbeck [18] and Taxman [19] and comes from solving the Boltzmann equation under certain approximations. Using this approach, one finds the following expressions for the viscosity and thermal conductivity coefficients:

$$\eta = \frac{5}{16} \frac{(\pi m k T)^{1/2}}{\pi \sigma^2 \langle \Omega^{(2, 2)*} \rangle} \quad (2)$$

and

$$\lambda = \frac{5}{2} \eta \left( \frac{3k}{2m} \right) + \rho D_{\text{int}} C_v^{\text{int}} - \eta \left( \frac{5}{2} - \frac{\rho D_{\text{int}}}{\eta} \right) \Delta, \quad (3)$$

where

$$\Delta = \frac{2}{\pi} \frac{C_v^{\text{int}}}{Z} \left( \frac{5}{2} - \frac{\rho D_{\text{int}}}{\eta} \right) \left[ 1 + \frac{2}{\pi Z} \left( \frac{5m C_v^{\text{int}}}{3k} + \frac{\rho D_{\text{int}}}{\eta} \right) \right]^{-1}.$$

In these expressions  $m$  is the mass of a molecule,  $T$  the absolute temperature,  $\rho$  the density,  $Z$  the rotational collision number (approximately the average number of collisions required to transfer one quantum of energy from the translational to rotational mode) and  $C_v^{\text{int}}$  is the specific heat per unit mass at constant volume due to internal degrees of freedom. The term  $D_{\text{int}}$  accounts for an internal 'diffusion' of energy and is given by

$$\rho D_{\text{int}} = \frac{3}{8} \frac{(\pi mkT)^{1/2}}{\pi \sigma^2 \langle \Omega_{\text{int}}^{(1,1)*} \rangle}. \quad (4)$$

The  $\langle \Omega^{(l,s)*} \rangle$  are complicated functions of temperature and the internal co-ordinates and energies of the colliding molecules. Detailed expressions for these have been given in the literature [14, 15].

Although these expressions are exact under the approximations of the Wang Chang-Uhlenbeck theory, several severe approximations must be made to use them in practical applications. These assumptions are

(1) The trajectories of colliding molecules are, on the average, insensitive to the details of an inelastic collision.

(2) The internal diffusion coefficient  $\rho D_{\text{int}}$  may be replaced by a diffusion coefficient for ordinary diffusion,  $\rho D_{11}$ .

(3) Terms of  $0(1/Z^2)$  and higher may be neglected in the thermal conductivity.

(4) The molecules collide with fixed relative orientations.

It is difficult to assess quantitatively what effect these assumptions have on the collision integral calculations but it seems likely that the fourth assumption (fixed orientations during collisions) places the greatest limitations on the model. For example, this assumption has been studied by Cross and Herschbach [20] for the case of an atom-diatom collision and has been shown to be inadequate. [The reason for this is that one is neglecting the angular torque which can give rise to out-of-plane scattering.] In spite of the limitations, it appears that the Mason-Monchick approach affords the best compromise between physical reality and practical utility at this time.

We shall also present calculations of the isotopic thermal diffusion factor,  $\alpha_0$ , even though an accurate expression for polyatomic molecules is not available. For these calculations, we use the monatomic gas expression with the collision integrals for polyatomic fluids  $\langle \Omega^{(l,s)} \rangle$  in place of those for a monatomic gas :

$$\alpha_0 = \frac{15(6C^* - 5)(2A^* + 5)}{2A^*(16A^* - 12B'^* + 55)} [1 + \delta], \quad (5)$$

where

$$A^* = \langle \Omega^{(2,2)*} \rangle / \langle \Omega^{(1,1)*} \rangle,$$

$$B'^* = \frac{5\langle \Omega^{(1,2)} \rangle - 4\langle \Omega^{(1,3)*} \rangle}{\langle \Omega^{(1,1)*} \rangle},$$

$$C^* = \langle \Omega^{(1,3)*} \rangle / \langle \Omega^{(1,1)*} \rangle$$

and  $\delta$  is a correction term involving further combinations of collision integrals. An expression for this term is given in reference [29].

Similarly, second-order corrections to the viscosity and self-diffusion coefficients have been calculated from the formulae

$$f_{\eta} = 1 + \frac{3}{196} \left( \frac{8 \langle \Omega^{(2,3)*} \rangle}{\langle \Omega^{(2,2)*} \rangle} - 7 \right)^2,$$

$$f_D = 1 + \frac{(6C^* - 5)^2}{16A^* + 40},$$

which are again identical to those for monatomic gases with the  $\Omega^{(l,s)*}$  replaced by  $\langle \Omega^{(l,s)*} \rangle$ .

### 3. THE MODEL POTENTIAL

The detailed form of the model potential (1) and the assumptions made in arriving at this model have been discussed in references [4] and [5]. Briefly, however, if the anisotropy in the repulsive and dispersive parts of the potential are neglected, one has

$$\Phi = \phi_{m-6-8}(|\mathbf{r}|) + \phi_{\text{quad}}(\mathbf{r}, \boldsymbol{\omega}_1, \boldsymbol{\omega}_2) + \phi_{\text{ind}}(\mathbf{r}, \boldsymbol{\omega}_1, \boldsymbol{\omega}_2, \mathbf{D}),$$

where  $\boldsymbol{\omega}_i$  denotes the set of angles describing the orientation of molecule  $i$  with respect to some arbitrary space-fixed coordinate system,  $\mathbf{D}$  is the dielectric displacement vector and  $\mathbf{r}$  is a vector connecting the centres of mass of the two interacting molecules. The spherical term  $\phi_{m-6-8}(|\mathbf{r}|)$  is given by [1]

$$\phi_{m-6-8}(|\mathbf{r}|) = \epsilon \left[ \frac{6+2\gamma}{m-6} \left( \frac{\sigma}{r} \right)^m d^m - \frac{m-\gamma(m-8)}{m-6} \left( \frac{\sigma}{r} \right)^6 d^6 - \gamma \left( \frac{\sigma}{r} \right)^8 d^8 \right], \quad (6)$$

where  $r \equiv |\mathbf{r}|$ ,  $d = r_{\text{min}}/\sigma$  with  $\sigma$  and  $r_{\text{min}}$  being defined by the conditions  $\phi_{m-6-8}(\sigma) = 0$  and  $\phi_{\text{min-6-8}}(r_m) = -\epsilon$  respectively. The parameters  $m$  and  $\gamma$  represent the 'hardness' of the repulsive term and the 'strength' of the inverse eighth attraction term, respectively.

The non-spherical portion of the potential consists of two terms  $\phi_{\text{quad}}$  and  $\phi_{\text{ind}}$  which represent the potential energy between two permanent quadrupoles and the electric fields and dipoles induced in the system, respectively. These are given by [21]

$$\phi_{\text{quad}} = \mathbf{Q}_1 : \mathbf{V}_{12} : \mathbf{Q}_2$$

and

$$\phi_{\text{ind}} = -\frac{1}{2}(\mathbf{D} - \mathbf{U}_{12} \cdot \mathbf{Q}_2) \cdot (1 - \boldsymbol{\alpha}_2 \cdot \mathbf{T}_{21})^{-1} \cdot \boldsymbol{\alpha}_1 \cdot (\mathbf{D} - \mathbf{U}_{12} \cdot \mathbf{Q}_2) \\ - \frac{1}{2}(\mathbf{D} - \mathbf{U}_{21} \cdot \mathbf{Q}_1) \cdot (1 - \boldsymbol{\alpha}_1 \cdot \mathbf{T}_{12})^{-1} \cdot \boldsymbol{\alpha}_2 \cdot (\mathbf{D} - \mathbf{U}_{21} \cdot \mathbf{Q}_1), \quad (7)$$

where  $\mathbf{T}$ ,  $\mathbf{U}$  and  $\mathbf{V}$  are the dipole-dipole, dipole-quadrupole and quadrupole-quadrupole interaction tensors and  $\boldsymbol{\alpha}_i$  and  $\mathbf{Q}_i$  are the molecular polarizability and quadrupole moment tensors, respectively.

Finally, in the calculation of the collision integrals, it is convenient to write out the anisotropic contribution to the potential in terms of the relative orientations of the two molecules, given by  $(\theta_1, \theta_2, \phi)$  [see reference [6]]. In this case we find with  $\mathbf{D} = 0$ ,

$$\phi_{\text{quad}} = \frac{3\Theta^2}{4r^5} [1 - 5 \cos^2 \theta_1 - 5 \cos^2 \theta_2 - 15 \cos^2 \theta_1 \cos^2 \theta_2 \\ + 2(4 \cos \theta_1 \cos \theta_2 - \sin \theta_1 \sin \theta_2 \cos \phi)^2] \quad (8)$$

and

$$\phi_{\text{ind}} = -\frac{9\bar{\alpha}\Theta^2}{8r^8} [\sin^4 \theta_1 + \sin^4 \theta_2 + 4 \cos^4 \theta_1 + 4 \cos^4 \theta_2], \quad (9)$$

where  $\bar{\alpha}$  is the mean molecular polarizability and  $\Theta$  is the scalar quadrupole moment. Note that we have only considered the first-order term in equation (7) and that we have neglected the anisotropy in the polarizability.

#### 4. CALCULATIONS FOR CO<sub>2</sub>

##### 4.1. Potential parameter selection

The potential of equation (1) is considered to have only four parameters,  $m$ ,  $\gamma$ ,  $\sigma$  (or  $r_{\text{min}}$ ) and  $\epsilon/k$ , all of which are associated with the spherical  $m$ -6-8 potential function. The quadrupole moment, molecular polarizability and polarizability anisotropy  $\kappa$  were taken from independent sources and are listed in table 1.

	$m$	$\gamma$	$10^{10}\sigma/m$	$r_{\text{min}}/\sigma$	$(\epsilon/k)/K$	$10^{24}\bar{\alpha}/\text{cm}^3$	$\kappa$	$10^{26}\Theta/\text{e.s.u.}$
reference [4] (a)	14	1.0	3.68	1.1048729	282.0	2.925 (b)	0.239 (c)	$4.3 \pm 0.2$ (d)
this work	11	0.5	3.775	1.1259862	217.0	2.925	0.239	$4.3 \pm 0.2$

e.s.u. of polarizability,  $\text{cm}^3 \approx 1.11265 \times 10^{-16} \text{ J}^{-1} \text{ C}^2 \text{ m}^2$ ; e.s.u. of quadrupole moment  $\approx 3.33564 \times 10^{-14} \text{ C m}^2$ .

(a) Based on a fit to viscosity data assuming a spherically symmetric potential function.

(b) LANDOLT, H. H., and BORNSTEIN, R., 1951, *Zahlenwerte und Funktionen* (Springer-Verlag).

(c) BRIDGE, N. J., and BUCKINGHAM, A. D., 1966, *Proc. R. Soc.*, **295**, 334.

(d) BUCKINGHAM, A. D., DISCH, R. L., and DUNMUR, D. A., 1968, *J. Am. chem. Soc.*, **90**, 3104.

Table 1. Model potential parameters for CO<sub>2</sub>.

A desirable method of determining potential parameters is to fit simultaneously several macroscopic properties [22]. It was found, however, that a suitable correlation for CO<sub>2</sub> could not be obtained by this procedure and it was decided, therefore, to select the potential parameters by fitting wide temperature range dilute gas viscosity data. Clearly, the parameters determined in this manner are dependent on the accuracy of the experimental viscosity data. The data used in this work were taken from the following sources. Johnston and McCloskey [23], Michels, Botzen and Schuurman [24], Kestin *et al.* [25, 26] and Smith *et al.* [27, 28]. Based on an evaluation of these data and on our experience with the results from these sources for other non-polar fluids [29, 30], it was felt that the data are accurate to within  $\pm 2$  per cent in the temperature range considered.

The spherical potential parameters were determined by the following procedure: (1) initial estimates of  $m$ ,  $\gamma$ ,  $\sigma$ , and  $\epsilon/k$  were obtained by fitting experimental viscosity data in the temperature range 200–1600 K with viscosities calculated using only the spherical  $m$ -6-8 potential. [These are the parameters given in [4] and are listed for the sake of comparison in table 1]; (2) new sets of collision integrals  $\langle \Omega^{(l, s)} \rangle$  calculated with the full potential ( $m$ -6-8 + anisotropic terms) were obtained for  $m = 11, 12, 13$ , and 14 and for several values of  $\gamma$ .

The upper limit of  $m = 14$  and the values of  $\epsilon/k$  and  $\sigma$  (which are required to reduce the quadrupole moment and polarizability, viz.  $\bar{\alpha}^* = \bar{\alpha}/\sigma^3$  and  $\Theta^{*2} = \Theta^2/\epsilon\sigma^5$ ) were determined by step (1). A comparison of the viscosities calculated with these collision integrals and experimental data led to a choice of  $m = 11$  and a closer estimate of  $\gamma$ ,  $\sigma$  and  $\epsilon/k$ ; (3) new sets of collision integrals were calculated with  $m = 11$  and several values of  $\gamma$ ,  $\sigma$  and  $\epsilon/k$ . This led to a choice of  $\gamma = 0.5$  and a closer estimate of  $\sigma$  and  $\epsilon/k$ ; (4) recalculations of the collision integrals with  $m = 11$  and  $\gamma = 0.5$  and comparison to the experiment led to final values of  $m = 11$ ,  $\gamma = 0.5$ ,  $\sigma = 3.775 \times 10^{-10}$  m and  $\epsilon/k = 217$  K $\dagger$ .

#### 4.2. Collision integral calculations

The collision integrals,  $\langle \Omega^{(l, s)^*} \rangle$ , required in this procedure are defined by

$$\langle \Omega^{(l, s)^*}(T) \rangle = \frac{1}{8\pi} \int_{-1}^1 d(\cos \theta_1) \int_{-1}^1 d(\cos \theta_2) \int_0^{2\pi} d\phi \Omega^{(l, s)^*}(\theta_1, \theta_2, \phi, T),$$

where the quantities  $\Omega^{(l, s)}(\theta_1, \theta_2, \phi, T)$  are the collision integrals calculated using the standard formulae [6] only with the full anisotropic potential evaluated at the fixed orientation given by  $(\theta_1, \theta_2, \phi)$  [see equations (8) and (9)]. At a given fixed orientation, the collision integrals were evaluated by the method of O'Hara and Smith [31, 32] and the triple integration over angles was performed by a three-fold application of a one-dimensional Chebyshev integration technique. The complete computer program has been described in detail elsewhere [33]. $\ddagger$

The final collision integrals obtained for CO<sub>2</sub> are listed in table 2. The accuracy of these calculations was checked by means of comparisons with previous results [34] for the 12-6 potential (without the induced dipole term) and by examining the divided differences calculated from table 2. Overall, the accuracy of these collision integrals is believed to be no worse than 0.1 per cent, which should be more than adequate for most applications.

#### 4.3. Second pressure and dielectric virial coefficients

The second pressure virial coefficient is defined by the expansion of the compressibility factor in powers of the density, viz.

$$\frac{P}{\rho RT} = 1 + B(T)\rho + C(T)\rho^2 + \dots,$$

where  $\rho$  is the density in mol/l,  $R$  is the gas constant and  $B(T)$  is the second pressure virial coefficient at a temperature  $T$ . For polyatomic molecules,  $B(T)$  is related to the intermolecular potential by the formula

$$B(T) = -\frac{1}{2} \iint (\exp[-\beta\Phi(\mathbf{R}_1, \mathbf{R}_2)] - 1) d\mathbf{R}_1 d\mathbf{R}_2$$

$\dagger$  It was observed that it made no difference in the final viscosity fit if the second-order correction to the viscosity was used or not;  $\sigma$  and  $\epsilon/k$  merely changed slightly to compensate for this correction.

$\ddagger$  The method of calculating the collision integrals used here is slightly different from that used originally by Smith *et al.* [34] in that the  $\Omega^{(l, s)}(\theta_1, \theta_2, \phi, T)$  were not found by an interpolation technique and that some small inconsistencies in the original O'Hara and Smith programme had been corrected.

$T^*$	$\langle \Omega^{(1, 1)*} \rangle$	$\langle \Omega^{(1, 2)*} \rangle$	$\langle \Omega^{(2, 2)*} \rangle$	$\langle \Omega^{(1, 3)*} \rangle$	$\langle \Omega^{(2, 3)*} \rangle$	$\langle \Omega^{(3, 3)*} \rangle$
0.6	1.918145	1.613920	2.099084	1.413648	1.868458	1.737636
0.7	1.781597	1.495825	1.959346	1.312793	1.737179	1.615179
0.8	1.670502	1.402237	1.843281	1.235088	1.630116	1.517277
0.9	1.578491	1.326852	1.745217	1.173889	1.541599	1.437453
1.0	1.501419	1.265064	1.661469	1.124538	1.467775	1.371155
1.2	1.379425	1.170187	1.527171	1.050241	1.352501	1.267839
1.4	1.287793	1.101245	1.424810	0.997062	1.267538	1.191492
1.6	1.216815	1.048836	1.344990	0.957022	1.202899	1.132985
1.8	1.160205	1.007845	1.281204	0.925622	1.152307	1.086740
2.0	1.114213	0.974865	1.229252	0.900202	1.111722	1.049305
2.2	1.075924	0.947650	1.186210	0.879102	1.078463	1.018400
2.4	1.043669	0.924712	1.150147	0.861197	1.050667	0.992463
2.6	1.016021	0.905053	1.119461	0.845736	1.027082	0.970327
2.8	0.992127	0.887999	1.093026	0.832190	1.006755	0.951195
3.0	0.971200	0.873005	1.069972	0.820172	0.989038	0.934444
3.2	0.952730	0.859702	1.049699	0.809396	0.973430	0.919624
3.4	0.936241	0.847772	1.031704	0.799642	0.959541	0.906391
3.6	0.921414	0.836984	1.015615	0.790743	0.947076	0.894480
3.8	0.908008	0.827166	1.001144	0.782569	0.935804	0.883683
4.0	0.895815	0.818171	0.988039	0.775017	0.925535	0.873834
5.0	0.847952	0.782120	0.937120	0.744143	0.884975	0.834838
6.0	0.814036	0.755630	0.901539	0.720850	0.855774	0.806696
7.0	0.788234	0.734855	0.874684	0.702208	0.833129	0.784873
8.0	0.767590	0.717827	0.853307	0.686699	0.814696	0.767116
9.0	0.750490	0.703430	0.835634	0.673439	0.799175	0.752175
10.0	0.735956	0.690979	0.820613	0.661872	0.785778	0.739293
15.0	0.685119	0.646018	0.767944	0.619504	0.737428	0.692923
20.0	0.652640	0.616311	0.733969	0.591144	0.705330	0.662260
25.0	0.628915	0.594251	0.708908	0.569969	0.681352	0.639418

Table 2. Angle average collision integrals for carbon dioxide.

where  $\beta = 1/kT$  and  $d\mathbf{R}_i = d\mathbf{R}_i d\omega_i$ . In general, the indicated angular integrations cannot be performed analytically, and therefore the non-spherical portion of the Boltzmann factor is expanded in powers of  $\beta$  [35], to yield, in our case

$$B(T) = B_0(T) + \frac{1}{2} \sum_{n=1}^{\infty} \sum_{m=0}^n \frac{(-\beta)^n}{n!} C_m^n \int \langle \phi_{\text{perm}}^m \phi_{\text{ind}}^{n-m} \rangle \exp(-\beta \phi_{m-6-8}) d\mathbf{r}$$

where  $C_m^n$  is the binomial coefficient and the brackets  $\langle \rangle$  indicate integration over the angular coordinates. The non-spherical contributions can then be treated as perturbations and the infinite series may be truncated at some (usually arbitrary) order. For most quadrupolar fluids, only a few terms need to be considered [36], however, owing to the magnitude of the quadrupole moment in CO<sub>2</sub> (see table 1), the series of terms  $\langle \phi_{\text{perm}}^n \rangle$  does not converge rapidly. In these calculations the series was truncated at  $n=2$  for cross-terms

$$\langle \langle \phi_{\text{perm}}^m \phi_{\text{ind}}^{n-m} \rangle \rangle$$

and pure induction terms  $\langle \phi_{\text{ind}}^{n-m} \rangle$ , and at  $n=5$  for pure permanent terms  $\langle \phi_{\text{perm}}^n \rangle$ . The resulting expression for the second virial coefficient is

$$B^*(T^*) = B(kT/\epsilon)/b_0 = B_{m-6-8}^* - \frac{9\alpha^*\Theta^{*2}}{T^*} I_8 + \frac{108\alpha^{*2}\Theta^{*2}}{25T^*} \kappa^2 I_{11} \\ + \frac{216\alpha^*\kappa\Theta^{*4}}{35T^{*2}} I_{13} - \frac{21\Theta^{*4}}{5T^{*2}} I_{10} + \frac{216\Theta^{*6}}{245T^{*3}} I_{15} - \frac{639\Theta^{*8}}{245T^{*4}} I_{20} + \frac{4608\Theta^{*10}}{4235T^{*5}} I_{28}. \quad (10)$$

The reduced quantities are defined by

$$\alpha^* = \bar{\alpha}/\sigma^3; \quad \Theta^{*2} = \Theta^2/\epsilon\sigma^5 \quad \text{and} \quad T^* = kT/\epsilon,$$

and  $b_0 = 2\pi N_0\sigma^3/3$ ,  $N_0$  is Avogadro's number and the  $I_n$  are dimensionless integrals given by

$$I_n = \int_0^\infty \exp[-\phi_{m-6-8}^*(x)/T^*] x^{-n+2} dx.$$

The polarizability anisotropy,  $\kappa$ , is defined by  $\kappa = (\alpha_L - \alpha_T)/3\bar{\alpha}$ , where  $\alpha_L$  and  $\alpha_T$  are the longitudinal and transverse components of the polarizability tensor, respectively.

In a similar way, the second dielectric virial coefficient is given by the expansion of the Clausius-Mossotti function in powers of the density, [37]

$$\frac{\epsilon - 1}{\epsilon + 2} \frac{1}{\rho} = A_D + B_D(T)\rho + \dots$$

where  $\epsilon$  is the static dielectric constant and  $B_D(T)$  is the second dielectric virial coefficient which is related to the intermolecular potential via [21, 38]

$$B_D^*(T) = B_D(T)/b_0^2 = 24\alpha^{*3}(1 + 2\kappa^2)I_6 + 12 \frac{(\alpha^{*2}\Theta^{*2})}{T^*} (1 + \frac{4}{5}\kappa^2)I_8. \quad (11)$$

All of the  $I_n(T^*)$  were calculated by means of a one-dimensional Chebyshev integration technique.

## 5. RESULTS

Given the spherical potential parameters and the molecular parameters  $\alpha$ ,  $\kappa$ , and  $\Theta$ , it is a straightforward task to evaluate the expressions for second pressure and dielectric virial coefficients. The primary computational difficulty lies in the evaluation of the collision integrals  $\langle \Omega^{(l, s)} \rangle$  since each potential tried required approximately 25 min on a CDC 7600 computer (versus approximately 4 s for a spherical potential). In order to assess the effect of the non-spherical terms on the collision integrals, figure 1 shows a deviation plot between angularly averaged and equivalent collision integrals for a spherical potential as a function of temperature. For the sake of comparison the 12-6-0 potential (Lennard-Jones 12-6) was used as the spherical potential. The solid curve was obtained using equations (6), (8)-(9) with  $\alpha^* = 0$  and  $\Theta^* = 1$  and the dashed curve shows the corresponding differences for  $\alpha^* = 0.05$  and  $\Theta^* = 1$ , parameters which roughly correspond to those of  $\text{CO}_2$ . It is observed that the primary effect of the non-spherical terms is to increase the collision integrals at a given  $T^*$  with the maximum effect around  $T^* = 2$ . The addition of an induced-dipole term in the potential makes a small but significant contribution.



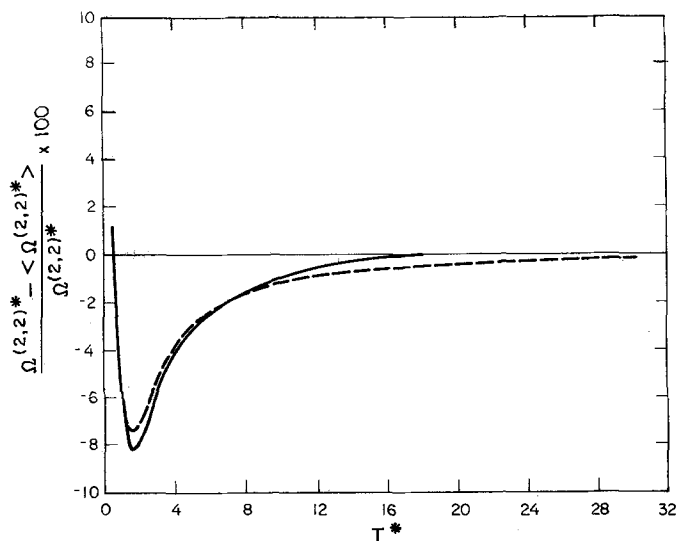


Figure 1. Percentage difference plot comparing collision integrals calculated with the spherical 12-6 potential and the 12-6 potential with non-spherical contributions. The solid curve shows the effect of the quadrupole moment and the dashed curve shows the effect of including the first-order induced dipole term (neglecting anisotropy).

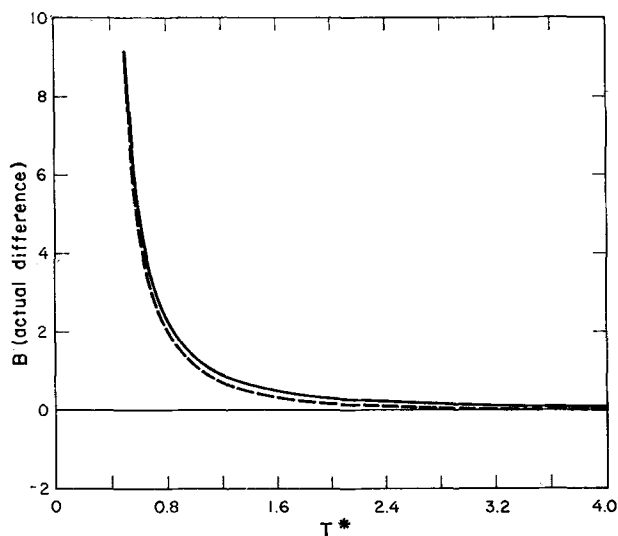


Figure 2. Corresponding plot to figure 1 only for the reduced pressure second virial coefficient.

It is interesting to note that the non-spherical contributions are most pronounced in the temperature range  $1 < T^* < 8$ . Since this corresponds to temperatures from 200 to 1750 K for CO<sub>2</sub>, and since the available experimental data lie within the range 250 to 1600 K, one would expect that a fit of viscosity

data and thus the potential parameters would be influenced by the anisotropic terms over the entire temperature range. In contrast, figure 2 shows the effect of the anisotropic term on the second pressure virial coefficient. In this case, as is well known, the non-spherical terms only make significant contributions for  $T^* < 2$  ( $\sim 400$  K).

Figures 3 and 4 show the deviations between the experimental viscosity and pressure second virial coefficients and those calculated using equations (2) and (10). The agreement with experimental data is generally satisfactory: the viscosity deviations are within the  $\pm 2$  per cent estimated experimental error. The pressure second virial coefficient deviations represent an improvement over previous calculated results [4]. The experimental pressure second virial coefficients were taken from references [39–44] and are estimated to be accurate

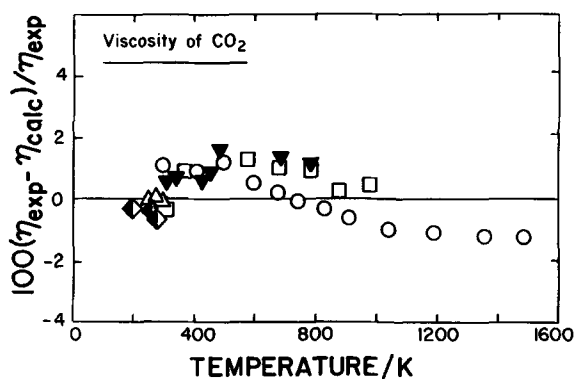


Figure 3. Percentage deviation plot for the viscosity of carbon dioxide. The calculated viscosities were obtained using equation (2) with second-order corrections and the intermolecular potential parameters listed in table 1. References:  $\blacklozenge$  [23],  $\circ$  [24],  $\triangle$  [25],  $\blacktriangle$  [26],  $\bullet$  [27],  $\square$  [28].

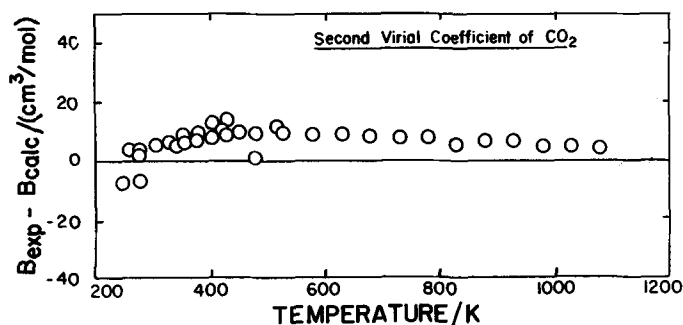


Figure 4. Difference between experimental and calculated values of the pressure second virial coefficient of  $\text{CO}_2$ . The calculated values were obtained using equation (10) and the potential parameters listed in table 1. The parameters  $m$ ,  $\gamma$ ,  $\sigma$  and  $\epsilon/k$  were determined by fitting the dilute gas viscosity, as described in § 4.1. Data, not distinguished, from references [39–44].

to within  $\pm 5$  per cent. Figure 5 compares the experimental thermal conductivity coefficient [45–52] with those calculated with equation (3). The required values for the internal specific heat  $C_v^{\text{int}}$  and rotational collisional number  $Z$  were taken from references [53] and [54], respectively. Figures 6 and 7 compare calculation and experiment for the isotopic thermal diffusion factor [55] and the second dielectric virial coefficient [56–61]. In an assessment of these later three figures it should be noted that the data are not very accurate: with the exception of a few isolated data points, the accuracy of the thermal conductivity coefficient data is about 5 per cent; the second dielectric virial coefficients data about 10 per cent; and about 25 per cent for the thermal diffusion data. With the exception of figure 5, which is discussed in the next section, the agreement between theory and experiment is within these experimental uncertainties.

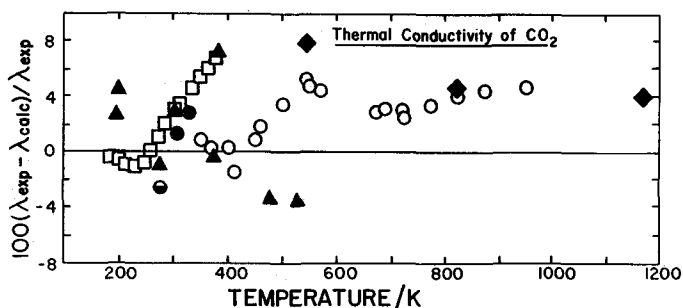


Figure 5. Percentage difference plot comparing the experimental thermal conductivities and those calculated using equation (3) with  $\rho D_{\text{int}} = \rho D_{11}$ . References:  $\square$  [45],  $\bullet$  [46–48],  $\blacktriangle$  [49],  $\bullet$  [50],  $\blacklozenge$  [51],  $\circ$  [52].

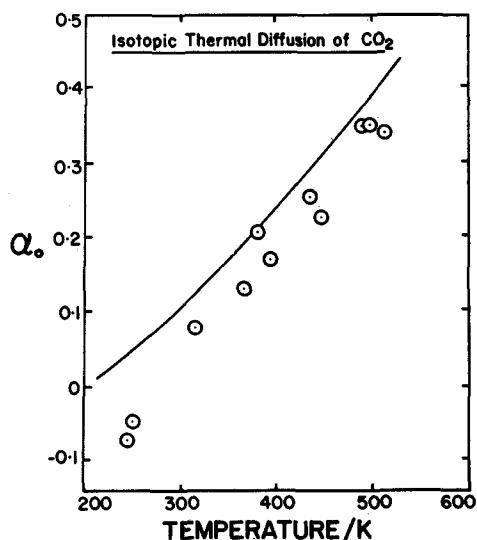


Figure 6. Isotopic thermal diffusion factor  $\alpha_0$  for  $\text{CO}_2$ . The experimental data were taken from reference [55] and the curve was calculated using equation (5).

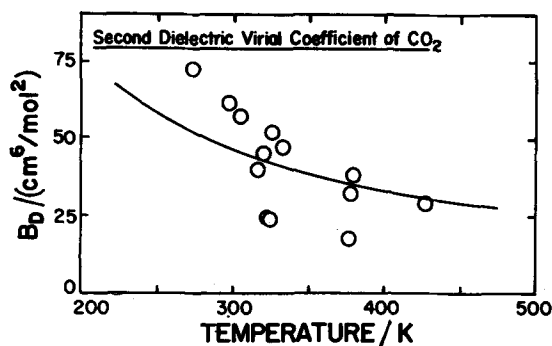


Figure 7. Dielectric second virial coefficient for CO<sub>2</sub>. The experimental data were critically evaluated by Olson [63] and the line was calculated using equation (11) with the parameters listed in table 1.

### 5.1. Discussion

Figures 3–7 effectively summarize the calculation of several quite different properties of CO<sub>2</sub> using the classical statistical mechanical formulae and the potential of equation (2). In general, we have reinforced the conclusion of our earlier work, viz. that the potential (2) is a reasonable, fairly simple model of the intermolecular potential for a simple quadrupolar gas. There are, however, two features of the results which require further consideration: (1) Systematic differences in figures 3 and 4, and (2) the thermal conductivity results, figure 5.

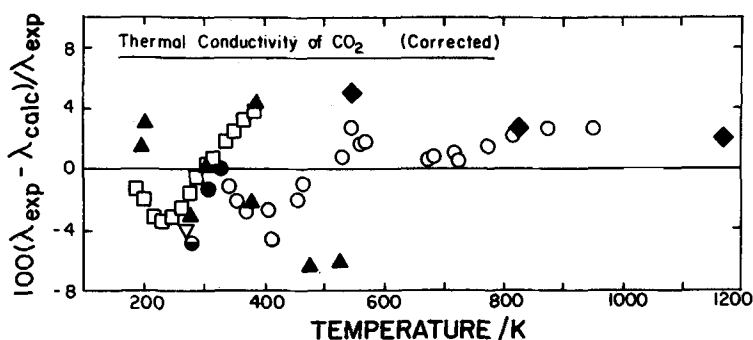


Figure 8. Recalculation of the thermal conductivity of CO<sub>2</sub> using Sandler's correction, equation (12) for  $\rho D_{int}$ . Compare to figure 5. The symbols refer to the same investigators as in figure 5.

Concerning the first point, the reasons for the small systematic differences in figures 3 and 4 have been examined. It is felt that the likely systematic errors in the data or in the calculation techniques would not give the deviation patterns observed. The deviations most probably arise either because the model potential is insufficiently flexible or because the assumptions used in the calculation of the collision integrals are not correct. It is also not obvious that the classical expansion of the second virial coefficient is converging at low temperatures. Unfortunately, these factors cannot be easily separated but we can

make several observations. (a) Other authors have suggested that terms accounting for anisotropy in the attractive and repulsive parts of the spherically symmetric part of the potential should be included. These terms were neglected in order to avoid having an empirically determined non-spherical parameter (the shape factor) in the potential. (b) The assumption that the molecules collide with fixed orientations is surely incorrect at low temperatures and low impact parameters.

With regard to the thermal conductivity, figure 5 shows that there is a systematic difference between the calculated and experimental thermal conductivity data. However, Sandler [62] has suggested that the difference between  $D_{11}$  (used for  $D_{\text{int}}$  in figure 5) and  $D_{\text{int}}$  is most pronounced for molecules with a rotational collision number  $Z$  which is less than three. According to Annis and Malinauskas [54],  $Z$  for carbon dioxide varies from 1 to 3 in the temperature range of interest here. Although Sandler's argument is for diatomic molecules the conclusion may also be valid for the linear CO<sub>2</sub> and as a matter of interest we have recalculated the thermal conductivity using his approximation for the internal diffusion coefficient (to  $1/Z$ ):

$$D_{\text{int}} = D_{11}(1 + 0.27/Z). \quad (12)$$

The resulting deviation curve is presented as figure 8 and one can see the improvement over the corresponding deviation pattern of figure 5.

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