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The Ratio D_{int}/D between the Coefficients for the Diffusion of Internal Energy and of Self Diffusion in Thermal Conductivity Data Correlations for Gases of Linear Molecules[1]

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Highly consistent sets of generalized cross sections are used to judge critically correlations of the thermal conductivity in the limit of zero density for nitrogen, carbon monoxide, and carbon dioxide. The correlations were developed by Millat, Vesovic, and Wakeham some years ago using restricted experimental information in order to deduce a set of generalized cross sections as consistent as possible for the extrapolation beyond the temperature range of the primary experimental data. Recently, the generalized cross sections needed have been evaluated by means of classical trajectory calculations for rigid rotors on the basis of accurate anisotropic *ab initio* potential energy hypersurfaces including a new improved way to take into account the vibrational degrees of freedom. It is shown that the ratio between the coefficients of internal energy and of self diffusion D_{int}/D was not appropriately chosen and that this effect was extensively compensated in a fortuitous way in the course of the development of the data correlations by a likewise unsuitable choice of the ratio A^* between the effective cross sections of viscosity and self-diffusion.

KEY WORDS: carbon monoxide; carbon dioxide; data correlation; diffusion coefficient of internal energy; nitrogen; thermal conductivity.

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1. INTRODUCTION

The formal exact kinetic theory of dilute polyatomic gases [1], which relates the transport and relaxation phenomena to a number of generalized cross sections, is well developed, but essentially more complicated than the theory for monatomic gases [2]. The complications are due to the internal energy states and to the potential energy hypersurfaces of the molecules. Nevertheless, extensive classical trajectory (CT) calculations using accurate intermolecular interaction potentials have been performed for such phenomena, but first have remained restricted to linear diatomic molecules treated under the assumption that they behave as rigid rotors. For viscosity and self diffusion it has been assumed that the effects of vibrational modes of motion can be neglected, because the vibrational state of a molecule does not practically influence the transport of mass and momentum, and that collisions characterized by an exchange of vibrational energy with translational or rotational energy are rare. However, in the case of thermal conductivity which measures the transport of *energy* through the gas, vibrational excitation of the molecule representing stored energy becomes important and the rigid-rotor assumption is much more questionable.

Heck and Dickinson as well as Heck et al. [3–5] performed rigid-rotor CT calculations for nitrogen and carbon monoxide using anisotropic *ab initio* potential energy hypersurfaces of van der Avoird et al. [6] (nitrogen) and of van der Pol et al. [7] (carbon monoxide). But in the following calculation procedure for thermal conductivity, they did not completely consider the effects of vibrational modes.

Bich et al. [8] proposed recently a distinctly improved way for the inclusion of the vibrational degrees of freedom into rigid-rotor calculations of the thermal conductivity of linear molecules and presented a re-evaluation of the results for nitrogen and carbon monoxide. The CT calculations were extended to carbon dioxide [9,10], since new *ab initio* potential-energy hypersurfaces for CO_2 were developed [11–13] and the effects of the vibrational modes on thermal conductivity have been expected to be of greater importance.

Correlations of thermal conductivity data in the limit of zero density for nitrogen and carbon monoxide were developed by Millat and Wakeham [14] and another one for carbon dioxide by Millat et al. [15] and by Vesovic et al. [16], all more than ten years ago. Unfortunately, the temperature range of selected primary experimental thermal conductivity data determined by means of the transient hot-wire technique was rather restricted (from 300 to 470 K for nitrogen and carbon dioxide and from 300 to 430 K for carbon monoxide). Hence, these authors included in their primary data sets a small number of data of significantly greater uncertainty. But they could not improve the worse situation with respect to reliable data at higher temperatures. To obtain thermal conductivity data correlations for temperature ranges similar to that for the viscosity, Millat, Vesovic, and Wakeham derived a consistent set of generalized cross sections for the real gases under discussion using auxiliary experimental data available for the complete temperature range intended. The theoretically-based procedure for the extrapolation to high temperatures was essentially based on the ratio between the coefficients for the diffusion of internal energy and of self diffusion D_{int}/D including two comparably rough approximations.

In this paper the reliability of the data correlations for the three gases is assessed by comparison with the results of the CT calculations. The correlations are particularly discussed with regard to the fact that the high-temperature limit for D_{int}/D used by Millat, Vesovic, and Wakeham should not be achieved at such low temperatures like 500 K.

2. THEORETICAL FORMULATION FOR A REAL GAS OF LINEAR MOLECULES

In the first-order approximation of the kinetic theory, the field-free thermal conductivity for a polyatomic gas is given according to the two-flux approach as the sum of the translational part $[\lambda_{\mathrm{tr}}]_1$ and internal part $[\lambda_{\mathrm{int}}]_1$.

$$[\lambda]_1 = [\lambda_{\mathrm{tr}}]_1 + [\lambda_{\mathrm{int}}]_1 = \frac{5k_{\mathrm{B}}^2 T}{2m\langle v\rangle_0} \left\{ \frac{S_{11}^{(1)} - rS_{21}^{(1)}}{S^{(1)}} + \frac{r^2 S_{22}^{(1)} - rS_{12}^{(1)}}{S^{(1)}} \right\}, \tag{1}$$

with $S^{(1)}$ the determinant,

$$S^{(1)} = \begin{vmatrix} \mathfrak{S}(1010) & \mathfrak{S}\begin{pmatrix}1010\\1001\end{pmatrix} \\ \mathfrak{S}\begin{pmatrix}1001\\1010\end{pmatrix} & \mathfrak{S}(1001) \end{vmatrix} \tag{2}$$

and $S_{ij}^{(1)}$ its minors. $\langle v\rangle_0$ is the average thermal velocity,

$$\langle v\rangle_0 = 4\left(\frac{k_{\mathrm{B}}T}{\pi m}\right)^{1/2} \tag{3}$$

where k_B is Boltzmann's constant, T is the temperature, and m is the mass of the molecule. r is given by

$$r = \left(\frac{2}{5}\frac{c_{\mathrm{int}}}{k_B}\right)^{1/2}. \tag{4}$$

Here c_{int} is the contribution of both the rotational, $c_{\mathrm{rot}} = k_B$, and the vibrational, c_{vib}, degrees of freedom to the isochoric heat capacity, c_V, for linear molecules.

$$c_{\mathrm{int}} = c_{\mathrm{rot}} + c_{\mathrm{vib}} \tag{5}$$

The generalized cross sections $\mathfrak{S}\begin{pmatrix} p\,q\,s\,t \\ p'q's't' \end{pmatrix}$ represent the collisional coupling between the microscopic tensor polarizations of the reduced molecular velocity $\mathbf{W}$ and the rotational angular momentum $\mathbf{j}$. The notation used in their labeling is fully given in McCourt et al. [1].

The two-term expansion given in Eq. (1) does not give an exact solution of the generalized Boltzmann equation [1,17], but it yields already a good approximation. There exist two independent second-order contributions to the thermal conductivity. Formulae for the second-order approximation resulting from the tensorial basis set function Φ^{10st} were reported by Maitland et al. [18]. This second-order contribution is only up to 1% related to the first-order contribution and has not been used in the development of the data correlations. The second contribution to the thermal conductivity coefficient, termed polarization contribution and considered in the data correlations, arises because the nonequilibrium distribution function for a polyatomic gas is generally anisotropic in the rotor angular momentum $\mathbf{j}$. The second-order approximation for the thermal conductivity in the field-free case, which includes only the main polarization contribution and is known as the Kagan-Afanasev approximation [19], can be formulated according to a proposal by Viehland et al. [20] as

$$[\lambda]'_2 = [\lambda_{\mathrm{tr}}]_1 + [\lambda_{\mathrm{int}}]_1\, S_\lambda \tag{6}$$

$$S_\lambda = 1 + \frac{\bar{\mathfrak{S}}\begin{pmatrix}1200\\1001\end{pmatrix}^2}{\mathfrak{S}(1001)\bar{\mathfrak{S}}(1200)^{(1)}} \tag{7}$$

Relations between unbarred and barred cross sections occurring in Eq. (7) are given in Ref. 1.

As already stated in Section 1, real gases of diatomic and triatomic molecules cannot be considered as composed of rigid rotors. Nevertheless, both the *ab initio* calculations of the intermolecular potential hypersurfaces and the CT calculations have been performed under this assumption. Hence, the generalized cross sections obtained from the CT calculations correspond to $\mathfrak{S}\begin{pmatrix} p & q & s & t \\ p' & q' & s' & t' \end{pmatrix}^{(k)}_{\text{rot}}$, whereas the theoretical formulation given above requires generalized cross sections $\mathfrak{S}\begin{pmatrix} p & q & s & t \\ p' & q' & s' & t' \end{pmatrix}^{(k)}_{\text{int}}$ taking into account all the internal degrees of freedom.

Recently Bich et al. [8] and Bock et al. [10] have proposed a very reasonable procedure for the modification of the rigid-rotor generalized cross sections needed for the calculation of the thermal conductivity. Here, the generalized cross sections can be expressed as

$$\mathfrak{S}\begin{pmatrix} p & q & s & t \\ p' & q' & s' & t' \end{pmatrix}_{\text{int}} = \left(\frac{c_{\text{rot}}}{c_{\text{int}}}\right)^{(t+t')/2} \mathfrak{S}\begin{pmatrix} p & q & s & t \\ p' & q' & s' & t' \end{pmatrix}_{\text{rot}}, \qquad t+t' \leqslant 1. \tag{8}$$

Then in the first-order approximation of thermal conductivity, i.e., in Eqs. (1) and (2), the cross section $\mathfrak{S}(1010)_{\text{int}}$ corresponds practically to $\mathfrak{S}(1010)_{\text{rot}}$ resulting from the CT calculations, whereas $\mathfrak{S}\begin{pmatrix} 1010 \\ 1001 \end{pmatrix}_{\text{int}}$ has to be deduced from $\mathfrak{S}\begin{pmatrix} 1010 \\ 1001 \end{pmatrix}_{\text{rot}}$ by means of Eq. (8). For cross sections of the type $t+t' \geqslant 2$, more complex expressions are obtained. Specifically, for the cross section $\mathfrak{S}(1001)_{\text{int}}$ also entering the first-order approximation, it results [8,10] in

$$\mathfrak{S}(1001)_{\text{int}} = \frac{c_{\text{rot}}}{c_{\text{int}}} \mathfrak{S}(1001)_{\text{rot}} + \frac{c_{\text{vib}}}{c_{\text{int}}} \mathfrak{S}'(1000)_{\text{rot}}. \tag{9}$$

$\mathfrak{S}'(1000)_{\text{rot}}$ corresponds to the so-called self-part for one molecule and is related to the self-diffusion coefficient.

3. METHODOLOGY OF DATA CORRELATION

To derive thermal conductivity data correlations for temperature ranges as large as possible, Millat and Wakeham [14] for nitrogen and carbon monoxide as well as Millat et al. [15] and Vesovic et al. [16] for carbon dioxide evaluated a consistent set of generalized cross sections using as auxiliary information the temperature dependences of the ideal-gas heat capacity, of the viscosity, and of the collisional numbers of the rotational and vibrational energy relaxation as well as data on the fractional change of the thermal conductivity in a magnetic field.

This analysis was based on the theoretical formulation described in the last section, i. e., on Eq. (6) including Eqs. (1), (2), and (7). In particular, expressions for the temperature dependence of the three generalized cross sections $\mathfrak{S}(1010)$, $\mathfrak{S}(1001)$, and $\mathfrak{S}\left(\begin{smallmatrix}1010\\1001\end{smallmatrix}\right)$ occurring in the first-order approximation are needed. Two of them are related to other generalized cross sections by means of the following exact relationships where the cross sections $\mathfrak{S}(0010)$ and $\mathfrak{S}(0001)$ are associated according to the conservation law of energy:

$$\mathfrak{S}(1010) = \frac{2}{3}\mathfrak{S}(2000) + \frac{5}{6}\mathfrak{S}(0010) = \frac{2}{3}\mathfrak{S}(2000) + \frac{25}{18}r^2\mathfrak{S}(0001) \quad (10)$$

$$\mathfrak{S}\begin{pmatrix}1010\\1001\end{pmatrix} = -\frac{1}{2r}\mathfrak{S}(0010) = -\frac{5r}{6}\mathfrak{S}(0001) \quad (11)$$

The ideal-gas heat capacities at constant pressure were used to get c_{int} as well as c_{rot} and c_{vib} using Eq. (5) for the corresponding gases.

Values of the generalized cross section $\mathfrak{S}(2000)$ were deduced from experimentally based viscosity data correlations of the gases via

$$[\eta]_1 = \frac{k_B T}{\langle v \rangle_0} \frac{1}{\mathfrak{S}(2000)} \quad (12)$$

The generalized cross section $\mathfrak{S}(0001)$ is related to the collisional number for internal energy relaxation by

$$\zeta_{\text{int}} = \frac{4}{\pi} \frac{\mathfrak{S}(2000)}{\mathfrak{S}(0001)} \quad (13)$$

Whereas $\mathfrak{S}(2000)$ and $\mathfrak{S}(0010)$ are practically not influenced by vibrational degrees of freedom, $\mathfrak{S}(0001)$ and ζ_{int} include contributions of rotational and vibrational degrees of freedom.

$$\frac{c_{\text{int}}}{\zeta_{\text{int}}} = \frac{c_{\text{rot}}}{\zeta_{\text{rot}}} + \frac{c_{\text{vib}}}{\zeta_{\text{vib}}} \quad (14)$$

The relationship Eq. (14) can in those cases, in which the vibrational collisional numbers are much larger than the rotational ones, be approximated by

$$\frac{c_{\text{int}}}{\zeta_{\text{int}}} \approx \frac{c_{\text{rot}}}{\zeta_{\text{rot}}} \quad (15)$$

Measurements of ζ_{vib} as well as of ζ_{rot} are needed to derive $\mathfrak{S}(0001)$ for the real gas by means of Eqs. (14) or (15). Since there existed only a limited number of measurements, such as the determination of thermomolecular pressure differences, which allow rotational collisional numbers ζ_{rot} to be deduced [21], Millat et al. [14,15] used a relationship by Brau and

Jonkman [22] to generate the temperature dependence of ζ_{rot} for the complete temperature range corresponding to that of $\mathfrak{S}(2000)$.

$$\zeta_{\text{rot}} = \zeta_{\text{rot}}^{\infty} \left[1 + \frac{\pi^{3/2}/2}{T^{*1/2}} + \frac{2+\pi^2/4}{T^*} + \frac{\pi^{3/2}}{T^{*3/2}} \right]^{-1} \tag{16}$$

Here T^* is the temperature reduced by an averaged energy scaling parameter. Millat, Vesovic, and Wakeham did not take into account the vibrational energy relaxation in the case of nitrogen and carbon monoxide by using Eq. (15), but for carbon dioxide, Millat et al. [15] considered ζ_{vib} values taken from the literature.

The relationships Eqs. (10) and (11) together with the deduced generalized cross sections $\mathfrak{S}(2000)$ and $\mathfrak{S}(0001)$ were used to get values of the cross sections $\mathfrak{S}\begin{pmatrix}1010\\1001\end{pmatrix}$ and $\mathfrak{S}(1010)$.

The cross sections needed for S_λ of the real gas in Eq. (6) including Eq. (7) are related to values measured in applied magnetic fields at saturation (high magnetic field to pressure ratio).

$$S_\lambda = 1 - \frac{5}{3}\left(1 + \frac{\lambda_{\text{tr}}}{\lambda_{\text{int}}}\right)\left(\frac{\Delta\lambda_{\parallel}}{\lambda}\right)_{\text{sat}} \tag{17}$$

$(\Delta\lambda_{\parallel}/\lambda)_{\text{sat}}$ represents the saturation value of the relative change of λ measured parallel to an applied magnetic field. Millat, Vesovic, and Wakeham employed experimental $(\Delta\lambda_{\parallel}/\lambda)_{\text{sat}}$ values, assumed to be almost temperature-independent, together with experimental thermal-conductivity data to derive $\mathfrak{S}(1001)$ values for the real gas. In this way they got a consistent set of generalized cross sections for the restricted temperature range of the primary data.

In order to extend the temperature range beyond that of the primary thermal conductivity data, particularly to high temperatures, Millat, Vesovic, and Wakeham tried to substitute the temperature function of the generalized cross section $\mathfrak{S}(1001)$ by that of the so-called diffusion coefficient of internal energy D_{int}, which was introduced and defined by Mason and Monchick [23], Monchick et al. [24], and Viehland et al. [20]:

$$[D_{\text{int}}]_1 = \frac{k_B T}{nm\langle v\rangle_0}\left[\frac{1}{\mathfrak{S}(1001)_{\text{int}} - \frac{1}{2}\mathfrak{S}(0001)_{\text{int}}}\right] \tag{18}$$

Here, n is the number density. Because D_{int} is practically not measurable, they replaced D_{int} by the ratio of the diffusion coefficient of internal energy to the self-diffusion coefficient including two very rough approximations. The ratio D_{int}/D as a function of temperature is exactly given in the first approximation of the kinetic theory by

$$\left[\frac{D_{\mathrm{int}}}{D}\right]_1 = \frac{\mathfrak{S}'(1000)_{\mathrm{rot}}}{\mathfrak{S}(1001)_{\mathrm{int}} - \frac{1}{2}\mathfrak{S}(0001)_{\mathrm{int}}} \tag{19}$$

One approximation of Millat, Vesovic, and Wakeham concerns the generalized cross section $\mathfrak{S}(1001)$ itself. For rigid-rotor molecules at high temperatures it has been shown [25,26] that $\mathfrak{S}(1001)_{\mathrm{rot}}$ can be approximated by

$$\mathfrak{S}(1001)_{\mathrm{rot}} \approx \mathfrak{S}^{\mathrm{sph}}(1001) + \frac{35}{12} r_{\mathrm{rot}}^2 \mathfrak{S}(0001)_{\mathrm{rot}} \tag{20}$$

where the spherical part of the effective cross section $\mathfrak{S}^{\mathrm{sph}}(1001)$ can be identified to be the self-diffusion cross section $\mathfrak{S}'(1000)_{\mathrm{rot}}$. Then the ratio of the diffusion coefficient of the rotational energy to the self-diffusion coefficient is approximately given in the high-temperature limit by

$$\left[\frac{D_{\mathrm{rot}}}{D}\right]_1 \approx \frac{\mathfrak{S}'(1000)_{\mathrm{rot}}}{\mathfrak{S}'(1000)_{\mathrm{rot}} + \left(\frac{35}{12} r_{\mathrm{rot}}^2 - \frac{1}{2}\right)\mathfrak{S}(0001)_{\mathrm{rot}}} \tag{21}$$

The limiting value of this ratio at very high temperature should approach unity from below, since $\mathfrak{S}(0001)_{\mathrm{rot}}$ will become zero at $T \rightarrow \infty$.

$$\lim_{T\rightarrow\infty}\left[\frac{D_{\mathrm{rot}}}{D}\right]_1 \approx 1 \tag{22}$$

It is to be stressed that this approximate relation was derived for the distorted wave Born approximation in the case of homonuclear or nearly homonuclear diatomic molecules [1,25,26]. It was also adopted by Millat, Vesovic, and Wakeham to be valid for real gases of linear molecules. This approximation is to be compared with values for the exact first-order approximation of a gas consisting of rigid-rotor molecules,

$$\left[\frac{D_{\mathrm{rot}}}{D}\right]_1 = \frac{\mathfrak{S}'(1000)_{\mathrm{rot}}}{\mathfrak{S}(1001)_{\mathrm{rot}} - \frac{1}{2}\mathfrak{S}(0001)_{\mathrm{rot}}} \tag{23}$$

as well as with values of $[D_{\mathrm{int}}/D]_1$ according to Eq. (19) for a real gas.

The second approximation is related to the self-diffusion coefficient for which only a limited number of measurements with moderate uncertainty in a restricted temperature range is available. In principle, D or better $\mathfrak{S}'(1000)$ could be substituted by means of the infinite-order sudden approximation (IOSA) or the Mason–Monchick approximation (MMA) as its classical limit [23,27,28]. In the framework of the MMA the generalized cross sections, which measure the rotational relaxation like $\mathfrak{S}(0001)$, are zero. Hence, the ratio $[D_{\text{rot}}/D]_1$ is equal to unity at all temperatures. The MMA is comparably more successful in evaluating the effective cross sections dominated by elastic and weakly inelastic collisions, that means $\mathfrak{S}(2000)$, $\mathfrak{S}'(1000)$, and their dimensionless ratio,

$$A^* = \frac{5}{6}\frac{\mathfrak{S}(2000)}{\mathfrak{S}'(1000)}, \tag{24}$$

as well as the relationship between the self-diffusion and viscosity coefficients:

$$[D]_1 = \frac{[\eta]_1}{nm}\frac{\mathfrak{S}(2000)}{\mathfrak{S}'(1000)} = \frac{[\eta]_1}{nm}\frac{6A^*}{5} \tag{25}$$

Millat, Vesovic, and Wakeham could not use the MMA result of the dimensionless ratio A^* for the corresponding intermolecular potential energy surfaces of the molecular gases under discussion and were forced to evaluate A^* according to the theorem of corresponding states for monatomic gases [2]. For monatomics, A^* is weakly dependent on the spherical pair potential between the molecules and also weakly dependent on temperature.

As a summary, the following relationship is to be considered as the working equation for the generalized cross section $\mathfrak{S}(1001)$:

$$\mathfrak{S}(1001) = \mathfrak{S}(2000)\left(\frac{2}{\pi\zeta_{\text{int}}} + \frac{1}{\left[\frac{D_{\text{int}}}{D}\right]_1 \frac{6}{5}A^*}\right) \tag{26}$$

In the temperature range of the primary thermal-conductivity data, the deduced $\mathfrak{S}(1001)$ values were applied to calculate and to correlate $[D_{\text{int}}/D]_1$ using the experimentally based values of $\mathfrak{S}(2000)$ and of ζ_{int} as well as A^* from the theorem of corresponding states. Surprisingly, Millat and Wakeham [14] found that $[D_{\text{int}}/D]_1$ already approached unity from below at 430 K for nitrogen and at 485 K for carbon monoxide, whereas Millat et al. [15] and Vesovic et al. [16] reported the same for carbon dioxide at 530 K. Consequently, above these temperatures $[D_{\text{int}}/D]_1$ was chosen to be unity for the thermal conductivity data correlations, so that $\mathfrak{S}(1001)_{\text{int}}$ was evaluated by means of $[D_{\text{int}}/D]_1 = 1$ for the purpose of extrapolation to high temperatures.

4. ANALYSIS AND DISCUSSION OF THE DATA CORRELATIONS

The conclusion by Millat, Vesovic, and Wakeham concerning $[D_{\text{int}}/D]_1$ is to be further considered. The argument that $[D_{\text{rot}}/D]_1$ becomes unity for rigid rotors within the distorted wave Born approximation in the limit of high temperatures is very weak. Figures 1 to 3 (Part A) make evident that the values of $[D_{\mathrm{rot}}/D]_1$ calculated according to Eq. (21) using the CT rigid-rotor calculations for the corresponding intermolecular potential-energy surfaces [6,7,12] are far from unity for all three gases. This holds even at the highest temperatures of the experimental thermal conductivity data or data correlations: 2100 K (nitrogen and carbon monoxide) and 1500 K (carbon dioxide). The closest approach to unity is found for nitrogen with 0.87 at 2100 K; the worst is given for carbon dioxide with 0.71 at 1500 K. The figures show also values for the first-order approximation of a gas consisting of rigid-rotor molecules (Eq. (23)) as well as values of $[D_{\mathrm{int}}/D]_1$ according to Eq. (19). A distinct increase of 10% and more can be seen for $[D_{\mathrm{rot}}/D]_1$ according to Eq. (23) compared with the Born approximation (Eq. (21)) for all three gases, but only for nitrogen is unity nearly approached at the highest temperatures. A further increase is illustrated for $[D_{\mathrm{int}}/D]_1$, particularly for carbon dioxide for which the vibrational degrees of freedom are of greater importance. The Parts A of the three figures demonstrate that the $[D_{\mathrm{int}}/D]_1$ values increase with a tendency to unity at high temperatures. Nevertheless, deviations of almost 5% (nitrogen at 430 K), 17% (carbon monoxide at 485 K), and nearly 9% (carbon dioxide at 530 K) are observed at those temperatures at which Millat, Vesovic, and Wakeham assumed that the ratio $[D_{\mathrm{int}}/D]_1$ already becomes unity.

Equation (26) elucidates that the deviations of $[D_{\mathrm{int}}/D]_1$ from unity can be compensated by a corresponding choice of the A^* values. In Parts B of Figs. 1–3, A^* values resulting for the theorem of corresponding states [2], for the Monchick-Mason approximation (MMA) [23,27,28], and for the CT calculations are illustrated for nitrogen, carbon monoxide, and carbon dioxide. It is to be mentioned that in the framework of the theorem of corresponding states the A^* values for nitrogen and carbon monoxide are equal and those for carbon dioxide are extrapolated beyond the validity range of the A^* functional ($T^* < 1$) at the lowest temperatures. All three figures show that the A^* values deduced for the theorem of corresponding states on the one hand and calculated for the MMA on the other hand are approximately the same. However, the A^* values resulting from the CT calculations of the generalized cross sections for the anisotropic potential-energy surfaces are higher by several per cent (3–5% for nitrogen, 5–7% for carbon monoxide, 8% for carbon dioxide). It is obvious that A^* for the molecular gases cannot be determined on the basis of the theorem of corresponding states of the monatomics or with the MMA. Furthermore, the smaller A^* values for the theorem of corresponding states are the main reason that Millat, Vesovic, and Wakeham

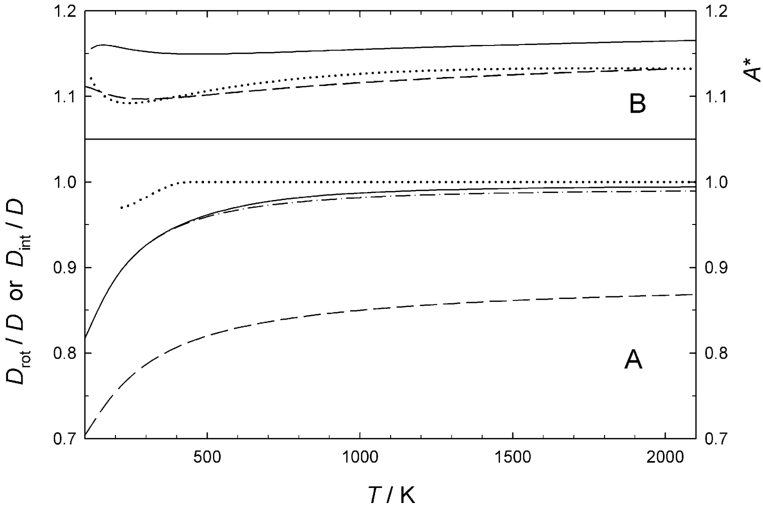

Fig. 1. Nitrogen. Part A: The ratio of the diffusion coefficient for rotational or internal energy to the self-diffusion coefficient as a function of temperature. ········· D_{int}/D according to Millat and Wakeham [14]; – – – – – $[D_{rot}/D]_1$, Eq. (21); –·–·–·–· $[D_{rot}/D]_1$, Eq. (23); ———— $[D_{int}/D]_1$, Eq. (19). Part B: The dimensionless ratio A^* (Eq. (24)) as a function of temperature. ········· according to the theorem of corresponding states [2]; – – – – – according to the Mason-Monchick approximation [23,27,28]; ———— according to the classical trajectory calculations for rigid rotors.

already obtained $[D_{int}/D]_1$ values near to unity at the higher temperatures of the range of the primary thermal conductivity data, i.e., at about 450–500 K. This statement is also of importance with respect to the discussion by Vesovic and Wakeham [28,29] that $[D_{int}/D]_1$ values above unity were deduced for methane and ethane using the analogous procedure for the development of thermal-conductivity data correlations for these gases.

Finally the choice and treatment of the collisional number ζ_{int} plays also a certain role for the $[D_{int}/D]_1$ values deduced by Millat, Vesovic, and Wakeham. Equation (26) reveals that its influence is smaller, because the contribution of the first summand in the brackets is about a tenth of the second in the case of ζ_{int} values of five to ten. In Fig. 4 ζ_{rot} values for carbon dioxide recommended by Millat et al. [15] and by Vesovic et al. [16] according to the Brau–Jonkman formula (Eq. (16)) are compared with ζ_{rot} values obtained from the exact classical trajectory calculations for rigid rotors. The figure includes also a comparison of the ζ_{int} values deduced with Eq. (14). Whereas for nitrogen and carbon monoxide the differences between the ζ_{int} values of Millat and Wakeham [14] and those resulting

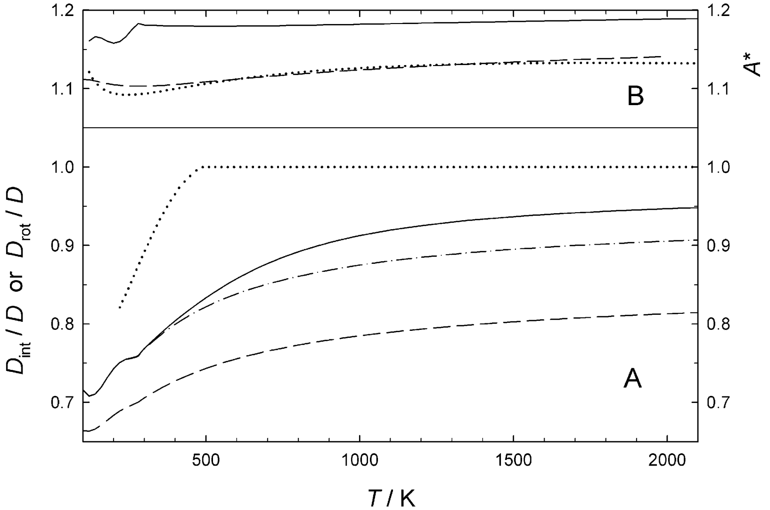

Fig. 2. Carbon monoxide. Part A: The ratio of the diffusion coefficient for rotational or internal energy to the self-diffusion coefficient as a function of temperature. Legend: the same as Fig. 1. Part B: The dimensionless ratio A^* (Eq. (24)) as a function of temperature. Legend: the same as Fig. 1.

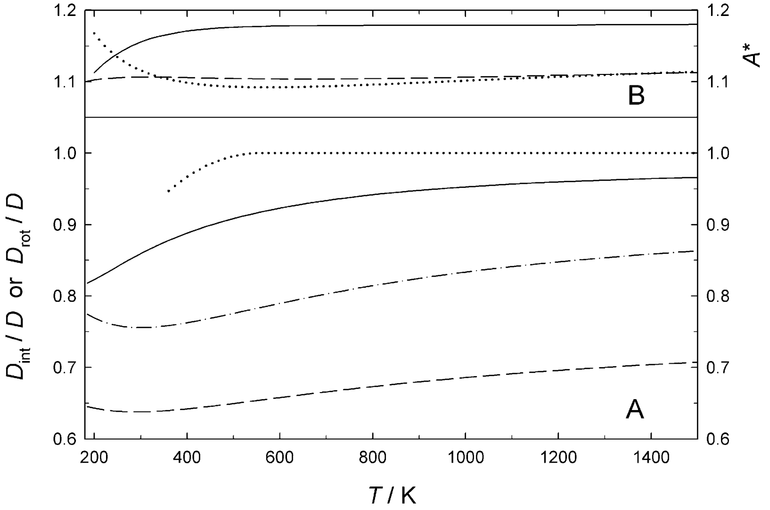

Fig. 3. Carbon dioxide. Part A: The ratio of the diffusion coefficient for rotational or internal energy to the self-diffusion coefficient as a function of temperature. ········· D_{int}/D according to Millat et al. [15] and Vesovic et al. [16]; further legend: the same as Fig. 1. Part B: The dimensionless ratio A^* (Eq. (24)) as a function of temperature. Legend: the same as Fig. 1.

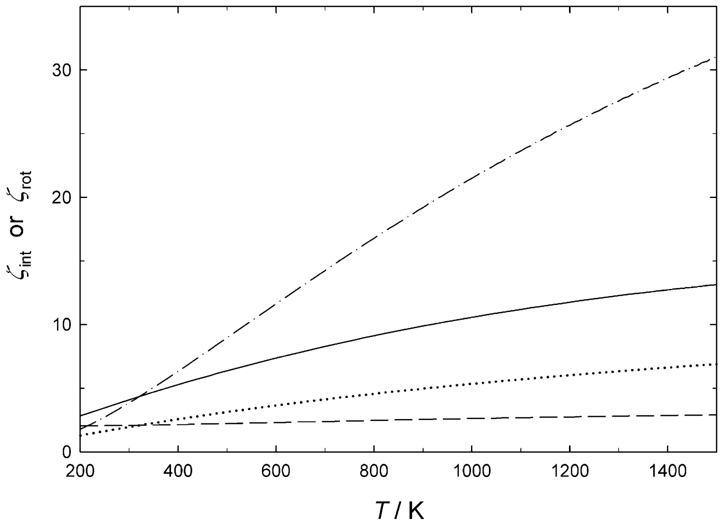

Fig. 4. Carbon dioxide. The collisional number for internal energy relaxation as a function of temperature. ········· ζ_{rot} values according to the Brau-Jonkman formula (Eq. (16)) by Millat et al. [15]; – – – – – ζ_{rot} values according to the CT calculations for rigid rotors; —·—·—· ζ_{int} values deduced with Eq. (14) via the Brau-Jonkman formula by Millat et al. [15]; ——— ζ_{int} values deduced with Eq. (14) using the CT calculations for rigid rotors.

from the classical trajectory calculations are comparably small and hence not shown, the ζ_{int} values for carbon dioxide differ by a factor of two at 1000 K. The reason is certainly that the Brau–Jonkman formula proposed for homonuclear diatomic molecules is not appropriate to model the rotational collisional number of a molecule like carbon dioxide.

The discussion shows that it is difficult to analyze in a complete manner the effects of the different input quantities used in the data correlations. Therefore, it seems to be reasonable to compare the values for the bracket expression of Eq. (26) obtained for the data correlations and following from the CT calculations. Figure 5 demonstrates for nitrogen and carbon monoxide that the corresponding differences of the bracket expression amount to approximately +4% (nitrogen) and −5% (carbon monoxide) at 700 K and decrease with increasing temperature to +2% (nitrogen) and −1% (carbon monoxide) at 2100 K. In the case of carbon dioxide (not shown here), the difference amounts to −3% at 700 K and about −1% at 1500 K. It is evident that the temperature dependence of the bracket expression is above 700 K within narrow limits the same for the correlations as well as for the CT calculations in the case of all three

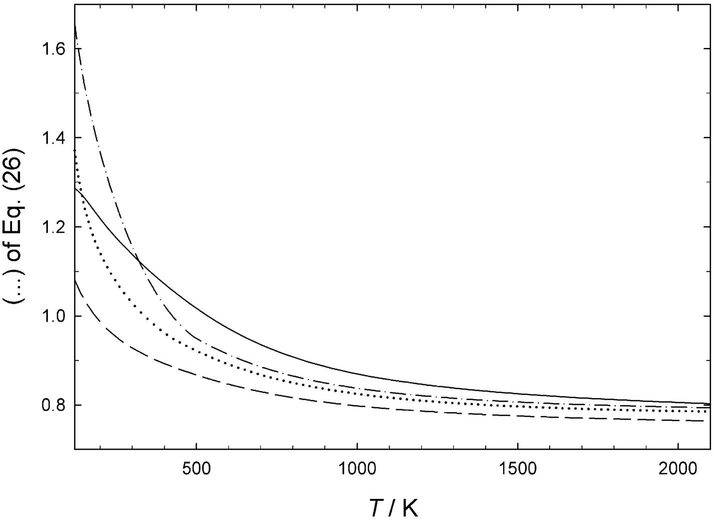

Fig. 5. Values of the bracket expression of Eq. (26) as a function of temperature. Nitrogen: ········· according to the data correlation by Millat and Wakeham [14]; — — — — — according to the CT calculations for rigid rotors. Carbon monoxide: — · — · — · — · according to the data correlation by Millat and Wakeham [14]; ———— according to the CT calculations for rigid rotors.

gases. This makes clear that the erroneous choice of $[D_{\rm int}/D]_1$ and of A^* in the course of the development of the data correlations has been mutually compensated in a fortuitous way.

5. CONCLUSIONS

More than ten years ago Millat, Vesovic, and Wakeham developed data correlations for the thermal conductivity of nitrogen, carbon monoxide, and carbon dioxide. To extend the temperature range of that correlations beyond the range of primary experimental data, the authors tried to obtain a consistent set of generalized cross sections from different experimental sources. Therefore, several approximations had to be introduced. Results of these correlations and the quality of the approximations used can now be compared with generalized cross sections evaluated by means of classical trajectory calculations for rigid rotors on the basis of accurate anisotropic *ab initio* potential energy hypersurfaces including a new improved way to take into account the vibrational degrees of freedom. The presented critical analysis makes evident that the ratio between the coefficients of internal energy and of self diffusion D_{int}/D used for the determination of the generalized cross section for the internal energy flux $\mathfrak{S}(1001)$ was not appropriately chosen. However, this effect was extensively compensated in a fortuitous way in the course of the development of the data correlations by a likewise unsuitable choice of the ratio A^* between the generalized cross sections of viscosity and self-diffusion.

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