

Calculation of the thermal conductivity of low-density CH₄-N₂ gas mixtures using an improved kinetic theory approach

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The thermal conductivity of low-density CH₄-N₂ gas mixtures has been calculated by means of the classical trajectory method using state-of-the-art intermolecular potential energy surfaces for the CH₄-CH₄, N₂-N₂, and CH₄-N₂ interactions. Results are reported in the temperature range from 70 K to 1200 K. Since the thermal conductivity is influenced by the vibrational degrees of freedom of the molecules, which are not included in the rigid-rotor classical trajectory computations, a new correction scheme to account for vibrational degrees of freedom in a dilute gas mixture is presented. The calculations show that the vibrational contribution at the highest temperature studied amounts to 46% of the total thermal conductivity of an equimolar mixture compared to 13% for pure nitrogen and 58% for pure methane. The agreement with the available experimental thermal conductivity data at room temperature is good, within $\pm 1.4\%$, whereas at higher temperatures larger deviations up to 4.5% are observed, which can be tentatively attributed to deteriorating performance of the measuring technique employed. Results are also reported for the magnitude and temperature dependence of the rotational collision number, Z_{rot} , for CH₄ relaxing in collisions with N₂ and N₂ relaxing in collisions with CH₄. Both collision numbers increase with temperature, with the former being consistently about twice the value of the latter.

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I. INTRODUCTION

The transport properties of low-density gases and their mixtures are governed solely by the dynamics of binary molecular collisions, which are determined by the intermolecular potential energy surfaces (PESs). In the kinetic theory of dilute polyatomic gases,¹ the transport properties are expressed in terms of temperature-dependent generalized collision cross sections. To compute these cross sections with good accuracy, intermolecular PESs based on high-level quantum-chemical *ab initio* calculations should be employed. Such calculations can provide a stringent test of the quality of a PES²⁻⁴ and allow us to supplement the available experimental transport property data at conditions where the data have large uncertainties or are nonexistent.⁵⁻⁹

In a previous study,¹⁰ we calculated the viscosity, η , and the product of the molar density and the binary diffusion coefficient, $\rho_m D$, for low-density mixtures of methane and nitrogen in the temperature range from 70 K to 1200 K using highly accurate PESs for the CH₄-CH₄,¹¹ N₂-N₂,¹² and CH₄-N₂¹⁰ interactions. The calculation of the generalized cross sections was performed classically within the rigid-rotor approximation, and no correction for the presence of vibrational degrees of freedom was made. This is appropriate for viscosity and diffusion, but not for the thermal conductivity, λ , which is strongly influenced by vibrational energy transport.

For pure gases, two schemes have been proposed to account for the influence of the vibrational degrees of freedom on the thermal conductivity. In both approaches, it is assumed that the vibrational states of the molecules do not change during collisions and that the influence of the vibrational motion on the collision trajectories is negligible. The latter assumption implies that knowledge of the intermolecular PES for the ground vibrational state of the molecules is sufficient to carry out the calculations of the thermal conductivity. For simple molecules, these are reasonable assumptions, which are supported by good agreement obtained so far^{3,4,7,8,12-14} between calculated and measured experimental thermal conductivity values.

In the scheme of Bich and co-workers,^{15,16} individual rigid-rotor cross sections are corrected for the effect of vibrational excitation, and the rotational contribution to the ideal-gas heat capacity, which enters the expression for the thermal conductivity, is replaced by the sum of the rotational and vibrational contributions. In an alternative approach, which was

proposed by Liang and Tsai^{17,18} for use in conjunction with molecular dynamics simulations and which was rigorously derived for the dilute-gas limit by two of the current authors¹⁴ using kinetic theory, the vibrational degrees of freedom are accounted for by means of an additive correction term to the rigid-rotor thermal conductivity,

$$\lambda = \lambda_{\text{rr}} + \lambda_{\text{vib}} = \lambda_{\text{rr}} + N_{\text{A}} C_{\text{vib}} \rho_{\text{m}} D_{\text{self}}. \quad (1)$$

Here, N_{A} is Avogadro's constant, C_{vib} is the vibrational contribution to the ideal-gas heat capacity per molecule, and $\rho_{\text{m}} D_{\text{self}}$ is the product of the molar density and the self-diffusion coefficient, which can be accurately determined using rigid-rotor cross sections. For the weakly polar molecules of interest to this work, the thermal conductivity values resulting from the two approaches differ by less than 0.1% and agree well with experimental data.¹²⁻¹⁴ However, as the polarity of the molecules increases, larger differences of up to 5% (water vapor) are observed.¹⁴ Since for polar fluids the results obtained using the scheme given by Eq. (1) are in much better agreement with experimental data,¹⁴ it is clear that this approach is to be preferred for correcting the classical rigid-rotor calculations for the presence of vibrational degrees of freedom.

In the present paper, we provide the extension of Eq. (1) to gas mixtures and report values for the thermal conductivity of dilute $\text{CH}_4\text{-N}_2$ mixtures as a function of mole fraction and temperature. The results are compared with the available experimental data. Furthermore, we analyze the rotational collision numbers for this mixture, as rotational relaxation plays an important role in determining the thermal conductivity of a gas.

II. THEORY

The transport properties of dilute gas mixtures can be calculated using the kinetic theory of polyatomic gases.^{1,19-25} For each transport coefficient, a system of linear equations needs to be solved. In the case of the thermal conductivity within the rigid-rotor approximation, λ_{rr} , the system of linear equations for a binary mixture of species A and B is given as

$$\begin{aligned} \sum_{q's't'} \left[\bar{S}_{(1q's't')}^{(1)}_{\text{AA}} X_{\text{A}}^{1q's't'} + \bar{S}_{(1q's't')}^{(1)}_{\text{AB}} X_{\text{B}}^{1q's't'} \right] &= x_{\text{A}} \delta_{q0} (\delta_{s1} \delta_{t0} C_{\text{A}}^{1010} + \delta_{s0} \delta_{t1} C_{\text{A}}^{1001}), \\ \sum_{q's't'} \left[\bar{S}_{(1q's't')}^{(1)}_{\text{BA}} X_{\text{A}}^{1q's't'} + \bar{S}_{(1q's't')}^{(1)}_{\text{BB}} X_{\text{B}}^{1q's't'} \right] &= x_{\text{B}} \delta_{q0} (\delta_{s1} \delta_{t0} C_{\text{B}}^{1010} + \delta_{s0} \delta_{t1} C_{\text{B}}^{1001}), \end{aligned} \quad (2)$$

where x_A and x_B are the mole fractions, and $X_A^{1q's't'}$ and $X_B^{1q's't'}$ are the resulting solutions of the coupled set of equations. The quantities C_α^{1010} and C_α^{1001} are given by

$$C_\alpha^{1010} = \left(\frac{5k_B T}{2m_\alpha} \right)^{1/2}, \quad C_\alpha^{1001} = \left(\frac{C_{\text{rot},\alpha} T}{m_\alpha} \right)^{1/2}, \quad (3)$$

where k_B is Boltzmann's constant, T is the temperature, and m_α and $C_{\text{rot},\alpha}$ are the molecular mass and the rotational contribution to the ideal-gas heat capacity per molecule, respectively, of component α . The coefficients $\bar{S}_{\alpha\beta}^{(p q s t)}(k)$ are given by

$$\bar{S}_{\alpha\beta}^{(p q s t)}(k) = \delta_{\alpha\beta} \sum_{\gamma} x_\alpha x_\gamma \langle v \rangle_{\alpha\gamma} \bar{\sigma}'_{\alpha\gamma}^{(p q s t)}(k) + x_\alpha x_\beta \langle v \rangle_{\alpha\beta} \bar{\sigma}''_{\alpha\beta}^{(p q s t)}(k), \quad (4)$$

where $\langle v \rangle_{\alpha\beta} = (8k_B T / \pi \mu_{\alpha\beta})^{1/2}$ is the average relative thermal speed of molecules of types α and β , $\mu_{\alpha\beta}$ is their reduced mass, and the index γ runs over both mixture components. The quantities $\bar{\sigma}'_{\alpha\beta}^{(p q s t)}(k)$ and $\bar{\sigma}''_{\alpha\beta}^{(p q s t)}(k)$ are temperature-dependent generalized cross sections for collisions between rigid-rotor molecules.^{1,10,22,25} Apart from the overbar and the added species subscripts, the present notation for the cross sections is identical to that introduced by Curtiss.²² In terms of the notation used by McCourt *et al.*,¹ we have

$$\bar{\sigma}'_{\alpha\alpha}^{(p q s t)}(k) + \bar{\sigma}''_{\alpha\alpha}^{(p q s t)}(k) \equiv \bar{\mathfrak{S}}_{\alpha\alpha}^{(p q s t | \alpha)}(k), \quad (5)$$

$$\bar{\sigma}'_{\alpha\beta}^{(p q s t)}(k) \equiv \bar{\mathfrak{S}}_{\alpha\beta}^{(p q s t | \alpha)}(k), \quad \alpha \neq \beta, \quad (6)$$

$$\bar{\sigma}''_{\alpha\beta}^{(p q s t)}(k) \equiv \bar{\mathfrak{S}}_{\alpha\beta}^{(p q s t | \beta)}(k), \quad \alpha \neq \beta. \quad (7)$$

The rigid-rotor thermal conductivity is obtained as the sum of a translational and a rotational contribution,

$$\lambda_{\text{rr}} = \lambda_{\text{tr}} + \lambda_{\text{rot}}, \quad (8)$$

with

$$\lambda_{\text{tr}} = k_B (x_A X_A^{1010} C_A^{1010} + x_B X_B^{1010} C_B^{1010}), \quad (9)$$

$$\lambda_{\text{rot}} = k_B (x_A X_A^{1001} C_A^{1001} + x_B X_B^{1001} C_B^{1001}). \quad (10)$$

The first-order approximation for λ_{rr} results from considering only the (qst) and $(q's't')$ sets (010) and (001) in Eqs. (2). For the second-order approximation, we also include the sets (020), (011), (002), (200), and (100). This definition of the second-order approximation is consistent with that given for pure gases in Ref. 14.

It is important to note that two different thermal conductivities, λ_0 and λ_∞ , can be defined for gas mixtures.^{26–28} The coefficient λ_0 would be obtained by measuring the heat flux due to an applied temperature gradient in a completely homogeneous mixture. The heat flux would then be affected by thermal diffusion, resulting in the build up of a concentration gradient until for each component the diffusive flux vanishes due to compensation of thermal diffusion by ordinary mass diffusion. As this steady state is reached very quickly, only the thermal conductivity under steady-state conditions, λ_∞ , can be determined experimentally. Contrary to intuition, even the transient hot-wire (THW) technique yields λ_∞ and not λ_0 .²⁸ The kinetic theory approach given here yields λ_∞ values. To obtain λ_0 , which is always larger than λ_∞ , one would have to additionally include the set (000) in Eqs. (2) and replace the coefficients $\bar{S}_{(1q's't'u')_{\alpha\beta}}^{(k)}$ by the coefficients $\tilde{S}_{(1q's't'u')_{\alpha\beta}}^{(k)}$ as given in Ref. 10.

To derive a scheme for the calculation of the vibrational contribution to the thermal conductivity, λ_{vib} , we define, following Ref. 14, generalized cross sections using basis functions that are products of rigid-rotor basis functions, $\Phi_k^{pqst|\alpha}$, and normalized Wang Chang–Uhlenbeck polynomials²⁹ of order u in the reduced vibrational energy. The system of linear equations for the thermal conductivity of a binary mixture with components A and B is then given as

$$\begin{aligned} & \sum_{q's't'u'} \left[\bar{S}_{(1q's't'u')_{AA}}^{(1)} X_A^{1q's't'u'} + \bar{S}_{(1q's't'u')_{AB}}^{(1)} X_B^{1q's't'u'} \right] \\ &= x_A \delta_{q0} \left(\delta_{s1} \delta_{t0} \delta_{u0} C_A^{10100} + \delta_{s0} \delta_{t1} \delta_{u0} C_A^{10010} + \delta_{s0} \delta_{t0} \delta_{u1} C_A^{10001} \right), \\ & \sum_{q's't'u'} \left[\bar{S}_{(1q's't'u')_{BA}}^{(1)} X_A^{1q's't'u'} + \bar{S}_{(1q's't'u')_{BB}}^{(1)} X_B^{1q's't'u'} \right] \\ &= x_B \delta_{q0} \left(\delta_{s1} \delta_{t0} \delta_{u0} C_B^{10100} + \delta_{s0} \delta_{t1} \delta_{u0} C_B^{10010} + \delta_{s0} \delta_{t0} \delta_{u1} C_B^{10001} \right), \end{aligned} \quad (11)$$

where $C_\alpha^{10100} = C_\alpha^{1010}$, $C_\alpha^{10010} = C_\alpha^{1001}$, and

$$C_\alpha^{10001} = \left(\frac{C_{\text{vib},\alpha} T}{m_\alpha} \right)^{1/2}. \quad (12)$$

The coefficients $\bar{S}_{(p'q's't'u')_{\alpha\beta}}^{(k)}$ are given by

$$\bar{S}_{(p'q's't'u')_{\alpha\beta}}^{(k)} = \delta_{\alpha\beta} \sum_{\gamma} x_\alpha x_\gamma \langle v \rangle_{\alpha\gamma} \bar{\sigma}'_{(p'q's't'u')_{\alpha\gamma}}^{(k)} + x_\alpha x_\beta \langle v \rangle_{\alpha\beta} \bar{\sigma}''_{(p'q's't'u')_{\alpha\beta}}^{(k)}. \quad (13)$$

The thermal conductivity is then obtained as

$$\lambda = \lambda_{\text{tr}} + \lambda_{\text{rot}} + \lambda_{\text{vib}}, \quad (14)$$

with

$$\lambda_{\text{tr}} = k_{\text{B}} (x_{\text{A}} X_{\text{A}}^{10100} C_{\text{A}}^{10100} + x_{\text{B}} X_{\text{B}}^{10100} C_{\text{B}}^{10100}), \quad (15)$$

$$\lambda_{\text{rot}} = k_{\text{B}} (x_{\text{A}} X_{\text{A}}^{10010} C_{\text{A}}^{10010} + x_{\text{B}} X_{\text{B}}^{10010} C_{\text{B}}^{10010}), \quad (16)$$

$$\lambda_{\text{vib}} = k_{\text{B}} (x_{\text{A}} X_{\text{A}}^{10001} C_{\text{A}}^{10001} + x_{\text{B}} X_{\text{B}}^{10001} C_{\text{B}}^{10001}). \quad (17)$$

If only the $(qstu)$ and $(q's't'u')$ sets (0100), (0010), and (0001) are considered in Eqs. (11), the first-order approximation for λ is obtained.

Again following the procedure summarized in Ref. 14, we can relate the generalized cross sections $\bar{\sigma}'_{\alpha\beta}(pqs't'u)^{(k)}$ and $\bar{\sigma}''_{\alpha\beta}(pqs't'u)^{(k)}$ to the rigid-rotor cross sections $\bar{\sigma}'_{\alpha\beta}(pqs't)^{(k)}$ and $\bar{\sigma}''_{\alpha\beta}(pqs't)^{(k)}$ if we assume that the vibrational motion does not influence the collision trajectories and that the vibrational states of the molecules do not change during a collision:

$$\bar{\sigma}'_{\alpha\beta}(pqs't'u)^{(k)} = \bar{\sigma}'_{\alpha\beta}(pqs't)^{(k)} \delta_{uu'}, \quad (18)$$

$$\bar{\sigma}''_{\alpha\beta}(pqs't'u)^{(k)} = \bar{\sigma}''_{\alpha\beta}(pqs't)^{(k)} \delta_{u0} \delta_{u'0}. \quad (19)$$

The coefficients of the system of linear equations (11) can then be simplified by substituting Eqs. (18) and (19) into Eq. (13) to obtain

$$\bar{S}_{\alpha\beta}(pqs't'u)^{(k)} = \delta_{uu'} \delta_{\alpha\beta} \sum_{\gamma} x_{\alpha} x_{\gamma} \langle v \rangle_{\alpha\gamma} \bar{\sigma}'_{\alpha\gamma}(pqs't)^{(k)} + \delta_{u0} \delta_{u'0} x_{\alpha} x_{\beta} \langle v \rangle_{\alpha\beta} \bar{\sigma}''_{\alpha\beta}(pqs't)^{(k)}. \quad (20)$$

Hence, for $u \neq u'$ as well as for the case that $u = u' \neq 0$ and $\alpha \neq \beta$, the coefficients are zero.

For $u = u' = 0$, we have

$$\bar{S}_{\alpha\beta}(pqs't'0)^{(k)} = \bar{S}_{\alpha\beta}(pqs't)^{(k)}, \quad (21)$$

while for $u = u' > 0$ we obtain

$$\bar{S}_{\alpha\alpha}(pqs't'u)^{(k)} = \sum_{\beta} x_{\alpha} x_{\beta} \langle v \rangle_{\alpha\beta} \bar{\sigma}'_{\alpha\beta}(pqs't)^{(k)}. \quad (22)$$

This greatly simplifies Eqs. (11). We obtain a system of linear equations for the rigid-rotor thermal conductivity (equivalent to Eqs. (2)) and for each component α an independent system of linear equations,

$$\sum_{q's't'} \bar{S}_{\alpha\alpha}(1qs't'1)^{(1)} X_{\alpha}^{1q's't'1} = x_{\alpha} \delta_{q0} \delta_{s0} \delta_{t0} C_{\alpha}^{10001}. \quad (23)$$

The solution coefficients X_{α}^{10001} yield the vibrational contribution, λ_{vib} , via Eq. (17). To obtain the first-order approximation for λ_{vib} , we only need to consider $(qst) = (q's't') =$

(000). For the second-order approximation, we also include the sets (010), (001), (200), and (100). This is consistent with the second-order approximation for pure gases given in Ref. 14.

For the first-order approximation, we obtain

$$[\lambda_{\text{vib}}]_1 = k_{\text{B}}T \sum_{\alpha} \frac{x_{\alpha} C_{\text{vib},\alpha}}{m_{\alpha}} \left(\sum_{\beta} x_{\beta} \langle v \rangle_{\alpha\beta} \sigma'(1000)_{\alpha\beta} \right)^{-1}, \quad (24)$$

where $\sigma'(1000)_{\alpha\beta}$ is a shorthand for $\bar{\sigma}'(1000)_{\alpha\beta}^{(1)}$.¹⁴ We can now introduce the first-order approximations for the self-diffusion coefficient of the pure component α ,^{1,14}

$$\rho_{\text{m}}[D_{\text{self},\alpha}]_1 = \frac{k_{\text{B}}T}{N_{\text{A}} m_{\alpha} \langle v \rangle_{\alpha\alpha} \sigma'(1000)_{\alpha\alpha}}, \quad (25)$$

and for the binary diffusion coefficient (which is independent of composition in the first-order approximation) of a mixture of unlike components ($\alpha \neq \beta$),

$$\rho_{\text{m}}[D_{\alpha\beta}]_1 = \frac{k_{\text{B}}T}{N_{\text{A}} m_{\alpha} \langle v \rangle_{\alpha\beta} \sigma'(1000)_{\alpha\beta}}, \quad (26)$$

yielding

$$[\lambda_{\text{vib}}]_1 = N_{\text{A}} \sum_{\alpha} x_{\alpha} C_{\text{vib},\alpha} \left(\frac{x_{\alpha}}{\rho_{\text{m}}[D_{\text{self},\alpha}]_1} + \sum_{\beta \neq \alpha} \frac{x_{\beta}}{\rho_{\text{m}}[D_{\alpha\beta}]_1} \right)^{-1}. \quad (27)$$

It can easily be shown that this expression holds not only for a binary mixture, but also for a multi-component one. A similar expression has already been derived by Hirschfelder³⁰ and by Monchick *et al.*²⁷ for a gas mixture consisting of spherical particles possessing internal degrees of freedom (as a simple model for polyatomic molecules). Following Hirschfelder, we define

$$\frac{1}{\rho_{\text{m}}[D_{\alpha}]_1} = \frac{x_{\alpha}}{\rho_{\text{m}}[D_{\text{self},\alpha}]_1} + \sum_{\beta \neq \alpha} \frac{x_{\beta}}{\rho_{\text{m}}[D_{\alpha\beta}]_1}. \quad (28)$$

Hirschfelder introduced D_{α} “for convenience of notation,”³⁰ but gave no physical interpretation. Since we assumed that the vibrational states of the molecules do not change during collisions, and since we are dealing with the thermal conductivity in the absence of diffusive fluxes, λ_{∞} , the only possible mechanism for the transport of vibrational energy is intradiffusion. Thus, $[D_{\alpha}]_1$ in Eq. (28) can be identified as the composition-dependent intradiffusion coefficient in the first-order approximation (we note that this relation is actually a variant of Blanc’s law^{31,32}). The total thermal conductivity of a multi-component mixture can then

be written for any order of approximation as

$$\lambda = \lambda_{\text{rr}} + N_{\text{A}} \sum_{\alpha} x_{\alpha} C_{\text{vib},\alpha} \rho_{\text{m}} D_{\alpha}. \quad (29)$$

This last expression is particularly useful for the determination of the thermal conductivity of gas mixtures by means of molecular dynamics simulations, as both the rigid-rotor thermal conductivity and the intradiffusion coefficients of the components in the mixture can be computed using established techniques.^{17,18,33,34} For a pure gas, Eq. (29) reduces to Eq. (1). Although we have derived these two equations only for the dilute-gas limit, we note that Liang and Tsai^{17,18} have demonstrated in their molecular dynamics studies of pure methane and pure carbon dioxide the suitability of Eq. (1) also for dense gases.

The scheme of Bich and coworkers^{15,16} to account for the vibrational degrees of freedom can, in the first-order approximation, easily be extended to mixtures as well. The resulting expressions for the generalized cross sections of a molecule–atom mixture have already been given by Dickinson *et al.*³⁵ The expressions for mixtures of molecular gases are provided in the supplementary material.³⁶

III. RESULTS

The generalized cross sections required for the evaluation of the thermal conductivity of dilute CH₄–N₂ mixtures were computed within the rigid-rotor approximation by means of the classical trajectory method using an extended version of the TRAJECT software code.^{10,24,25} Accurate CH₄–CH₄, N₂–N₂, and CH₄–N₂ PESs based on high-level quantum-chemical *ab initio* calculations and fine tuned to the best experimental data for the pure and cross second virial coefficients^{10–12} were employed for these calculations. The details of the trajectory calculations are given in Ref. 10 and are therefore not repeated here. The vibrational contributions to the ideal-gas heat capacities of methane and nitrogen were determined using the reference equations of state for these fluids.^{37,38}

A. Thermal conductivity

The computed values for the thermal conductivity in the second-order approximation, $[\lambda]_2$, are tabulated for 155 temperatures from 70 K to 1200 K and 11 mole fractions in the

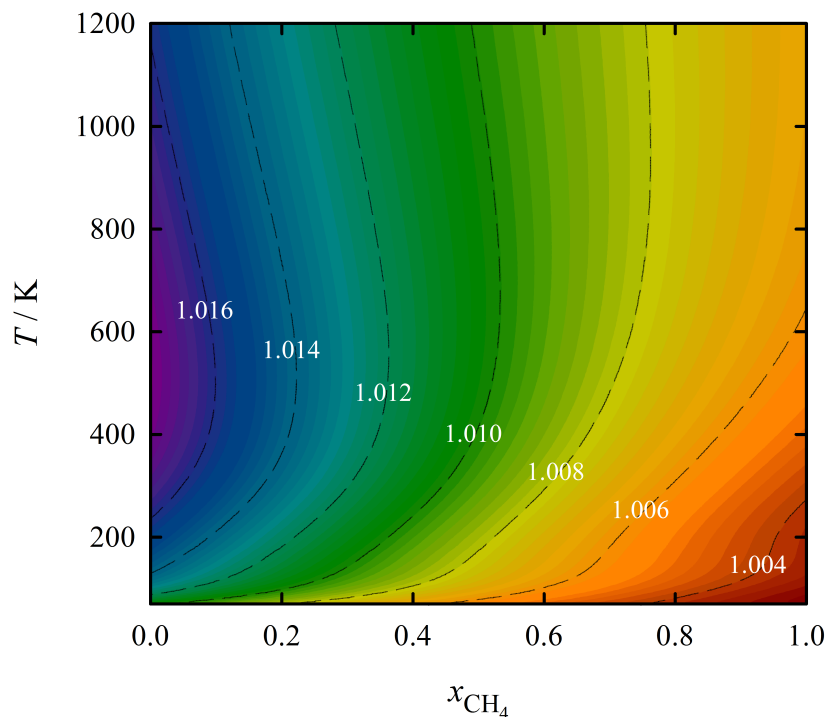


FIG. 1. Contour plot of the ratio of the thermal conductivity in the second-order approximation, $[\lambda]_2$, to that in the first-order approximation, $[\lambda]_1$, as a function of temperature and composition.

supplementary material.³⁶ The standard uncertainty of these values due to the Monte Carlo integration scheme used in the TRAJECT program to obtain ensemble averages of the cross sections is estimated to be smaller than 0.2% at all temperatures and mole fractions. The thermal conductivity values calculated for the pure components are slightly more accurate than the previously published ones,^{12,13} which were obtained using less accurate Monte Carlo integrations.

Figure 1 shows the ratio of the thermal conductivity in the second-order approximation to that in the first-order approximation. The ratio is always larger than unity, but does not exceed 1.018. We estimate that relative contributions from third- and higher-order approximations are of the order of 0.1%.

The ratio of the vibrational contribution in the second-order approximation, $[\lambda_{\text{vib}}]_2$, to the total thermal conductivity in the second-order approximation, $[\lambda]_2 = [\lambda_{\text{tr}}]_2 + [\lambda_{\text{vib}}]_2$, is shown in Fig. 2. At 300 K, the vibrational contribution amounts to 0.1%, 4.0%, and 7.0% of the total thermal conductivity of pure nitrogen, an equimolar mixture, and pure

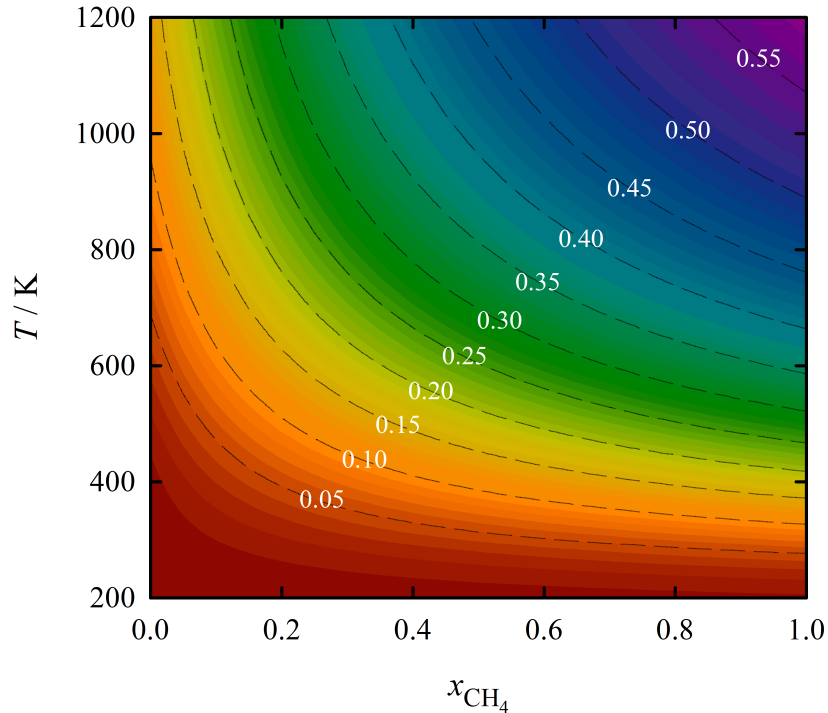


FIG. 2. Contour plot of the ratio of the vibrational contribution in the second-order approximation, $[\lambda_{\text{vib}}]_2$, to the total thermal conductivity in the second-order approximation, $[\lambda]_2$, as a function of temperature and composition.

methane, respectively, whereas the contribution at 1200 K amounts to 13%, 46%, and 58%, respectively. The vibrational contributions to the ideal-gas heat capacities are $C_{\text{vib},\text{N}_2}/k_{\text{B}} = 0.003$ and $C_{\text{vib},\text{CH}_4}/k_{\text{B}} = 0.30$ at 300 K and $C_{\text{vib},\text{N}_2}/k_{\text{B}} = 0.56$ and $C_{\text{vib},\text{CH}_4}/k_{\text{B}} = 5.67$ at 1200 K.

First-order thermal conductivity values resulting from the scheme of Bich and co-workers^{15,16} and from the approach of the present paper differ by less than 0.02% in the full range of temperature and composition.

We have also evaluated the thermal conductivity using the approach of Thijsse *et al.*,³⁹ who used a different set of expansion vectors to solve the generalized Boltzmann equation. The resulting first-order expressions for the thermal conductivity of pure gases³⁹ and mixtures^{40,41} are much simpler, and so far all results for pure gases consisting of simple non-polar or weakly polar molecules^{13,16,42} or model chain-like molecules⁴³ indicate that the two approaches give nearly identical values for the thermal conductivity, the largest rela-

tive deviations being 0.6%.² We have employed both the cross sections evaluated within the rigid-rotor approximation and the cross sections corrected for the vibrational degrees of freedom by the scheme of Bich and co-workers^{15,16,36} for the calculation of the thermal conductivity of CH₄-N₂ mixtures using the approach of Thijsse *et al.* The agreement with the thermal conductivity values obtained using the common first-order approximation, $[\lambda]_1$, is remarkably good; the difference never exceeds 0.17% either for a calculation using the corrected or the rigid-rotor cross sections.

For completeness, we have also calculated values for λ_0 . They are always within 0.05% of the values for the thermal conductivity under steady-state conditions, λ_∞ , in the range of temperatures and compositions studied in this work.

B. Dimensionless parameters

There are a number of dimensionless parameters that appear in traditional kinetic theory formulations of dilute gases. They are of interest because there is a body of evidence, based primarily on spherically symmetric pair potentials, that indicates that these parameters are only weakly dependent on temperature and nearly independent of the PES.⁴⁴ In our previous work on the calculation of the viscosity and the binary diffusion coefficient of dilute CH₄-N₂ mixtures,¹⁰ we examined the behavior of the dimensionless parameter A^* . The results concur with those for pure polyatomic species,^{2,5,43,45,46} where it was observed that the values of A^* are on average a few percent higher than those calculated for spherically symmetric potentials.^{44,47} Here, we present the first results for the parameters B^* and K^* for a binary mixture consisting of two molecular species. These two parameters appear in the practical expressions for the thermal conductivity of mixtures.^{27,44,48} Their definitions in terms of generalized cross sections^{48,49} or, for B^* , also as a ratio of traditional collision integrals^{27,44,47,50} are readily available and are not given here for brevity. Figure 3 illustrates the behavior of B^* as a function of temperature and provides a comparison with the values obtained from the universal correlation of Bzowski *et al.*⁴⁷ (using the energy scaling parameter $\varepsilon = 125$ K recommended in Ref. 47 for the CH₄-N₂ system). We observe that the B^* values obtained in this work show a similar trend as those obtained from the universal correlation, but are on average (2–3)% larger in magnitude. The parameter K^* , which is zero for a spherically symmetric potential, is small at all temperatures; it never exceeds a value of 0.023. This is

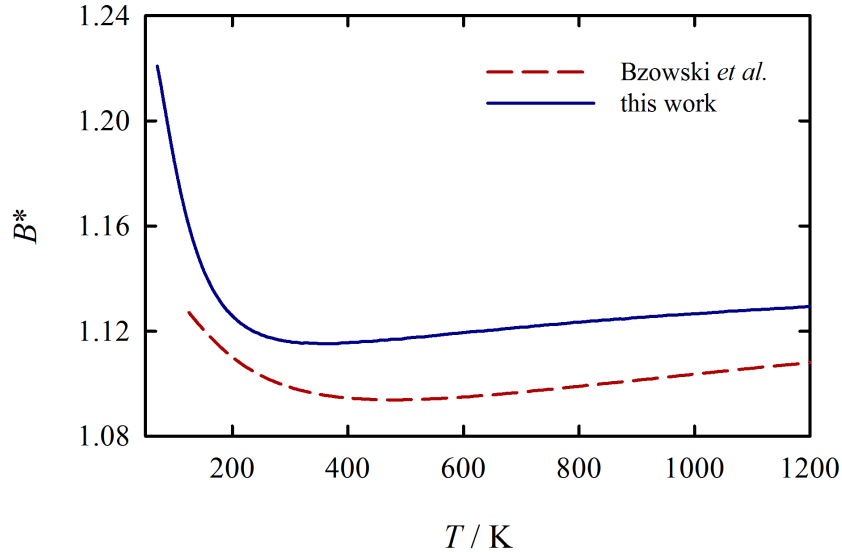


FIG. 3. Dimensionless parameter B^* as a function of temperature.

in line with previous studies on the thermal conductivity of the N_2 -He system,⁵¹ which also found K^* to be close to zero.

C. Rotational collision number

Rotational relaxation plays an important role in determining the thermal conductivity of a molecular gas. An easy measure of its efficiency is the rotational collision number (also known as rotational relaxation number), Z_{rot} , which also appears in the practical expressions for predicting the thermal conductivity.^{48,49} As Z_{rot} is also of relevance to other fields and as the literature on rotational relaxation due to molecule-molecule collisions is scant, we complete our discussion by presenting the first results for the magnitude and temperature dependence of Z_{rot} in unlike molecule-molecule interactions that do not involve hydrogen or its isotopes. Unlike the pure gas case, where one rotational collision number suffices for molecules, we need to consider two of them, $Z_{\text{rot}N_2,CH_4}$ and $Z_{\text{rot}CH_4,N_2}$, for binary collisions between methane and nitrogen. The former describes the rotational relaxation of nitrogen due to collisions with methane and the latter the rotational relaxation of methane due to collisions with nitrogen. Here, we kept to the notation introduced in Refs. 48 and 49, which also provide the full definition in terms of the cross sections, namely that $Z_{\text{rot}A,B}$ is inversely

proportional to the product of the cross section $\sigma'(0001)_{AB}$ and the interaction viscosity η_{AB} .

Figure 4 shows $Z_{\text{rotN}_2,\text{CH}_4}$ and $Z_{\text{rotCH}_4,\text{N}_2}$ as a function of temperature. Although both are determined by the same intermolecular PES, we observe that N_2 relaxes much faster (lower Z_{rot} values) than CH_4 . The difference in Z_{rot} can be attributed partly to the different moments of inertia of the relaxing molecules. To demonstrate this, we have performed additional classical trajectory computations with the moment of inertia of the methane molecule, I_{CH_4} , artificially tripled so that its value is almost equal to that of nitrogen. As illustrated in Fig. 4, this reduces $Z_{\text{rotCH}_4,\text{N}_2}$ considerably, but it is still higher than $Z_{\text{rotN}_2,\text{CH}_4}$ (which is, as expected, almost unaffected by the artificial change of the moment of inertia of CH_4 ; the resulting curve is therefore not shown in the figure). We have also performed calculations with the moment of inertia of CH_4 tripled and its mass increased to that of N_2 . However, this mass increase affects both collision numbers only by a few percent. To fully account for the observed differences, we also have to take into account that the tetrahedral methane molecule is more spherical in shape than nitrogen. As a consequence, the PES is less anisotropic with respect to the angular orientation of methane than to that of nitrogen. Therefore, even when the moments of inertia are made equal, nitrogen relaxes faster than methane since the efficiency of rotational relaxation increases with anisotropy.

IV. COMPARISON WITH EXPERIMENTAL THERMAL CONDUCTIVITY DATA

Our current best estimate for the combined expanded uncertainty (coverage factor $k = 2$) of the computed thermal conductivity values for both pure components, based on extensive comparisons with experimental data,^{12,13} is 1% between 300 K and 700 K, increasing to 2% at both 70 K and 1200 K. This estimate should also be valid for the mixtures since the PES for the $\text{CH}_4\text{-N}_2$ interaction¹⁰ is of a similar quality as the $\text{CH}_4\text{-CH}_4$ ¹¹ and $\text{N}_2\text{-N}_2$ ¹² PESs.

In Fig. 5, we compare the calculated thermal conductivity values with the available experimental data in the dilute gas phase.⁵²⁻⁵⁵ The three data points of Clingman *et al.*⁵² for nitrogen-rich mixtures at 273.15 K (pressure not given but probably 1 atm) were measured with a commercial thermal conductivity detector (calibrated against helium-argon mixtures) and agree surprisingly well with the calculated values; the deviations do not exceed 1.4%. The three data points in the limit of zero density of Kestin *et al.*⁵³ at 300.65 K for methane

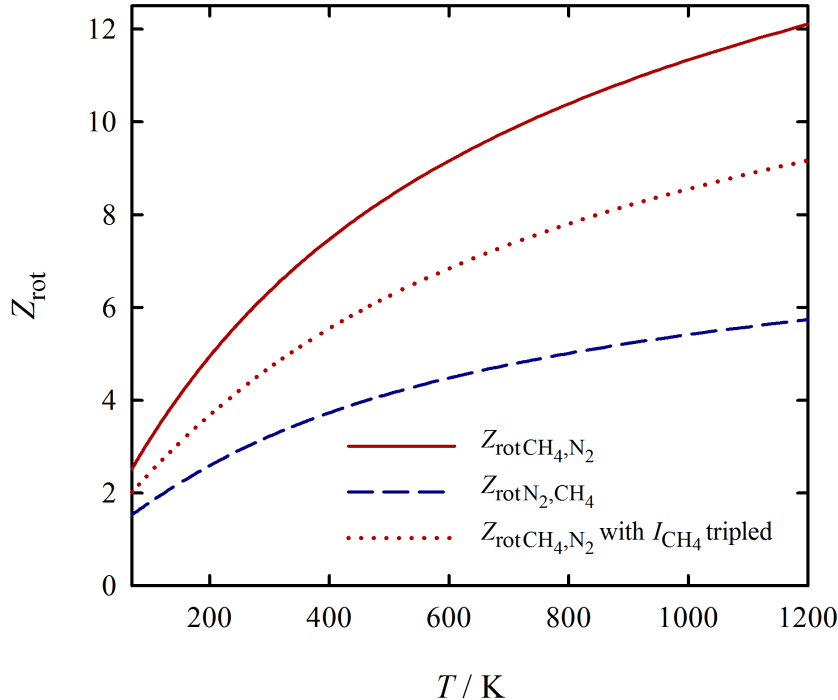


FIG. 4. Rotational collision number, Z_{rot} , as a function of temperature.

mole fractions of 0.2564, 0.5432, and 0.7707 were obtained using a THW apparatus and have a stated uncertainty of 0.3%. The agreement with our calculated values is within mutual uncertainties. Pátek *et al.*⁵⁵ also employed a THW instrument to determine the thermal conductivity at six temperatures from 300 K to 425 K for methane mole fractions of 0.25, 0.50, and 0.75 as well as for pure nitrogen. Measurements for pure methane with the same instrument at eight temperatures from 290 K to 360 K were also reported⁵⁴ (for the latter, we only show the deviations at 300 K and 350 K in the figure). The claimed uncertainty is 0.7% for pure methane⁵⁴ and 1.0% for pure nitrogen and the mixtures.⁵⁵ At 300 K, the agreement of the measured thermal conductivity with our calculated values is within the quoted experimental uncertainties for the pure gases and the three mixtures. However, at higher temperatures, we observe larger deviations for the mixtures, which increase with temperature and, to a lesser extent, with an increase in the mole fraction of methane, reaching a maximum value of +4.5%. It is not clear at the moment what causes the observed differences between the calculated and measured values. In our opinion, it is highly unlikely that the vibrational degrees of freedom were somehow not properly taken

into account in the mixture calculation considering that the two schemes employed give practically identical results. Furthermore, the approximations made regarding vibrational energy exchange are the same as for pure gases, which led to good predictions of the thermal conductivity.^{3,4,7,8,12-14} The uncertainty in the CH₄-N₂ potential is also unlikely to explain the observed high temperature increase in the deviations, as the same potential function was successfully used to predict the viscosity and the cross second virial coefficient.¹⁰ The most likely explanation is that the uncertainty of the measurements of Pátek *et al.* for the three investigated mixture compositions is higher than 1% despite the good agreement for the pure gases. In the last two decades, evidence has been emerging that measurements by means of the THW technique performed at low densities and at temperatures higher than ambient suffer from a systematic error.^{56,57} Although a large effort has gone into establishing the source of the error,⁵⁶ no credible hypothesis has been put forward that would explain the observed effect.⁵⁷ Thus, the currently circumstantial evidence is based primarily on the inability of the accepted theory for the THW technique to fully account for the observed behavior⁵⁷ and on the discrepancies between the measured thermal conductivity using THW instruments and other methods for a number of pure gases.^{4,8,13,58} There is thus an urgent need for accurate measurements of the thermal conductivity of this and similar systems using a primary instrument that is not based on the THW principle.

V. CONCLUSIONS

A method for correcting the thermal conductivity of a low-density gas mixture consisting of rigid-rotor molecules for the influence of vibrational degrees of freedom has been developed. The resulting equations, which have their basis in the kinetic theory of polyatomic gases, show that the vibrational contribution can be approximated by an additive term that depends only on the mole fractions, the vibrational contributions to the ideal-gas heat capacities, and the intradiffusion coefficients of the mixture components. The proposed correction should be most appropriate for mixtures of simple polyatomic molecules consisting of few atoms.

We have used previously reported PESs for the CH₄-CH₄,¹¹ N₂-N₂,¹² and CH₄-N₂¹⁰ interactions to compute the thermal conductivity of CH₄-N₂ mixtures in the temperature range from 70 K to 1200 K by means of the classical trajectory method. The agreement with

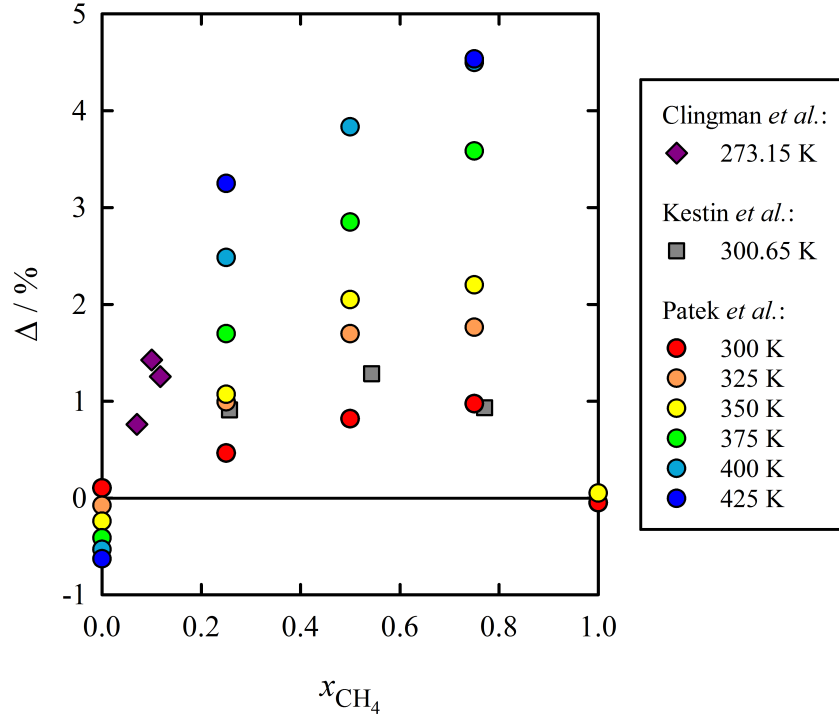


FIG. 5. Deviations, $\Delta = (\lambda_{\text{exp}} - [\lambda]_2) / [\lambda]_2$, of experimental thermal conductivity data (Refs. 52–55) from values obtained using second-order kinetic theory.

experimental data at room temperature is good; the observed deviations of at most 1.4% are within the combined overall uncertainty of the experimental data and the calculated values. At temperatures of 325 K and above, we observe a systematic increase in the deviations, reaching a maximum of 4.5%. The cause of this discrepancy is not fully understood, but there is emerging evidence that seems to indicate that thermal conductivity measurements at low densities by means of the THW technique are less accurate at elevated temperatures than at room temperature.

The calculations performed indicate that, as expected, the vibrational contribution to the thermal conductivity increases strongly with temperature and the mole fraction of methane in the mixture. For an equimolar mixture at 1200 K, it amounts to 46% of the total thermal conductivity compared to 13% for pure nitrogen and 58% for pure methane. The second-order thermal conductivity correction does not exceed 1.8% in the whole temperature and composition range, while the third-order correction is expected to be negligible. We have also calculated the thermal conductivity in the first-order order approximation using the

approach of Thijsse *et al.*³⁹ It gives nearly identical results, with deviations of at most 0.17% between the two approaches. The dimensionless parameter B^* shows a similar trend as for monoatomic systems, but is on average (2 – 3)% larger in magnitude, while the dimensionless parameter K^* is close to zero at all temperatures.

Results have also been obtained, for the first time, for the magnitude and temperature dependence of the rotational collision number, Z_{rot} , for CH_4 in collisions with N_2 and for N_2 in collisions with CH_4 . Both collision numbers increase with temperature, and the former is consistently about twice the value of the latter. The differences can be ascribed to an interplay between the anisotropy of the PES and the moment of inertia of the rotationally relaxing molecule.

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