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Thermal Conductivity of Multicomponent Polyatomic Dilute Gas Mixtures[1]

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A new expression for the thermal conductivity of an N-component polyatomic gas mixture in the dilute-gas limit has been derived, based on the Thijsse approximation. The results are presented in terms of experimentally accessible quantities to allow for easier calculation of the thermal conductivity and easier interpretation of the experimentally available data. The resulting expressions are much simpler than other formulae hitherto available. An additional new expression for the thermal conductivity of an N-component polyatomic gas mixture has been derived by replacing the effective cross-section by their spherical limits. These results are cast in a form which is analogous with, and no more complicated than, the corresponding expressions for purely monatomic mixtures.

KEY WORDS: Kinetic theory; mixture; thermal conductivity.

1. INTRODUCTION

The development of the kinetic-theory expressions for the thermal conductivity of dilute gases and their mixtures has a long and interesting history. At the beginning of this century, the foundations of the kinetic theory were laid and the expressions for the thermal conductivity of N-component

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monatomic mixtures were derived [1]. It took another 40 years for the formal kinetic theory of polyatomic gases to be developed [2]. The difficulties were essentially twofold: first, how to incorporate the internal modes of molecules into the framework and allow for the transfer of energy between translational and internal (rotational and vibrational) mode; second, how to calculate the dynamics of the molecular collisions taking place on the nonspherical intermolecular potential surface. One of the more successful approaches [2, 3] was a semiclassical treatment of Wang–Chang Uhlenbeck and de Boer (WCUB), where the solution of the generalized Boltzmann equation for a nonuniform dilute polyatomic gas is obtained by using two expansion vectors, one proportional to the translational energy and other proportional to the internal energy. The WCUB solution resulted in a set of expressions relating the transport properties of pure gases to the effective cross sections, which contain all the dynamic information about the manner in which binary molecular collisions influence appropriate transport properties. One of the criticisms of the WCUB treatment is that it is unable to account for the polarisation of angular momentum which occurs in polyatomic gases. This phenomenon [2] is of interest only if one is concerned with the influence of magnetic and electrical fields on transport properties. For the traditional transport properties, such as thermal conductivity, the WCUB equation gives the same results as the more exact Waldman–Snider equation [2] in the semiclassical limit. The advantage of the WCUB formalism is that it is rather straightforward to generalize the results to include all internal energy modes, rather than just rotational. This is important because the vibrational contribution to the thermal conductivity is significant and its neglect can lead to large errors [4].

In the early sixties Monchick et al. [5] extended the WCUB formalism to mixtures of polyatomic gases. The resulting formal expressions were sufficiently complicated and lengthy, involving a large number of cross sections, that it was not possible to make use of them in practical applications. In pioneering work Mason and his collaborators showed [6–8], based on physical arguments, that a number of cross sections entering expressions for the transport properties are of a low relative magnitude and can be neglected, while the remaining cross sections can be related, at least in principle, to experimentally measured properties. Although for the thermal conductivity of the polyatomic mixtures the expressions were still lengthy [8], this work laid the foundations for all subsequent attempts to calculate the thermal conductivity or to analyze experimental data. As such, it has had a lasting influence on the development of thermal conductivity of dilute gas mixtures.

In the late seventies Thijsse et al. [9] showed that it is possible to obtain much simpler expressions for the thermal conductivity of pure gases.

First, they showed that it is possible to obtain the expression for the thermal conductivity equivalent to the WCUB result if different expansion vectors are used. The essence of the proposal [2, 9] was that, in the solution of the generalized Boltzmann equation for a nonuniform, dilute polyatomic gas, the expansion vectors chosen for the solution should consist of one proportional to the total heat flux (translational and internal) and one proportional to the difference of the translational and internal heat fluxes. It was then showed that a greatly simplified approximate expression would be obtained if only one expansion vector was used, namely, the one proportional to the total energy flux. A number of numerical tests carried out [4, 10] for pure gases indicated that the results obtained with Thijsse's approximation are very accurate. Subsequently, Ross et al. [11] derived formal expressions for the thermal conductivity of a dilute, multicomponent polyatomic gas mixture based on Thijsse's total-energy flux approach. Recently [12] the formal expressions were examined for the simplest polyatomic mixture, namely, an atom–molecule system. The numerical tests, based on classical trajectory studies, indicated again that the Thijsse approximation is very accurate and leads to a simple final expression for the thermal conductivity of an atom–molecule system. Furthermore, it has been shown [12] that such an expression can be cast in the form analogous to that for the thermal conductivity of a monatomic mixture. Although, useful in its own right, the derived expressions contained a number of cross sections that were not readily available, which made predictions difficult for practical purposes. Hence, a further approximation was made [13] based on replacing a number of cross sections by their equivalent spherical limit. The numerical tests, using rigorous theoretical results, again indicated that such an approximation is justifiable, to within ±1%, for a number of systems studied. Finally, the resulting expressions for the thermal conductivity of an atom–molecule mixture in the spherical limit were tested against the available, accurate experimental thermal conductivity data [14]. The results were very encouraging as these rather simple expressions [14] predicted most of the data to within ±2%.

In order to confirm the more general applicability of the formulation that successfully predicted the thermal conductivity of atom–molecule mixtures, it is necessary to extend the theoretical development to encompass multicomponent polyatomic mixtures. The present paper reports on the results of such theoretical investigations and proposes two formulations of the thermal conductivity of N-component mixtures; the first based only on Thijsse approximation and the second based on replacing the cross sections of the former formulation by their spherical limit.

2. THEORY

2.1. The Formal Results of the Kinetic Theory

The thermal conductivity of a dilute N-component polyatomic gas mixture, λ^{X}, at temperature, T, can be expressed in the following form [11]:

$$\lambda^{X} = \frac{5}{2} k_{\mathrm{B}}^{2} T \sum_{q} \sum_{q'} (\mathrm{S})_{qq'}^{-1} \frac{x_q x_{q'} (1 + r_q^2)(1 + r_{q'}^2)}{\sqrt{m_q m_{q'}}} \tag{1}$$

where $(\mathrm{S})_{qq'}^{-1}$ denotes the qq' element of the inverse of $N \times N$ square matrix S. The matrix S is given by

$$\mathrm{S} = \mathrm{S}^{EE} - \mathrm{S}^{ED} (\mathrm{S}^{DD})^{-1} \mathrm{S}^{DE} \tag{2}$$

where the S^{XY} are $N \times N$ matrices whose elements are given by

$$S_{qq'}^{XY} = (1 + r_q^2)^{1/2} (1 + r_{q'}^2)^{1/2} \left[x_q x_{q'} \bar{c}_{qq'} \mathfrak{S} \begin{pmatrix} 1 & 0 & X & | & q \\ 1 & 0 & Y & | & q' \end{pmatrix}_{qq'} + \delta_{qq'} \sum_{\mu \neq q} x_\mu x_q \bar{c}_{q\mu} \mathfrak{S} \begin{pmatrix} 1 & 0 & X & | & q \\ 1 & 0 & Y & | & q \end{pmatrix}_{q\mu} \right] \tag{3}$$

where

$$r_q = \left(\frac{2 c_{\mathrm{int},\, q}}{5 k_{\mathrm{B}}} \right)^{1/2} \tag{4}$$

and

$$\bar{c}_{qq'} = \left(\frac{8 k_{\mathrm{B}} T}{\pi} \frac{(m_q + m_{q'})}{m_q m_{q'}} \right)^{1/2} \tag{5}$$

In these equations, q, q', and μ denote the molecular species, x_q is the mole fraction of species q, m its molecular mass, $c_{\mathrm{int},\, q}$ its internal, isochoric heat capacity, and k_{B} the Boltzmann constant, while $\delta_{qq'}$ represents the Kronecker delta. The effective cross sections, $\mathfrak{S}\left(\begin{smallmatrix} 1 & 0 & X & | & q \\ 1 & 0 & Y & | & q' \end{smallmatrix}\right)_{qq'}$ and $\mathfrak{S}\left(\begin{smallmatrix} 1 & 0 & X & | & q \\ 1 & 0 & Y & | & q \end{smallmatrix}\right)_{q'\mu}$, are those proposed originally by Thijsse et al. [2, 9] and generalized for mixtures [11]. The above result, Eqs. (1)–(5), is equivalent to, although much simpler, than, the traditional first-order expression for the thermal conductivity of a multicomponent gas mixture [15] which was first derived by Mason and his collaborators [5].

It is useful to cast Eq. (1) in a determinant form, in order to facilitate an easier comparison with the traditional expression of the thermal conductivity of monatomic mixture. If the elements of matrix **S** are replaced by the elements of matrix **L**,

$$S_{qq'} = \frac{5}{2} k_B^2 T \frac{(1+r_q^2)(1+r_{q'}^2)}{\sqrt{m_q m_{q'}}} L_{qq'}^{(1)} \tag{6}$$

then the expression for the thermal conductivity, Eq. (1), can be cast into the following form:

$$\lambda' = \sum_q \sum_{q'} (\mathbf{L})_{qq'}^{-1} x_q x_{q'} = \frac{\mathbf{x}^{\mathrm{T}} \mathrm{adj}(\mathbf{L}) \mathbf{x}}{\det(\mathbf{L})} \tag{7}$$

where **x** is a $1 \times N$ column vector of mole fractions, x, $\mathbf{x}^{\mathrm{T}}$ is its transpose, and adj(**L**) is the adjoint of matrix **L**. The numerator of the right-hand side of Eq. (7) can be expressed in the determinant form and one ends up with a simple expression for the thermal conductivity of the N-component polyatomic mixture,

$$\lambda' = - \begin{vmatrix} L_{11}^{(1)} & \cdots & L_{1n}^{(1)} & x_1 \\ \vdots & & \vdots & \vdots \\ L_{n1}^{(1)} & \cdots & L_{nn}^{(1)} & x_n \\ x_1 & \cdots & x_n & 0 \end{vmatrix} \Bigg/ \begin{vmatrix} L_{11}^{(1)} & \cdots & L_{1n}^{(1)} \\ \vdots & & \vdots \\ L_{n1}^{(1)} & \cdots & L_{nn}^{(1)} \end{vmatrix} \tag{8}$$

This expression is analogous to the one for the mixture of monatomic species [15]. Here we have used superscript 1 on the elements of matrix **L** to indicate that Eq. (8) is a full first-order result and no further approximations have been made in its derivation.

2.2. The Thijsse Approximation

The full formal first-order results presented above have limited practical use, since a large number of different effective cross sections that enter the expressions render any calculations or analysis of experimental thermal conductivity data very difficult. Nevertheless, it has been shown [8], based on physical arguments, that the contributions from a number of effective cross sections are likely to be very small and can be safely neglected. In order to proceed with the elimination of the relevant effective cross sections, it is necessary to evoke approximations which both simplify the thermal conductivity expression and preserve its accuracy. In the case of pure polyatomic gases [4, 9] and atom–molecule mixtures [12], it has been shown that remarkably simple and accurate formulas can be derived if Thijsse's approximation is made. The Thijsse approximation [2, 9] is based on the simple physical hypothesis that for polyatomic molecules the transfer of the total energy (translational and internal) during collisions is a primary factor in determining the thermal conductivity. Thus, any expansion vectors chosen for the solution of the generalized Boltzmann equation should be based on the total energy, rather than depending separately upon the translational and internal energy [2].

In the context of the thermal conductivity of polyatomic gas mixtures, the Thijsse approximation is equivalent to neglecting the second term in the expression for matrix S, Eq. (2) [12], and hence replacing Eq. (2) by

$$\mathbf{S} = \mathbf{S}^{EE} \tag{9}$$

If the elements of matrix $\mathbf{S}^{EE}$, Eq. (3), are then substituted into Eq. (6), the following result is obtained for the thermal conductivity:

$$\lambda'_E = -\begin{vmatrix} L_{11} & \cdots & L_{1n} & x_1 \\ \vdots & & \vdots & \vdots \\ L_{n1} & \cdots & L_{nn} & x_n \\ x_1 & \cdots & x_n & 0 \end{vmatrix} \Bigg/ \begin{vmatrix} L_{11} & \cdots & L_{1n} \\ \vdots & & \vdots \\ L_{n1} & \cdots & L_{nn} \end{vmatrix} \tag{10}$$

Here we use the symbol λ'_E, in line with our earlier notation [12], to denote the thermal conductivity based on the Thijsse approximation. The determinant elements are given by

$$L_{qq'} = \frac{2}{5k_B^2 T} \frac{\sqrt{m_q m_{q'}}}{(1+r_{q'}^2)^{1/2}(1+r_q^2)^{1/2}} x_q x_{q'} \bar{c}_{qq'} \mathfrak{S}\begin{pmatrix} 1 & 0 & E & | & q \\ 1 & 0 & E & | & q' \end{pmatrix}_{qq'}, \quad q \neq q' \tag{11}$$

$$L_{qq} = \frac{x_q^2}{\lambda_q} + \frac{2}{5k_B^2 T} \frac{m_q}{(1+r_q^2)} \sum_{\mu \neq q} x_\mu x_q \bar{c}_{\mu q} \mathfrak{S}(10E \mid q)_{q\mu} \tag{12}$$

where λ_q is the thermal conductivity of the pure component q, which, within the Thijsse approximation, is given by [2, 4, 9]

$$\lambda_q = \frac{5k_B^2 T(1+r_q^2)}{2} \frac{1}{m_q \bar{c}_{qq} \mathfrak{S}(10E \mid q)_{qq}} \tag{13}$$

For pure gases [4, 7] and for atom–diatom mixtures [12], the effective cross section entering the thermal conductivity expressions can be calculated directly from the intermolecular potential. Thus, one can estimate the accuracy of the Thijsse approximation by evaluating the thermal conductivity both in the first-order form, λ', and within the Thijsse approximation, λ'_E. Such calculations are, at present, computationally prohibitively expensive for even binary diatomic mixtures and it is therefore not possible to make comparisons between predictions of Eqs. (10)–(12) and Eqs. (1)–(5) based on kinetic theory calculations.

In order to estimate the accuracy of Eqs. (10)–(12) for predicting the thermal conductivity of polyatomic mixtures, one has to compare their predictions with the available experimental data. To facilitate such a comparison and also to have a more practical set of equations, it is necessary to eliminate from Eqs. (11)–(12) the effective cross sections in favor of measurable or more readily available quantities [8, 12, 13].

2.3. The Practical Formulation

The kinetic-theory expressions for the effective cross sections for molecule–molecule interaction have been derived by Köhler and 't Hoft [16]. They have limited their derivation to rigid rotors only and have not considered vibrational energy transfer. Recent calculations have shown [4, 7, 13] that neglect of vibrational degrees of freedom can lead to large discrepancies between calculated and experimentally available thermal conductivity. We have thus generalized the results of Ref. 16 to include vibrational degrees of freedom, for the effective cross sections where the angular momentum polarization is zero, which covers all the cross sections of interest here. Such cross sections are derivable from the semi classical WCUB kinetic equation, which allows for a relatively straightforward generalization of results to include all internal degrees of freedom. Thus, it is possible to replace the rotational energy, ε_{rot}, by the total internal energy, ε_{int}, in all the effective cross sections of interest without loss of rigor [12].

Following this generalization, it is relatively straightforward, although algebraically lengthy, to relate the Thijsse cross sections, Eqs. (11) and (12), to the traditional ones given in Ref. 16 and, by examining each term in turn, to express it in terms of experimentally accessible quantities. For the sake of brevity we present here only the final results, and the details of the derivations are given in Ref. 17.

The elements $L_{qq'}$ of the determinant that enter the expression for the thermal conductivity, Eq. (10), are then given as

$$
\begin{aligned}
L_{qq} = {} & \frac{x_q^2}{\lambda_q} + \sum_{\mu \neq q} \frac{x_q x_\mu}{2(1+r_q^2)^2 A_{q\mu}^* \lambda_{q\mu}} \\
& \times \left[\frac{25}{4} y_\mu^4 + \frac{15}{2} y_q^4 - 3 y_\mu^4 B_{q\mu}^* + 4 y_q^2 y_\mu^2 A_{q\mu}^* + \frac{5}{2} r_q^2 \frac{D_{q\mu}}{D_{\text{int}\, q,\mu}} \right. \\
& + 10 y_\mu^2 K_{q\mu}^* - \frac{2}{\pi} r_q^2 y_q^2 (5 - 3/y_\mu^2) \frac{A_{q\mu}^*}{Z_{\text{int}\, q,\mu}} \\
& \left. + \frac{10}{\pi} r_\mu^2 y_q^2 \frac{A_{q\mu}^*}{Z_{\text{int}\, \mu,q}} + \frac{10}{3\pi} (r_q + r_\mu)^2 y_q^2 (5 y_\mu^2 - 3) \frac{A_{q\mu}^*}{Z_{\text{tot int},\, q\mu}} \right]
\end{aligned}
\qquad (14)
$$

$$L_{qq'} = -\frac{x_q x_{q'} y_q^2 y_{q'}^2}{2A^*_{qq'}\lambda_{qq'}(1+r_q^2)(1+r_{q'}^2)}$$
$$\times \left\{\frac{55}{4} - 3B^*_{qq'} - 4A^*_{qq'} + \frac{5}{y_{q'}^2} K^*_{qq'} + \frac{5}{y_q^2} K^*_{q'q} + \frac{5}{4y_q^2 y_{q'}^2} \frac{D_{qq'}}{D_{\mathrm{dif\,int},\,qq'}} + \frac{2A^*_{qq'}}{\pi y_q^2 y_{q'}^2}\right.$$
$$\left.\times \left[\frac{r_q^2(5y_q^2-1)}{Z_{\mathrm{int}\,q,\,q'}} + \frac{r_{q'}^2(5y_{q'}^2-1)}{Z_{\mathrm{int}\,q',\,q}} - \frac{(r_q + r_{q'})^2\,(25y_q^2 y_{q'}^2-3)}{3Z_{\mathrm{tot\,int},\,qq'}}\right]\right\} \tag{15}$$

where y_q is the mass ratio of species q, given by

$$y_q^2 = \frac{m_q}{(m_q + m_{\mu})} \tag{16}$$

and $\lambda_{qq'}$ is the interaction thermal conductivity [12–15].

The quantities $A^*_{qq'}$, $B^*_{qq'}$, $K^*_{qq'}$, and $K^*_{q'q}$ are the ratios of effective cross sections, $D_{qq'}$ is the binary mass-diffusion coefficient, $D_{\mathrm{int}\,q,\,q'}$, $D_{\mathrm{int}\,q'q}$, and $D_{\mathrm{dif\,int}\,qq'}$ are different measures of diffusion of internal energy, and $Z_{\mathrm{int}\,q,\,q'}$, $Z_{\mathrm{int}\,q',\,q}$, and $Z_{\mathrm{tot\,int},\,qq'}$ are different measures of the relaxation of internal energy. For completeness, the definitions of all the above quantities in terms of Köhler and 't Hooft bracket integrals [2, 16] are given in the Appendix.

The ratios of the effective cross-sections $A^*_{qq'}$ and $B^*_{qq'}$ are analogous to those for monatomic gases. In the limit of zero internal energy or spherical intermolecular potential they tend to the well-known monatomic expressions [15]. Although not directly experimentally accessible, these two ratios, which are very weakly temperature dependent, can be obtained from the available corresponding-states correlations [15, 18]. The other ratios of effective cross section, $K^*_{qq'}$ and $K^*_{q'q}$ do not have monatomic analogous and are nonzero only for polyatomic molecules. All the calculations, based on atom–diatom systems [4, 19], performed so far indicate that they are vanishingly small and are unlikely to influence the overall thermal conductivity to any great extent.

The quantities $D_{\mathrm{int}\,q,\,q'}$ and $D_{\mathrm{int}\,q',\,q}$ are the diffusion coefficients of internal energy of molecule q in species q' and internal energy of molecule q' in species q, respectively. Their definition is equivalent to the original definition proposed by Monchick et al. [8]. The definition implicitly assumes that only the internal energy of a molecule that diffuses changes in a collision. Although this is true in atom–molecule encounters, there is a possibility that when two molecules collide the internal energy of both will change. Hence, for polyatomic gas mixtures there is a need for an additional diffusion coefficient that can measure the diffusion of the total internal energy change. Such, a diffusion coefficient is labeled $D_{\mathrm{tot\,int},\,qq'}$ and its definition is given in the Appendix. This coefficient does not enter the expressions for the thermal conductivity, Eqs. (11) and (12), explicitly but, rather, through $D_{\text{dif int},\,qq'}$, which is defined as

$$\frac{1}{D_{\text{dif int},\,qq'}}=\frac{r_q^2+r_{q'}^2}{D_{\text{tot int},\,qq'}}-\frac{r_q^2}{D_{\text{int}\,q,\,q'}}-\frac{r_{q'}^2}{D_{\text{int}\,q',\,q}} \tag{17}$$

For atoms and in the limit of spherical intermolecular potential all three internal energy diffusion coefficients, $D_{\text{int}\,q,\,q'}$, $D_{\text{int}\,q',\,q}$, and $D_{\text{tot int},\,qq'}$, tend to the value of the mass diffusion coefficient, $D_{qq'}$. Consequently, the reciprocal of $D_{\text{dif int},\,qq'}$ tends to zero, Eq. (17). At present there are no calculations of $D_{\text{dif int},\,qq'}$ so it is difficult to estimate its influence on the thermal conductivity of polyatomic mixtures, but it is worth pointing out that for atom–molecule mixtures, there are no terms involving $D_{\text{dif int},\,qq'}$, since if one of the species is an atom, the reciprocal of $D_{\text{dif int},\,qq'}$ vanishes, Eq. (17). Although, the three nonvanishing internal diffusion coefficients are, in principle, accessible to direct measurements, no measurements have been performed to date, even for atom–molecule mixtures. In fact the perceived difficulties associated with experimentally identifying the three separate contributions to the diffusion of internal energy might render the experimental identification impossible. It is thus essential to perform some calculations of the appropriate effective cross section using realistic intermolecular potential surfaces in order to estimate their values relative to the mass diffusion coefficient.

The quantities $Z_{\text{int}\,q,\,q'}$ and $Z_{\text{int}\,q',\,q}$ are the collision numbers for the relaxation of internal energy of molecule q in species q' and internal energy of molecule q' in species q, respectively [2, 17, 19]. The quantity $Z_{\text{tot int},\,qq'}$ is the collision number for the relaxation of the combined internal energy of molecules q and q' and its definition in terms of bracket integrals [2, 16] and the internal energy exchanged is given in the Appendix. In the spherical limit all three collision numbers tend to infinity, because for the spherical potentials there is no possibility of internal energy exchange, and hence it would, in principle, take an infinite number of collisions to relax the internal energy of a molecule. The collision numbers enter the expressions for the thermal conductivity, Eqs. (11) and (12), as reciprocals, so the larger the collision number, the smaller its influence is on the overall thermal conductivity. For atom (q')–molecule (q) collisions the total collision number, $Z_{\text{tot int},\,qq'}$, is equivalent to the collision number for the relaxation of the internal energy of the molecule, $Z_{\text{int}\,q,\,q'}$. The experimental identification of all three separate collision numbers might prove difficult and the computational approach directly from the intermolecular potential might be a more feasible way of estimating the relative sizes of different collision numbers.

It is worth pointing out that Eqs. (14) and (15) can be further simplified if one makes the plausible assumption that complex collisions are rare and can be neglected, in which case the term $D_{qq'}/D_{\text{dif int},\, qq'}$ in Eq. (15) will vanish and $Z_{\text{tot int},\, qq'}$ will be expressible in terms of the other two collision numbers. Although this assumption is usually made in phenomenological theories of relaxation of gases and has also been made by Mason and his collaborators [8] in simplifying the traditional WCUB expressions, we are reluctant to make it at present until the computational evaluation of the relevant cross sections justifies its use.

The general expressions for the thermal conductivity of N-component polyatomic mixtures are given in Eqs. (10) and (12). For binary mixtures, where one of the species is an atom, the formulation reduces to the one given in Ref. 4, while for N-component monatomic mixture it reduces to the traditional expressions given in Ref. 15.

2.4. The Spherical Approximation

Presently, the use of Eqs. (10)–(12) to calculate the thermal conductivity is hampered by a lack of available experimental information on a number of quantities entering Eqs. (10)–(12). Furthermore, no calculations of the effective cross sections for unlike molecule–molecule interactions directly from the intermolecular potential are yet available. Very little is known about the relative sizes of different internal energy diffusion coefficients and collision numbers, and thus it is not possible to estimate the contribution of different terms to the overall thermal conductivity. In fact, most of the information available relates to the simplest polyatomic system, namely, atom–diatom. Although molecule–molecule systems require rather more information, study of the behavior of atom–molecule systems can give us some general indications of what further assumptions and simplifications can be made. Recent work [13, 14] has shown that the thermal conductivity of the binary atom–molecule mixture can be predicated to within a few percent by making use of thermal-conductivity expressions where the ratios of effective cross sections have been replaced by their spherical limits.

For completeness we present here the expressions for the thermal conductivity of an N-component polyatomic gas mixture in the spherical limit. The elements, $L_{qq'}$, of the determinant that enter the expression for the thermal conductivity, Eq. (10), are then given as

$$L_{qq} = \frac{x_q^2}{\lambda_q} + \sum_{\mu \neq q} \frac{x_q x_\mu}{2(1 + r_q^2)^2 A_{q\mu}^* \lambda_{q\mu}} \left[\frac{25}{4} y_\mu^4 + \frac{15}{2} y_q^4 - 3 y_\mu^4 B_{q\mu}^* \right.$$

$$\left. + 4 y_q^2 y_\mu^2 A_{q\mu}^* + \frac{5}{2} r_q^2 \right] \tag{18}$$

$$L_{qq'} = -\frac{x_q x_{q'} y_q^2 y_{q'}^2}{2A_{qq'}^* \lambda_{qq'} (1 + r_q^2)(1 + r_{q'}^2)} \left[\frac{55}{4} - 3B_{qq'}^* - 4A_{qq'}^* \right] \tag{19}$$

Evaluation of the thermal conductivity in this approximation now requires data on the thermal conductivity and the internal heat capacity of pure components, which are readily available, the interaction thermal conductivity, $\lambda_{qq'}$, and two effective cross section ratios, $A_{qq'}^*$ and $B_{qq'}^*$, all of which can be calculated from corresponding-states correlations [5, 18]. Such calculations are currently being performed for a number of polyatomic gas mixtures in order to compare the predicted thermal conductivity with the experimentally available one. Only then shall we know if the general formulation given by Eqs. (10), (18), and (19), is accurate enough for the prediction of the thermal conductivity of all polyatomic mixtures.

3. CONCLUSION

A new expression for the thermal conductivity of an N-component polyatomic gas mixture in a dilute-gas limit has been derived. The derived formulation is based on the Thijsse approximation and the final expressions, Eqs. (10)–(12), turn out to be much simpler than those presently available. Future numerical tests have to be performed in order to ascertain that the present formulation is as accurate as the traditional ones, but judging by the results for pure gases and binary atom–molecule mixtures, all indications are that it is.

Furthermore, the derived expressions were rewritten in terms of experimentally accessible quantities to allow for easier calculation of the thermal conductivity and easier interpretation of the experimentally available data. Presently, there is insufficient information on a number of quantities entering the expressions for the thermal conductivity to make this formulation readily usable. There is therefore a need for more computational studies and experimental data on unlike molecule–molecule interactions.

Finally, a new expression for the thermal conductivity of an N-component polyatomic gas mixture in a dilute-gas limit has been derived by replacing the effective cross sections by their spherical limit, Eqs. (10), (18), and (19). This formulation is rather simple and all the input quantities are readily available. Presently, the calculations are being performed for a number of polyatomic mixtures for which accurate experimental data are available in order to ascertain the accuracy of the proposed formulae.

APPENDIX

This appendix contains the definitions of the quantities appearing in Eqs. (14) and (15) in terms of Köhler and 't Hoft bracket integrals [16], symbolized by $\{\ldots\}$.

$$A^*_{qq'} \equiv \frac{5y_q^2}{3y_{q'}^2} \frac{\mathfrak{S}^{(2)}_{\eta q}}{\mathfrak{S}^{(1)}_{\eta}} \tag{A1}$$

$$B^*_{qq'} \equiv \frac{5y_q^2}{3y_{q'}^4} \frac{(y_{q'}^3 \mathfrak{S}_{dq} - \mathfrak{S}_{aq})}{\mathfrak{S}^{(1)}_{\eta}} \tag{A2}$$

$$K^*_{qq'} \equiv -y_q^2 \frac{\mathfrak{S}_{cq}}{\mathfrak{S}^{(1)}_{\eta}} \tag{A3}$$

$$Z_{\mathrm{int}\, q,\, q'} \equiv \frac{2}{\pi y_{q'}^4} \frac{\mathfrak{S}^{(2)}_{\eta q}}{\mathfrak{S}_{\zeta q}} \tag{A4}$$

$$Z_{\mathrm{tot\ int},\, qq'} \equiv \frac{2}{\pi y_{q'}^4} \frac{\mathfrak{S}^{(2)}_{\eta q}}{\mathfrak{S}_{\zeta\,\mathrm{tot}}} \tag{A5}$$

$$\frac{D_{qq'}}{D_{\mathrm{int}\, q,\, q'}} \equiv 2y_q^2 \frac{\mathfrak{S}_{bq}}{\mathfrak{S}^{(1)}_{\eta}} \tag{A6}$$

$$\frac{D_{qq'}}{D_{\mathrm{tot\ int},\, qq'}} \equiv 2y_q y_{q'} \frac{\mathfrak{S}_{b\,\mathrm{tot}}}{\mathfrak{S}^{(1)}_{\eta}} \tag{A7}$$

where the effective cross sections are given by

$$\mathfrak{S}^{(1)}_{\eta} \equiv \frac{4}{3} y_q^2 y_{q'}^2 \{\sigma_{qq'}(\gamma^2 + \gamma'^2 - 2\gamma\gamma' \cos\chi)\} \tag{A8}$$

$$\mathfrak{S}^{(2)}_{\eta q} \equiv \frac{4}{15} y_{q'}^4 \{\sigma_{qq'}(3\gamma^2\gamma'^2(1 - \cos^2\chi) + (\Delta\varepsilon)^2)\} \equiv \frac{y_{q'}^4}{y_q^4} \mathfrak{S}^{(2)}_{\eta q'} \tag{A9}$$

$$\mathfrak{S}_{aq} \equiv \frac{4}{15} y_{q'}^6 \{\sigma_{qq'}(\gamma^6 + \gamma'^6 - 2\gamma^3\gamma'^3 \cos\chi)\} \equiv \frac{y_{q'}^6}{y_q^6} \mathfrak{S}_{aq'} \tag{A10}$$

$$\mathfrak{S}_{dq} \equiv \frac{4}{3} y_{q'}^3 \{\sigma_{qq'}(\gamma^4 + \gamma'^4 - \gamma\gamma'(\gamma^2 + \gamma'^2) \cos\chi)\} \equiv \frac{y_{q'}^3}{y_q^3} \mathfrak{S}_{dq'} \tag{A11}$$

$$\mathfrak{S}_{cq} \equiv \frac{8}{15} y_{q'}^2 \{\sigma_{qq'}(\gamma'(\gamma'^2 - 2.5)[\gamma'(\varepsilon'_q - \bar{\varepsilon}_q) - \gamma(\varepsilon_q - \bar{\varepsilon}_q) \cos\chi])\} \tag{A12}$$

$$\mathfrak{S}_{\zeta q} \equiv \frac{2}{5} \frac{1}{r_q^2} \{\sigma_{qq'}(\varepsilon'_q - \varepsilon_q)^2\} \tag{A13}$$

$$\mathfrak{S}_{\zeta\,\mathrm{tot}} \equiv \frac{2}{5}\frac{1}{(r_q+r_{q'})^2}\{\sigma_{qq'}(\Delta\varepsilon)^2\} \tag{A14}$$

$$\begin{aligned}\mathfrak{S}_{bq} \equiv \frac{4}{15}\frac{y_{q'}^2}{r_q^2}\{&\sigma_{qq'}(\gamma^2(\varepsilon_q-\bar{\varepsilon}_q)^2+\gamma'^2(\varepsilon'_q-\bar{\varepsilon}_q)^2\\ &-2\gamma\gamma'\cos\chi(\varepsilon_q-\bar{\varepsilon}_q)(\varepsilon'_q-\bar{\varepsilon}_q))\}\end{aligned} \tag{A15}$$

$$\mathfrak{S}_{b\,\mathrm{tot}} \equiv \frac{4}{15}\frac{y_q y_{q'}}{(r_q^2+r_{q'}^2)}\{\sigma_{qq'}(\gamma^2(\Delta\bar{\varepsilon})^2+\gamma'^2(\Delta\bar{\varepsilon}')^2-2\gamma\gamma'\cos\chi\,\Delta\bar{\varepsilon}\,\Delta\bar{\varepsilon}')\} \tag{A16}$$

and

$$\Delta\varepsilon=\varepsilon'_q+\varepsilon'_{q'}-\varepsilon_q-\varepsilon_{q'} \tag{A17}$$

$$\Delta\bar{\varepsilon}=\varepsilon_q+\varepsilon_{q'}-\bar{\varepsilon}_q-\bar{\varepsilon}_{q'} \tag{A18}$$

$$\Delta\bar{\varepsilon}'=\varepsilon'_q+\varepsilon'_{q'}-\bar{\varepsilon}_q-\bar{\varepsilon}_{q'} \tag{A19}$$

where ε and γ are the reduced internal and kinetic energy, respectively, $\sigma_{qq'}$ is the differential cross section, χ is the deflection angle, a prime indicates the final state, and an overbar indicates the kinetic average. For more details the reader is referred to Refs. 16 and 17.

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