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Highlights

1) Kinetic model for state-resolved transport coefficients.
2) Dependence of the molecular diameters on the vibrational state
3) Dependence of the transport coefficients on the vibrational stat
4) Wave propagation for gases with vibrational excitations.

The influence of vibrational state-resolved transport coefficients on the wave propagation in diatomic gases

Gilberto M. Kremer[1]*, Olga V. Kunova[2]†, Elena V. Kustova[1]‡ George P. Oblapenko[2]§

[1]Departamento de Física, Universidade Federal do Paraná,
Caixa Postal 19044 81531-980 Curitiba, Brazil

[2]Saint Petersburg State University, 7/9 Universitetskaya nab., St. Petersburg, 199034, Russia

Abstract

A detailed kinetic-theory model for the vibrationally state-resolved transport coefficients is developed taking into account the dependence of the collision cross section on the size of vibrationally excited molecule. Algorithms for the calculation of shear and bulk viscosity, thermal conductivity, thermal diffusion and diffusion coefficients for vibrational states are proposed. The transport coefficients are evaluated for single-component diatomic gases N_2, O_2, NO, H_2, Cl_2 in the wide range of temperature, and the effects of molecular diameters and the number of accounted states are discussed. The developed model is applied to study wave propagation in diatomic gases. For the case of initial Boltzmann distribution, the influence of vibrational excitation on the phase velocity and attenuation coefficient is found to be weak. We expect more significant effect in the case of initial thermal non-equilibrium, for instance in gases with optically pumped selected vibrational states.

1 Introduction

In the modern fluid dynamics, state-to-state simulations become a powerful tool for modelling strongly non-equilibrium flows. The model is based on the assumption that the rates of vibrational relaxation and chemical reactions are comparable with the rate of fluid dynamic parameters variation whereas translational and rotational energies attain equilibrium much faster. Under such conditions, the set of governing equations includes the master equations for the vibrational level populations coupled with the conservation equations for mass, momentum and total energy. In the early works [1, 2, 3, 4], only inviscid flows were considered in the state-to-state approach and effects of strong vibrational and chemical non-equilibrium on the vibrational level populations, pressure and temperature were studied. Later, a general model for state-specific transport properties [5, 6] and reaction rates [7, 8] suitable for viscous flows was developed and applied for evaluations of heat and mass transfer under different non-equilibrium conditions in diatomic [9, 10, 11, 12, 13, 14] and polyatomic [15, 16] gas mixtures. Since direct implementation of the state-to-state transport coefficients in the computational fluid dynamics is still extremely time-consuming, the majority of heat flux estimates were carried out using post-processing techniques.

The transport model proposed in [5, 6] has some limitations. In order to obtain easy-to-implement systems for the transport coefficients it is assumed that rotational energy of molecules does not depend on the vibrational one; moreover, the cross sections of elastic collisions are set independent of the vibrational state of colliding particles. This last assumption has to be used with precautions since it is known that the size of excited molecules increases considerably with the vibrational energy [17, 18, 19]; the situation is worse for electronically excited states [20]. Recently several models of transport processes taking into account increasing size of excited particles were developed for gases with electronic [21, 22, 23] and vibrational [24, 25, 26, 27] excitation. For the latter case, preliminary estimates of shear viscosity coefficients were carried out using various potentials.

The objectives of the present study are to extend the model proposed in [25] to calculate all transport coefficients including thermal conductivity, bulk viscosity, diffusion and thermal diffusion; to evaluate the effects of varying

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*kremer@fisica.ufpr.br

†kunova.olga@gmail.com

‡e.kustova@spbu.ru

§kunstmord@kunstmord.com

molecular diameters and number of accounted vibrational states on the transport and transition rate coefficients; and to apply the developed model to investigate the wave propagation in a single-component diatomic gas. To fulfill these objectives, some simplifications are used in the state-to-state model: anharmonicity is neglected, rotational and vibrational degrees of freedom are assumed to be independent, and the hard spheres are used to calculate the elastic cross sections depending on the vibrational state. Several diatomic species such as nitrogen N_2, nitric oxide NO, oxygen O_2, hydrogen H_2, and chlorine Cl_2 are considered, and the peculiarities of transport coefficients, phase velocities and attenuation coefficient are discussed for these gases.

The paper is structured as follows. The basic equations of the state-to-state model are introduced in Section 2. In Section 3 it is shown the effect of the vibrational states on the molecular diameters and on the transport coefficients of shear and bulk viscosities, thermal conductivity, diffusion and thermal diffusion for single-component diatomic gases N_2, O_2, NO, H_2, Cl_2 in a wide range of temperature. As an application, the influence of vibrational excitations in the wave propagation is discussed in Section 4. The conclusions of the work are given in Section 5. Bulk tables of computed values of transport coefficients and wave propagation phase velocities and attenuation coefficients are given in the Appendix.

2 The state-to-state model

In this work we are interested in analyzing the influence of the molecular vibrational distributions on the field equations of a single diatomic gas and for that end we shall base our description on the state-to-state kinetic model. This model is characterized by the assumption that the rates of the vibrational relaxation and chemical reactions are of the same order as the rate of variation of the macroscopic flow variables which describe the dynamics of the gas, whereas the translational and rotational degrees of freedom attain their equilibrium states much faster.

Here the description of a single diatomic gas which takes into account the molecular vibrational distributions will be characterized by the particle number densities of the molecules at the vibrational level i, denoted by n_i, the hydrodynamic velocity $\mathbf{v}$ and the temperature T. The total particle number density of the gas is obtained by summing over all vibrational levels, i.e., $n = \sum_i n_i$.

The system of balance equations for the determination of the fields is composed by the equations of continuity, momentum and energy coupled with the equations for the vibrational particle number densities, which reads [5, 12]

$$\frac{dn}{dt} + n\nabla \cdot \mathbf{v} = 0, \tag{1}$$

$$\rho\frac{d\mathbf{v}}{dt} + \nabla \cdot \mathbf{P} = 0, \tag{2}$$

$$\rho\frac{dU}{dt} + \nabla \cdot \mathbf{q} + \mathbf{P} : \nabla\mathbf{v} = 0. \tag{3}$$

$$\frac{dn_i}{dt} + n_i\nabla \cdot \mathbf{v} + \nabla \cdot (n_i\mathbf{V}_i) = R_i, \qquad i = 0, \ldots, i_{\max} - 1, \tag{4}$$

In the above equations $\mathbf{P}$ is the pressure tensor, U the total specific energy, $\mathbf{q}$ the heat flux, $i_{\max}$ the number of vibrational levels, $\mathbf{V}_i$ the diffusion velocity related to the i-th vibrational state and R_i the rate of production of n_i due to vibrational transitions. There exist only $i_{\max} - 1$ linearly independent diffusion velocities, since they are constrained by $\sum_i n_i\mathbf{V}_i = \mathbf{0}$.

The system of balance equations (1)–(4) becomes a system of field equations for n, $\mathbf{v}$, T and n_i if constitutive equations for $\mathbf{P}$, $\mathbf{q}$, U, $\mathbf{V}_i$ and R_i are specified. The total specific energy U is given by the sum of the specific translational U_{tr}, rotational U_{rot} and vibrational U_{vibr} energies. In the case of a diatomic gas where the rotational degrees of freedom are totally excited the specific energies are given by

$$U_{\mathrm{tr}} = \frac{3}{2}\frac{kT}{m}, \qquad U_{\mathrm{rot}} = \frac{kT}{m}, \qquad U_{\mathrm{vibr}} = \frac{1}{mn}\sum_{i=0}^{i_{\max}} \varepsilon_i n_i. \tag{5}$$

Here k denotes the Boltzmann constant, m the mass of a molecule of the gas and the non-equilibrium level populations n_i are found from (4). Since in this work we will consider only low vibrational levels, the anharmonicity can be neglected, and the vibrational energy ε_i of the i-th level is that of the harmonic oscillator:

$$\varepsilon_i = hc\omega_e\left(i + \frac{1}{2}\right), \tag{6}$$

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('r') where h is the Planck's constant, c the light speed and ω_e the vibrational frequency of the harmonic oscillator.

The determination of the constitutive equations for the diffusion velocities, pressure tensor and heat flux follows from the Chapman-Enskog method applied to the Boltzmann equation The first-order correction to the distribution function is written in terms of the macroscopic flow parameters and their gradients; the unknown functions are found from the linear integral equations, and the transport coefficients are expressed via integral brackets (for a detailed description of the method, see [5]). Constitutive relations, coupled with equations (1)–(4), form a closed set of equations . Their linear expressions as functions of the gradients of velocity, temperature and molar fractions $x_i = n_i/n$ are given by

$$\mathbf{V}_i = -\sum_{k=0}^{i_{\max}} D_{ik}\mathbf{d}_k - D_i^T \nabla \ln T, \qquad \mathbf{P} = (p - \zeta \nabla \cdot \mathbf{v} - p_{rel})\,\mathbf{I} - \eta \left[\nabla\mathbf{v} + (\nabla\mathbf{v})^T - \frac{2}{3}(\nabla \cdot \mathbf{v})\,\mathbf{I} \right], \qquad (7)$$

$$\mathbf{q} = -\lambda' \nabla T - p \sum_{i=0}^{i_{\max}} D_i^T \mathbf{d}_i + \sum_{i=0}^{i_{\max}} \left(\frac{7}{2}kT + \varepsilon_i \right) n_i \mathbf{V}_i. \qquad (8)$$

In the above equations it was introduced the scalar coefficients: diffusion D_{ik}, thermal diffusion D_i^T, partial thermal conductivity λ', bulk ζ and shear η viscosities. Furthermore, the pressure tensor at equilibrium reduces to the hydrostatic pressure $p = nkT$ and p_{rel} is the relaxation pressure. The diffusive driving force for molecules at the i-th vibrational level is related to the concentration gradient $\mathbf{d}_i = \nabla x_i$ and due to the constraint $\sum_i \mathbf{d}_i = 0$ there exist only $i_{\max} - 1$ linearly independent diffusive forces.

It is worth to note that the heat flux in the state-to-state model is not only specified by the heat conduction – which is associated with the transfer of rotational and translational energies – but also by a contribution of the diffusive forces which refers to the diffusion of the vibrational states. The total number of vibrational states determines the number of independent diffusion and thermal diffusion coefficients.

We consider that the vibrational relaxation is due to single-quantum transitions for vibrational energy exchanges (VV) and for vibrational-translational energy transitions (VT). The VV processes, where molecules with vibrational states i and k collide and their post-collisional states become i' and k', are written as follows:

$$M(i) + M(k) \to M(i') + M(k'). \qquad (9)$$

The rate coefficients for these processes are defined as

$$k_{ii'}^{kk'} = 8\sqrt{\frac{kT}{\pi m}} \int \gamma^3 \exp\left(-\gamma^2\right) \sigma_{ii'}^{kk'}\, d\gamma, \qquad (10)$$

where γ is the dimensionless relative velocity, and $\sigma_{ii'}^{kk'}$ is the integral cross-section of the VV transitions during which the first molecule changes its vibrational state from i to i' and the second molecule changes its vibrational state from k to k'. The VT processes, where a molecule with vibrational state i collides with a molecule with vibrational state k and its vibrational state changes to i' can be written as follows:

$$M(i) + M(k) \to M(i') + M(k). \qquad (11)$$

Here the rate coefficients for VT processes $k_{ii'}^k$ are defined as

$$k_{ii'}^k = 8\sqrt{\frac{kT}{\pi m}} \int \gamma^3 \exp\left(-\gamma^2\right) \sigma_{ii'}^k\, d\gamma, \qquad (12)$$

where $\sigma_{ii'}^k$ is the integral cross-section of the VT transition from the vibrational level i to i' when the collision partner is in the vibrational state k. It is worth noting that usually the rates of VT processes do not depend on the internal state of the collision partner, but since we account for the influence of the vibrational state on the molecular diameter, the cross-section will depend on the vibrational level of the collision partner k.

Hence, the rate of production R_i due to VV and VT vibrational transitions is then defined as

$$R_i = \sum_{i'k} n_k \left(n_{i'} k_{i'i}^k - n_i k_{ii'}^k \right) + \sum_{ki'k'} \left(n_{i'} n_{k'} k_{i'i}^{k'k} - n_i n_k k_{ii'}^{kk'} \right). \qquad (13)$$

Thus, the set of equations considered in this paper is formed by the equations (1)–(4), coupled with constitutive relations (5), (7)–(8) and (10), (12)–(13).

3 The transport coefficients

The evaluation of the transport coefficients from the state-to-state algorithm is described in details in Refs. [5, 6, 8]. According to the method used there, the scalar coefficients – which came out from the first-order approximation of the non-equilibrium distribution function – are expanded in terms of Sonine-Waldmann-Trübenbacher polynomials, so that all transport coefficients can be expressed in terms of bracket integrals. Furthermore, the bracket integrals are determined by the cross sections of rapid processes, i.e. elastic collisions, and those resulting in the rotational energy exchange [5].

Before we analyze the transport coefficients we shall discuss the influence of vibrational states on the diameters of diatomic molecules.

3.1 Influence of vibrational state on molecular diameters and the collision integrals

We consider that the diameters of the molecules are dependent on the vibrational state. It has been shown that the influence of rotational levels on the molecular diameter is extremely small (less than 0.5 %) [25], and therefore, we do not account for it. We use the following expression to obtain the diameter d_i, which is based on the work [17]:

$$d_i = R_e + b_e + \frac{9}{2}\beta l_\alpha^2 \exp\left[2\sqrt{\beta l_\alpha}(i-1)\right], \tag{14}$$

by neglecting the contribution of the rotational levels. Here R_e is the equilibrium bond length of the molecule, $b_e \approx 2.25\text{Å}$ and β is the Morse constant in the Morse potential. The quantity l_α is given by the formula

$$l_\alpha = \sqrt{\frac{16.863}{\omega_e \mu}}, \tag{15}$$

where μ is the relative atomic mass, ω_e the vibrational constant. The values of the spectroscopic constants for the diatomic molecules considered in this work are given in Table 1.

	R_e, Å	ω_e, cm^{-1}	μ, g/mol	β, 10^{10} m
N$_2$	1.097	2358.6	28	2.6986
NO	1.151	1904.2	30	2.7534
O$_2$	1.207	1580.2	32	2.6636
H$_2$	0.741	4401.2	2	1.9506
Cl$_2$	1.987	559.7	70.9	2.0087

Table 1: Spectroscopic constants for diatomic molecules in the ground electronic state [18, 28]

Although the hard sphere model gives only rough estimates for the collision integrals, other more realistic molecular interaction models based on the Lennard-Jones or Born-Meyer potentials give the same dependence on the molecular diameters [12, 21], but have the disadvantage that there is no analytical expressions for the $\Omega_{ik}^{(l,r)}$ integrals which appear in the transport coefficients. Hence the use of the hard-sphere model for the $\Omega_{ik}^{(l,r)}$ integrals permits to describe qualitatively the main features of the effect of molecular diameters on the state-resolved transport properties. In this work we shall introduce dimensionless ratios of the transport coefficients to the corresponding coefficients calculated neglecting variation of molecular diameters in order to eliminate the inaccuracy introduced by the hard sphere model.

The cross-sections for hard-spheres with diameters which depend only on the vibrational levels i, k are given by $\sigma_{ik} = \pi(d_i + d_k)^2/4$, and the collision integrals become

$$\Omega_{ik}^{(1,1)} = \frac{1}{4}\sqrt{\frac{\pi kT}{m}}\left(d_i + d_k\right)^2, \qquad \Omega_{ik}^{(1,2)} = \frac{3}{4}\sqrt{\frac{\pi kT}{m}}\left(d_i + d_k\right)^2, \tag{16}$$

$$\Omega_{ik}^{(1,3)} = 3\sqrt{\frac{\pi kT}{m}}\left(d_i + d_k\right)^2, \qquad \Omega_{ik}^{(2,2)} = \frac{1}{2}\sqrt{\frac{\pi kT}{m}}\left(d_i + d_k\right)^2. \tag{17}$$

In the collision integral $\Omega_{ik}^{(2,2)}$ we have regarded that the difference of the rotational energy levels at collision associated with the rotational energy resonance defect can be neglected, since according to [12] its contribution is about 1%.

In the next subsections we shall use the state-to-state algorithm for the determination of the transport coefficients for gases whose cross-sections can be modeled by hard-spheres with diameters which depend on the vibrational levels of the molecules.

3.2 The shear viscosity

If we consider binary collisions between two molecules of the same species with mass m and whose vibrational levels are denoted by i, k, the shear viscosity coefficient η is given in terms of the scalar coefficients b_i of the first Sonine-Waldmann-Trübenbacher polynomial representation by (see [12])

$$\eta = \frac{kT}{2} \sum_{i=0}^{i_{\max}} x_i b_i. \tag{18}$$

Here $x_i = n_i/n$ is the molar fraction of molecules at the i-th vibrational state, $i_{\max}$ is the maximum number of considered vibrational levels.

The vibrational level populations in non-equilibrium flows are found from the master equations (4) and strictly speaking can take arbitrary form. For particular evaluations of state-resolved transport properties performed in this work we use the thermal equilibrium Boltzmann distributions:

$$x_i = \frac{n_i}{n} = \frac{1}{Z^{\mathrm{vibr}}} \exp\left(-\frac{\varepsilon_i}{kT}\right), \qquad Z^{\mathrm{vibr}} = \sum_i \exp\left(-\frac{\varepsilon_i}{kT}\right), \tag{19}$$

where the vibrational energies ε_i are determined by (6).

The scalar coefficients b_i are determined from the the system of algebraic equations of the bracket integrals H_{ik} which result from the Chapman-Enskog method applied to the Boltzmann equation. When only the first non-vanishing terms in the expansions are taken into account, this system of algebraic equations reads

$$\sum_{k=0}^{i_{\max}} H_{ik} b_k = \frac{2}{kT} x_i, \qquad i = 0, ..., i_{\max}. \tag{20}$$

For the hard sphere model whose diameters depend on the vibrational levels the bracket integrals H_{ik} are

$$H_{ik} = -\frac{4}{15}\sqrt{\frac{\pi}{mkT}} x_i x_k \left(\mathsf{d}_i + \mathsf{d}_k\right)^2, \qquad H_{ii} = \frac{16}{15}\sqrt{\frac{\pi}{mkT}} x_i \left[\sum_{k \neq i} x_k \left(\mathsf{d}_i + \mathsf{d}_k\right)^2 + 3 x_i \mathsf{d}_i^2\right]. \tag{21}$$

If we introduce the dimensionless scalar coefficients

$$\widetilde{b}_i = \frac{8}{5}\sqrt{\frac{\pi kT}{m}} x_i \mathsf{d}_i^2 b_i, \tag{22}$$

the system of algebraic equations (20) for the determination of $\widetilde{b}_i$ reads

$$\sum_{k \neq i} \left[\left(1 + \frac{\mathsf{d}_k}{\mathsf{d}_i}\right)^2 \frac{x_k}{x_i} + 3\right] \widetilde{b}_i - \frac{1}{4}\sum_{k \neq i} \left(1 + \frac{\mathsf{d}_i}{\mathsf{d}_k}\right)^2 \widetilde{b}_k = 3, \tag{23}$$

by taking into account (21).

If the diameters of vibrationally excited states are assumed constant,

$$\mathsf{d}_i = \mathrm{const} = \mathsf{d}_0 \quad \forall i, \tag{24}$$

the bracket integrals can be simplified as

$$H_{ik} = -\frac{16}{15}\sqrt{\frac{\pi}{mkT}} x_i x_k \mathsf{d}_0^2, \qquad H_{ii} = \frac{16}{15}\sqrt{\frac{\pi}{mkT}} x_i \left(4 - x_i\right) \mathsf{d}_0^2, \tag{25}$$

and the system of equations (20) becomes

$$-\frac{16}{15}\sqrt{\frac{\pi}{mkT}}\mathsf{d}_0^2 x_i\left(\sum_{k=0}^{i_{max}}x_k b_k - 4b_i\right) = \frac{2}{kT}x_i, \qquad i = 0, ..., i_{\max}. \tag{26}$$

One can see that both left- and right-hand sides of the latter equations include x_i linearly and therefore the equations can be divided by x_i. The resulting equations for any i contain the only value depending on i, namely the coefficient b_i. This yields that all the coefficients b_i are equal and therefore do not depend on the vibrational state,

$$b_i = b \quad \forall i, \tag{27}$$

and the system (26) can be solved analytically. The shear viscosity coefficient η_0 corresponding to the case of constant diameters is then given by the expression

$$\eta_0 = \frac{5}{16\mathsf{d}_0^2}\sqrt{\frac{mkT}{\pi}}. \tag{28}$$

This latter coefficient coincides with the shear viscosity coefficient calculated in the one-temperature thermal equilibrium approach [12, 29] using the hard sphere model for molecular interactions.

Now we can build from (18) and (28) the ratio of the shear viscosity coefficient with respect to its value obtained under assumption (24). This ratio is a function of the dimensionless scalar coefficients $\widetilde{b}_i$:

$$\frac{\eta}{\eta_0} = \sum_{i=0}^{i_{max}}\left(\frac{\mathsf{d}_0}{\mathsf{d}_i}\right)^2 \widetilde{b}_i. \tag{29}$$

Here we shall explain the methodology adopted for the calculation of the shear viscosity ratio η/η_0 and this methodology is quite the same for the other transport coefficients. In the first step the diameters are calculated in the interval $[0, i_{\max}]$ for the diatomic molecules at different temperatures by using the expression (14). Next the values of the diameters and state-to-state vibrational distributions obtained from the solution of Eqs. (1)–(4) are substituted into the linear system of equations (23) which is solved for $\widetilde{b}_i$. From the knowledge of $\widetilde{b}_i$ the ratios (29) for the shear viscosity coefficients can be obtained.

In this work we restrict ourselves to the case where $i_{\max} = 4$, i.e., we consider only the five first vibrational levels for molecular nitrogen, nitric oxide, oxygen, hydrogen and chlorine: N_2, NO, O_2, H_2 and Cl_2. Also we use the thermal equilibrium Boltzmann distributions (19) to calculate x_i. By considering only the five first vibrational levels the results found for all molecules is that $\eta \approx \eta_0$. In the case analyzed in [25, 26] the number of the vibrational levels adopted were 19 for N_2 and Cl_2, 18 for NO and O_2 and 11 for H_2 and it was found that the influence of vibrational excitation becomes important only for high temperatures greater than $10\,000$ K. The shear viscosity coefficient becomes smaller and the difference could reach 10 to 25% at $T = 20\,000$ K. Calculations performed in [27] for a more realistic model of molecular diameters showed that even at high temperatures the effect of varying diameter on the shear viscosity coefficient is rather weak.

3.3 The thermal conductivity

If we consider the first Sonine-Waldmann-Trübenbacher polynomial representation the thermal conductivity coefficient λ' can be expressed in terms of two scalar coefficients a_i^{10} and a_i^{01} (see [12]), namely

$$\lambda' = \frac{5}{4}k\sum_i x_i\left[a_i^{10} + \frac{2}{5}\frac{m\mathsf{c}_i^{\mathrm{rot}}}{k}a_i^{01}\right]. \tag{30}$$

Here and below all sums that are not specified are in the range $[0, i_{max}]$, $\mathsf{c}_i^{\mathrm{rot}}$ is the rotational specific heat for a given vibrational state i. For the rigid rotator model, $\mathsf{c}_i^{\mathrm{rot}}$ does not depend on the vibrational state,

$$\mathsf{c}_i^{\mathrm{rot}} = \mathsf{c}^{\mathrm{rot}} = k/m \qquad \forall i. \tag{31}$$

The scalar coefficients a_i^{pq} are obtained from the following system of algebraic equations

$$\sum_k \sum_{p'q'} \Lambda_{ik}^{pp'qq'} a_k^{p'q'} = \frac{15}{2} kT x_i \left[\delta_{p1}\delta_{q0} + \frac{2}{5}\delta_{p0}\delta_{q1} \right] \quad \text{for all} \quad i,p,q. \tag{32}$$

Here, δ_{pi} is the Kronecker delta. The bracket integrals $\Lambda_{ik}^{pp'qq'}$ follow from the application of the Chapman-Enskog method to the Boltzmann equation and one has to consider that the coefficients a_i^{00} are constrained by

$$\sum_i x_i a_i^{00} = 0. \tag{33}$$

Note that the constraint (33) takes the above form since for a single species, the molar and mass fraction coincide (all excited states have the same mass), $x_i = \rho_i/\rho$.

Here we are interested in the first approximation of λ' where the only non-vanishing terms in the expansions that will be considered are those where the indices (p,q) in (32) assume the values $(0,0)$, $(1,0)$ and $(0,1)$. Hence from (32) it follows the system of algebraic equations for a_i^{00}, a_i^{10} and a_i^{01}:

$$\sum_k \left(\Lambda_{ik}^{0000} a_k^{00} + \Lambda_{ik}^{0001} a_k^{01} + \Lambda_{ik}^{0100} a_k^{10} \right) = 0, \qquad i = 0,...,i_{\max}, \tag{34}$$

$$\sum_k \left(\Lambda_{ik}^{1000} a_k^{00} + \Lambda_{ik}^{1001} a_k^{01} + \Lambda_{ik}^{1100} a_k^{10} \right) = \frac{15}{2} x_i kT, \qquad i = 0,...,i_{\max}, \tag{35}$$

$$\sum_k \left(\Lambda_{ik}^{0010} a_k^{00} + \Lambda_{ik}^{0011} a_k^{01} + \Lambda_{ik}^{0110} a_k^{10} \right) = 3 x_i kT, \qquad i = 0,...,i_{\max}. \tag{36}$$

If we assume that the contribution of the resonance defect to the thermal conductivity is small and that the diffusion coefficient of the rotational energy can be approximated by the ordinary diffusion coefficient the bracket integrals $\Lambda_{ik}^{pp'qq'}$ can be simplified (see [12] for more details). Indeed in this case we have $\Lambda_{ik}^{1001} = \Lambda_{ik}^{0001} = 0$ for all k and the system of algebraic equations (34)–(36) becomes

$$\sum_k \left(\Lambda_{ik}^{0000} a_k^{00} + \Lambda_{ik}^{0100} a_k^{10} \right) = 0, \quad \sum_k \left(\Lambda_{ik}^{1000} a_k^{00} + \Lambda_{ik}^{1100} a_k^{10} \right) = \frac{15 x_i kT}{2}, \quad \sum_k \Lambda_{ik}^{0011} a_k^{01} = 3 x_i kT, \quad i = 0,...,i_{\max} \tag{37}$$

thanks to the relationships $\Lambda_{ik}^{0010} = \Lambda_{ki}^{0001}$ and $\Lambda_{ik}^{0110} = \Lambda_{ki}^{1001}$.

The bracket integrals $\Lambda_{ik}^{pp'qq'}$ for hard sphere molecules by taking into account the previous assumptions reduce to

$$\Lambda_{ik}^{0000} = -\sqrt{\pi m kT} x_i \mathsf{d}_i^2 x_k \left(1 + \frac{\mathsf{d}_k}{\mathsf{d}_i} \right)^2, \qquad \Lambda_{ii}^{0000} = \sqrt{\pi m kT} x_i \mathsf{d}_i^2 \sum_{k \neq i} x_k \left(1 + \frac{\mathsf{d}_k}{\mathsf{d}_i} \right)^2, \tag{38}$$

$$\Lambda_{ik}^{1000} = \frac{\sqrt{\pi m kT}}{4} x_i \mathsf{d}_i^2 x_k \left(1 + \frac{\mathsf{d}_k}{\mathsf{d}_i} \right)^2, \qquad \Lambda_{ii}^{1000} = -\frac{\sqrt{\pi m kT}}{4} x_i \mathsf{d}_i^2 \sum_{k \neq i} x_k \left(1 + \frac{\mathsf{d}_k}{\mathsf{d}_i} \right)^2, \tag{39}$$

$$\Lambda_{ik}^{1100} = -\frac{27}{16} \sqrt{\pi m kT} x_i \mathsf{d}_i^2 x_k \left(1 + \frac{\mathsf{d}_k}{\mathsf{d}_i} \right)^2, \qquad \Lambda_{ii}^{0011} = \sqrt{\pi m kT} x_i \mathsf{d}_i^2 \left[\sum_{k \neq i} x_k \left(1 + \frac{\mathsf{d}_k}{\mathsf{d}_i} \right)^2 + 4 x_i \right], \tag{40}$$

$$\Lambda_{ik}^{0100} = \Lambda_{ik}^{1000}, \qquad \Lambda_{ii}^{1100} = \sqrt{\pi m kT} x_i \mathsf{d}_i^2 \left[\frac{59}{16} \sum_{k \neq i} x_k \left(1 + \frac{\mathsf{d}_k}{\mathsf{d}_i} \right)^2 + 8 x_i \right]. \tag{41}$$

By using the relationships $\Lambda_{ik}^{1000} = \Lambda_{ki}^{1000} = \Lambda_{ik}^{0100} = \Lambda_{ki}^{0100}$ and $\Lambda_{ik}^{0000} = -4\Lambda_{ik}^{1000}$, the coefficient a_i^{00} can be eliminated from $(37)_1$ and $(37)_2$ and it follows a system of equations for the determination of a_i^{10} that reads

$$\sum_k \left(\Lambda_{ik}^{0100} + 4\Lambda_{ik}^{1100} \right) a_k^{10} = 30 x_i kT, \qquad i = 0,...,i_{\max}. \tag{42}$$

Hence, the scalar coefficients a_i^{10} and a_i^{01} that appear in the thermal conductivity coefficient (30) can be obtained from the system of algebraic equations composed by $(37)_3$ and (42).

Now by introducing the dimensionless coefficients

$$\widetilde{a}_i^{pq} = \mathsf{d}_i^2 \sqrt{\frac{\pi m}{kT}} x_i a_i^{pq}, \tag{43}$$

the system of algebraic equations $(37)_3$ and (42) can be rewritten as

$$-\frac{13}{2}\sum_{k\neq i}\left(1+\frac{\mathsf{d}_i}{\mathsf{d}_k}\right)^2 \widetilde{a}_k^{10} + \widetilde{a}_i^{10}\left[\frac{29}{2}\sum_{k\neq i}\frac{x_k}{x_i}\left(1+\frac{\mathsf{d}_k}{\mathsf{d}_i}\right)^2 + 32\right] = 30, \qquad \widetilde{a}_i^{01}\left[\sum_{k\neq i}\frac{x_k}{x_i}\left(1+\frac{\mathsf{d}_k}{\mathsf{d}_i}\right)^2 + 4\right] = 3,$$
$$i = 0,...,i_{\max}. \tag{44}$$

For a molecular gas of hard spheres under assumptions of rigid rotator (31) and constant molecular diameter (24), each linear equation of (44) involve the only variable depending on i — the coefficient a_i^{pq}, similarly to the case of shear viscosity (see Eqs. (25)–(27)). Therefore the coefficients a_i^{pq} are equal for all i and do not depend on the vibrational state, and the system (34)–(36) can be solved analytically. Its solution provides the following expression for the corresponding thermal conductivity coefficient λ_0

$$\lambda_0 = \lambda_0^{\mathrm{tr}} + \lambda_0^{\mathrm{rot}} = \frac{5}{2}\left[\mathsf{c}^{\mathrm{tr}}\eta + \frac{2}{5}\mathsf{c}^{\mathrm{rot}}\rho D_0\right], \tag{45}$$

where λ_0^{tr} and λ_0^{rot} are the thermal conductivities due to the contribution of translational and rotational degrees of freedom, respectively, D_0 is the self-diffusion coefficient. Expression (45) is the modification of the Eucken formula for the thermal conductivity coefficient in the state-to-state approach under assumption of constant diameters and for the rigid rotator model [6].

By simple transformations, the above expression for the thermal conductivity coefficient λ_0 reduces to

$$\lambda_0 = \frac{99}{64}\frac{k}{\mathsf{d}_0^2}\sqrt{\frac{kT}{\pi m}}, \tag{46}$$

if we use the following values for the shear viscosity η_0, self-diffusion coefficient D_0, translational c^{tr} and rotational $\mathsf{c}^{\mathrm{rot}}$ specific heats [12]:

$$\eta_0 = \frac{5}{16\mathsf{d}_0^2}\sqrt{\frac{mkT}{\pi}}, \qquad D_0 = \frac{3}{8n\mathsf{d}_0^2}\sqrt{\frac{kT}{m\pi}}, \qquad \mathsf{c}^{\mathrm{tr}} = \frac{3k}{2m}, \qquad \mathsf{c}^{\mathrm{rot}} = \frac{k}{m}. \tag{47}$$

By following the same strategy as for the shear viscosity coefficient we build from (30) and (45) the ratio of the thermal conductivity coefficient with respect to its value obtained at constant diameters (24) and rotational specific heats (31). The ratio is a function of the scalar coefficients $\widetilde{a}_i^{10}$ and $\widetilde{a}_i^{01}$:

$$\frac{\lambda'}{\lambda_0} = \frac{80}{99}\sum_{i=0}^{i_{max}}\left(\frac{\mathsf{d}_0}{\mathsf{d}_i}\right)^2\left[\widetilde{a}_i^{10} + \frac{2}{5}\widetilde{a}_i^{01}\right]. \tag{48}$$

If we consider only the five first vibrational levels we get that $\lambda' \approx \lambda_0$ for the diatomic gases N_2, NO, O_2, H_2 and Cl_2. As in the case of the shear viscosity coefficient it was shown in the paper [26] that the influence of the vibrational excitations become important only for temperatures greater than $10\,000$ K, for the vibrational levels specified at the end of the last subsection. The thermal conductivity coefficient becomes smaller at high temperatures and the difference could also reach 10 to 25% at $T = 20\,000$ K.

3.4   The bulk viscosity

From the Boltzmann equation through the Chapman-Enskog method the bulk viscosity coefficient ζ is given in terms of the scalar coefficients f_k^{10} by [12]

$$\zeta = -kT\sum_k x_k f_k^{10}. \tag{49}$$

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The scalar coefficients f_k^{10} are calculated from the system of equations

$$\sum_k \left(\beta_{ik}^{1100} f_k^{10} + \beta_{ik}^{1001} f_k^{01} \right) = -\frac{2}{5} x_i, \qquad \sum_k \left(\beta_{ik}^{0110} f_k^{10} + \beta_{ik}^{0011} f_k^{01} \right) = \frac{2}{5} x_i, \qquad i = 0, ..., i_{\max}, \tag{50}$$

and the coefficients f_k^{10} and f_k^{01} are subjected to the constraint

$$\sum_k x_k \left(\frac{3}{2} f_k^{10} + f_k^{01} \right) = 0. \tag{51}$$

For hard sphere molecules, the β's coefficients in the above equations read

$$\beta_{ik}^{1100} = -\sqrt{\frac{\pi k T}{m}} x_i x_k \left(\mathsf{d}_i + \mathsf{d}_k \right)^2 \left[1 - \frac{8}{5\pi\zeta_{\rm rot}(T)} \right], \tag{52}$$

$$\beta_{ii}^{1100} = \sqrt{\frac{\pi k T}{m}} \left[\sum_{k \neq i} x_i x_k \left(\mathsf{d}_i + \mathsf{d}_k \right)^2 \left(1 + \frac{8}{5\pi\zeta_{\rm rot}(T)} \right) + \frac{64}{5\pi\zeta_{\rm rot}(T)} x_i^2 \mathsf{d}_i^2 \right], \tag{53}$$

$$\beta_{ik}^{0110} = -\frac{8}{5\pi\zeta_{\rm rot}(T)} \sqrt{\frac{\pi k T}{m}} x_i x_k \left(\mathsf{d}_i + \mathsf{d}_k \right)^2, \tag{54}$$

$$\beta_{ii}^{0110} = -\frac{8}{5\pi\zeta_{\rm rot}(T)} \sqrt{\frac{\pi k T}{m}} \left[\sum_{k \neq i} x_i x_k \left(\mathsf{d}_i + \mathsf{d}_k \right)^2 + 8 x_i^2 \mathsf{d}_i^2 \right], \tag{55}$$

$$\beta_{ik}^{0011} = 0, \qquad \beta_{ii}^{0011} = \frac{16}{5\pi\zeta_{\rm rot}(T)} \sqrt{\frac{\pi k T}{m}} \left[\sum_{k \neq i} x_i x_k \left(\mathsf{d}_i + \mathsf{d}_k \right)^2 + 4 x_i^2 \mathsf{d}_i^2 \right]. \tag{56}$$

Furthermore, the relationship $\beta_{ik}^{0110} = \beta_{ki}^{1001}$ holds and here we adopt that $\zeta_{\rm rot}(T)$ is given by Parker's formula [30]

$$\zeta_{\rm rot}(T) = \frac{\zeta^\infty}{F(T)}, \quad \text{where} \quad F(T) = 1 + \frac{\pi^{\frac{3}{2}}}{2} \left(\frac{\varepsilon}{kT} \right)^{\frac{1}{2}} + \left(\frac{\pi^2}{4} + 2 \right) \left(\frac{\varepsilon}{kT} \right) + \pi^{\frac{3}{2}} \left(\frac{\varepsilon}{kT} \right)^{\frac{3}{2}}. \tag{57}$$

The parameters in the Parker's formula have the following values [30, 31, 32, 33]:

	N$_2$	NO	H$_2$	O$_2$	Cl$_2$
ζ^∞	21.9	22.6	788.9	22.0	116.9
ε/k	97.5 K	119.0 K	38.0 K	107.4 K	497.0 K

Table 2: Parameters ζ^∞ and ε/k for N$_2$, NO, H$_2$, O$_2$ and Cl$_2$.

If we introduce the dimensionless coefficients

$$\widetilde{f}_k^{pq} = \sqrt{\frac{\pi k T}{m}} \mathsf{d}_k^2 x_k f_k^{pq}, \tag{58}$$

the system of equations for the determination of $\widetilde{f}_k^{10}$ and $\widetilde{f}_k^{01}$, obtained from (50) together with (52)–(56) reads

$$\sum_{k \neq i = 0}^{i_{\max}} \left(1 + \frac{\mathsf{d}_i}{\mathsf{d}_k} \right)^2 \left[\widetilde{f}_k^{10} - \frac{8}{5\pi\zeta_{\rm rot}(T)} \left(\widetilde{f}_k^{10} - \widetilde{f}_k^{01} \right) \right] - \frac{64}{5\pi\zeta_{\rm rot}(T)} \left(\widetilde{f}_i^{10} - \widetilde{f}_i^{01} \right)$$

$$- \left[\widetilde{f}_i^{10} + \frac{8}{5\pi\zeta_{\rm rot}(T)} \left(\widetilde{f}_i^{10} - \widetilde{f}_i^{01} \right) \right] \sum_{k \neq i = 1}^{n} \frac{x_k}{x_i} \left(1 + \frac{\mathsf{d}_k}{\mathsf{d}_i} \right)^2 = \frac{2}{5}, \qquad i = 0, ..., i_{\max}, \tag{59}$$

$$\frac{8}{5\pi\zeta_{\rm rot}(T)} \sum_{k \neq i = 0}^{i_{\max}} \left(1 + \frac{\mathsf{d}_i}{\mathsf{d}_k} \right)^2 \widetilde{f}_k^{10} + \frac{8}{5\pi\zeta_{\rm rot}(T)} \left(\widetilde{f}_i^{10} - 2\widetilde{f}_i^{01} \right) \sum_{k \neq i = 1}^{n} \frac{x_k}{x_i} \left(1 + \frac{\mathsf{d}_k}{\mathsf{d}_i} \right)^2$$

$$+ \frac{64}{5\pi\zeta_{\rm rot}(T)} \left(\widetilde{f}_i^{10} - \widetilde{f}_i^{01} \right) = -\frac{2}{5}, \qquad i = 0, ..., i_{\max}. \tag{60}$$

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To solve the above equations one has to consider from the constraint (51) that

$$\sum_{k=0}^{i_{\max}} \left(\frac{\mathsf{d}_0}{\mathsf{d}_k}\right)^2 \left(\frac{3}{2}\widetilde{f}_k^{10} + \widetilde{f}_k^{01}\right) = 0. \tag{61}$$

Once the coefficients $\widetilde{f}_k^{10}$ are determined from the above equations we can build the ratio of bulk and shear viscosity coefficients

$$\frac{\zeta}{\eta_0} = -\frac{16}{5} \sum_k \left(\frac{\mathsf{d}_0}{\mathsf{d}_k}\right)^2 \widetilde{f}_k^{10}. \tag{62}$$

In table 3 it is given the ratio of bulk and shear viscosities for the molecular gases N_2, H_2, O_2, NO and Cl_2 at different temperatures by considering only the ground vibrational state, i.e. when $i_{\max} = 0$. If we consider only the five first vibrational levels we get that $\zeta/\eta_0 \approx \zeta_0/\eta_0$ for the gases N_2, H_2, O_2, NO and Cl_2.

	T=2 500 K	T=5 000 K	T=10 000 K	T=15 000 K	$T = 20\,000\,K$
ζ_0/η_0 (N_2)	1.5585	1.8469	2.0802	2.1918	2.2608
ζ_0/η_0 (H_2)	69.7359	77.4283	83.3141	86.0436	87.7071
ζ_0/η_0 (O_2)	1.5202	1.8170	2.0590	2.1752	2.2473
ζ_0/η_0 (NO)	1.5123	1.8249	2.0819	2.2061	2.2831
ζ_0/η_0 (Cl_2)	4.0546	5.8846	7.7137	8.7006	9.3465

Table 3: Ratios of the bulk and shear viscosities for N_2, H_2, O_2, NO and Cl_2 at different temperatures by considering only the first term in the sum (62).

The values for the ratios of the bulk and shear viscosities are given in Table 4, for the cases analyzed in the works [25, 26] where the number of the vibrational levels adopted for N_2 and Cl_2 were 19, 18 for NO and O_2 and 11 for H_2. We infer from this table that the bulk viscosity coefficient decreases with the increase in the temperature, and at $T = 20\,000$K the discrepancy can reach 10% to 24%. Thus we can conclude that the number of accounted vibrational states is important in the bulk viscosity evaluations at high temperatures.

	T=2 500 K	T=5 000 K	T=10 000 K	T=15 000 K	$T = 20\,000\,K$
ζ_{19}/ζ_0 (N_2)	0.9997	0.9983	0.9796	0.9390	0.8976
ζ_{11}/ζ_0 (H_2)	0.9994	0.9951	0.9450	0.8667	0.8038
ζ_{18}/ζ_0 (O_2)	0.9990	0.9982	0.9110	0.8362	0.7862
ζ_{18}/ζ_0 (NO)	0.9995	0.9950	0.9496	0.8893	0.8425
ζ_{19}/ζ_0 (Cl_2)	0.9805	0.9074	0.8212	0.7847	0.7654

Table 4: Ratios of the bulk viscosities for N_2, H_2, O_2, NO and Cl_2 at different temperatures by considering different vibrational levels.

3.5 The thermal-diffusion coefficients

The determination of the thermal-diffusion coefficients follows from the Chapman-Enskog method applied to the Boltzmann equation and they are given in terms of the scalar coefficients a_i^{00} by [12]

$$D_i^T = -\frac{1}{2n} a_i^{00}. \tag{63}$$

The system of equations for the determination of a_i^{00} follows from $(37)_1$ by considering the constraint (33). First we subtract from the ith equation the nth equation of $(37)_1$, yielding

$$\sum_{k=0}^{i_{\max}} \left(\Lambda_{ik}^{0000} - \Lambda_{i_{\max}k}^{0000}\right) a_k^{00} + \sum_{k=0}^{i_{\max}} \left(\Lambda_{ik}^{0100} - \Lambda_{i_{\max}k}^{0100}\right) a_k^{10} = 0, \qquad i = 0,...,i_{\max}. \tag{64}$$

Next by considering the constraint $\sum_i x_i a_i^{00} = 0$, we can rewrite the above equation as

$$\sum_{k=0}^{i_{\max}-1} \left(\frac{\Lambda_{ik}^{0000}}{x_k} - \frac{\Lambda_{nk}^{0000}}{x_k} - \frac{\Lambda_{in}^{0000}}{x_n} + \frac{\Lambda_{nn}^{0000}}{x_n} \right) x_k a_k^{00} + \sum_{k=0}^{i_{\max}} \left(\Lambda_{ik}^{0100} - \Lambda_{nk}^{0100} \right) a_k^{10} = 0, \tag{65}$$

where $0 \leq i \leq i_{\max} - 1$. Now by considering the expressions for Λ_{ik}^{0000} and Λ_{ik}^{0100} given by (38) and (39), the system of equations (65) becomes

$$\sum_{k \neq i=0}^{i_{\max}-1} \left(1 + \frac{\mathsf{d}_i}{\mathsf{d}_k} \right)^2 \widetilde{a}_k^{00} - \sum_{k=0}^{i_{\max}-1} \frac{x_n}{x_i} \left(1 + \frac{\mathsf{d}_n}{\mathsf{d}_k} \right)^2 \widetilde{a}_k^{00} - \widetilde{a}_i^{00} \sum_{k \neq i=0}^{i_{\max}-1} \frac{x_k}{x_i} \left(1 + \frac{\mathsf{d}_k}{\mathsf{d}_i} \right)^2$$

$$- \left[\left(1 + \frac{\mathsf{d}_i}{\mathsf{d}_n} \right)^2 + \sum_{k=0}^{i_{\max}-1} \frac{x_k}{x_i} \left(1 + \frac{\mathsf{d}_k}{\mathsf{d}_n} \right)^2 \right] \sum_{k=0}^{i_{\max}-1} \left(\frac{\mathsf{d}_n}{\mathsf{d}_k} \right)^2 \widetilde{a}_k^{00} - \frac{1}{4} \sum_{k \neq i=0}^{i_{\max}} \left(1 + \frac{\mathsf{d}_i}{\mathsf{d}_k} \right)^2 \widetilde{a}_k^{10}$$

$$+ \frac{\widetilde{a}_i^{10}}{4} \sum_{k \neq i=0}^{i_{\max}} \frac{x_k}{x_i} \left(1 + \frac{\mathsf{d}_k}{\mathsf{d}_i} \right)^2 + \frac{1}{4} \sum_{k=0}^{i_{\max}-1} \frac{x_n}{x_i} \left(1 + \frac{\mathsf{d}_n}{\mathsf{d}_k} \right)^2 \widetilde{a}_k^{10} - \frac{\widetilde{a}_n^{10}}{4} \sum_{k=0}^{i_{\max}-1} \frac{x_k}{x_i} \left(1 + \frac{\mathsf{d}_k}{\mathsf{d}_n} \right)^2 = 0. \tag{66}$$

In the above equation the coefficients $\widetilde{a}_i^{10}$ follow from $(44)_1$.

By introducing the self-diffusion coefficient D_0 given by $(47)_2$ we can build the ratios of the thermal-diffusion and self-diffusion coefficients:

$$\widetilde{D}_i^T = \frac{D_i^T}{D_0} = -\frac{4}{3} \frac{\widetilde{a}_i^{00}}{x_i} \left(\frac{\mathsf{d}_0}{\mathsf{d}_i} \right)^2, \qquad 0 \leq i \leq i_{\max} - 1, \qquad \widetilde{D}_n^T = \frac{D_n^T}{D_0} = \frac{4}{3} \sum_{k=0}^{i_{\max}-1} \frac{\widetilde{a}_k^{00}}{x_n} \left(\frac{\mathsf{d}_0}{\mathsf{d}_k} \right)^2. \tag{67}$$

Once the coefficients $\widetilde{a}_i^{00}$ are known from the system of equations (66) the ratios of the thermal-diffusion and self-diffusion coefficients can be determined from (67) for different temperatures and different molecular gases. The dimensionless thermal-diffusion coefficients for the selected states are plotted in Fig. 1. One can see that the absolute value of $\widetilde{D}_i^T$ increases with the vibrational level. For low levels, the ratio is non-monotonic with temperature. For Cl_2 the dimensionless thermal-diffusion coefficients show different qualitative behaviour compared to other species. The ratios of the thermal-diffusion coefficients for N_2, H_2, O_2, NO and Cl_2 at different temperatures for the first five vibrational levels are given in Appendix (see Table A.1).

It should be noted that for a single-component gas under assumption of constant diameters (24) all thermal diffusion coefficients vanish. It follows from the fact that in this case, the coefficients a_i^{00} become independent of the vibrational state; consequently the constraint (33) becomes

$$\sum_i x_i a_i^{00} = a^{00} \sum_i x_i = a^{00} = 0. \tag{68}$$

Therefore in a single-component gas, thermal diffusion exists only when diameters of vibrationally excited states are different.

3.6   The diffusion coefficients

According to the Chapman-Enskog method applied to the Boltzmann equation the diffusion coefficients for the single-component gas are given in terms of the scalar coefficients $d_{i,0}^k$ by [12]

$$D_{ik} = \frac{1}{2n} d_{i,0}^k. \tag{69}$$

Furthermore, the coefficients $d_{i,0}^k$ can be calculated from the system of equations

$$\sum_{k=0}^{i_{\max}} \Lambda_{ik}^{0000} d_{k,0}^n = 3kT(\delta_{in} - x_i), \qquad i,n = 0, \ldots, i_{\max}, \tag{70}$$
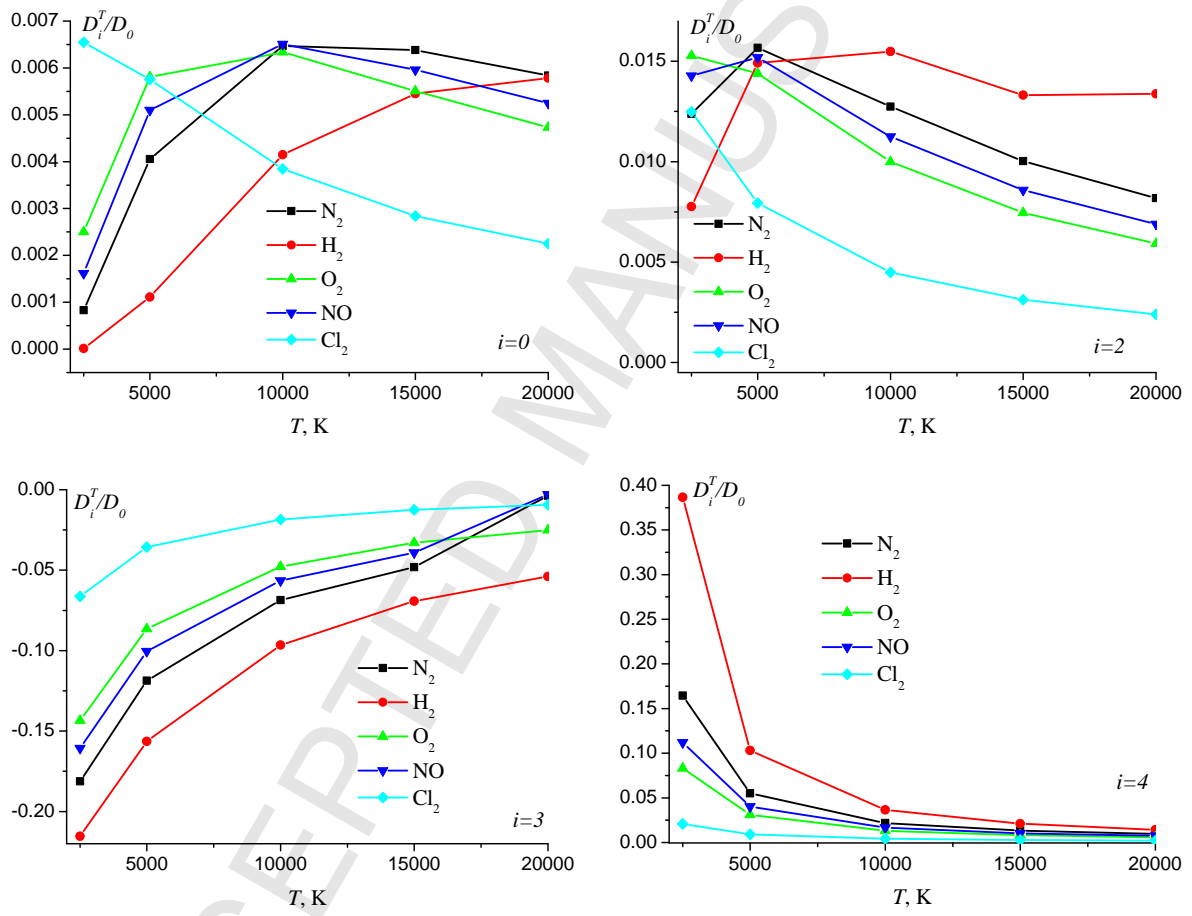
11

Figure 1: Dimensionless thermal-diffusion coefficients as functions of T.
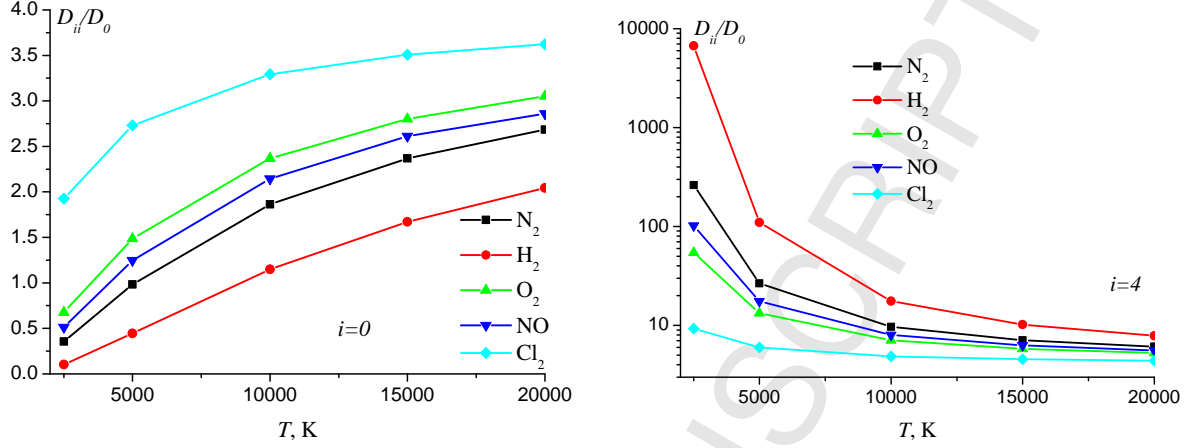
Figure 2: Dimensionless self-diffusion coefficients as functions of T.

and are subjected to the constraint

$$\sum_{k=0}^{i_{max}} x_k d_{k,0}^n = 0, \quad \forall n = 0, \ldots, i_{max}. \tag{71}$$

By introducing the dimensionless coefficient

$$\widetilde{d}_{k,0}^n = \sqrt{\frac{\pi m}{kT}} \mathsf{d}_k^2 x_k d_{k,0}^n, \tag{72}$$

we can rewrite the system of equations (70) and the constraint (71) as

$$-\sum_{k \neq i=0}^{i_{max}} \left(1 + \frac{\mathsf{d}_i}{\mathsf{d}_k}\right)^2 \widetilde{d}_{k,0}^n + \widetilde{d}_{i,0}^n \sum_{k \neq i=0}^{i_{max}} \frac{x_k}{x_i} \left(1 + \frac{\mathsf{d}_k}{\mathsf{d}_i}\right)^2 = 3 \left(\frac{\delta_{in}}{x_i} - 1\right), \qquad i, n = 0, \ldots, i_{max}, \tag{73}$$

$$\sum_{k=0}^{i_{max}} \left(\frac{\mathsf{d}_0}{\mathsf{d}_k}\right)^2 \widetilde{d}_{k,0}^n = 0, \quad \forall n = 0, \ldots, i_{max}. \tag{74}$$

Here we can also build the ratio of the diffusion coefficients and the self-diffusion coefficient, yielding

$$\widetilde{D}_{ik} = \frac{D_{ik}}{D_0} = \frac{4}{3} \left(\frac{\mathsf{d}_0}{\mathsf{d}_i}\right)^2 \frac{\widetilde{d}_{i,0}^k}{x_i}. \tag{75}$$

Once the coefficients $\widetilde{d}_{i,0}^k$ are determined from the system of equations (73) subjected to the constraint (74) the ratio of the diffusion and self-diffusion coefficients can be obtained from (75) for different temperatures and different molecular gases. In table A.2 of Appendix, the ratios of the diffusion and self-diffusion coefficients $\widetilde{D}_{ii}, (i = 0, \ldots 4)$ for N_2, H_2, O_2, NO and Cl_2 at different temperatures are given by considering the first five vibrational levels. For the others coefficients, namely for $i \neq j$, we have obtained that $D_{ij} \approx -D_0$. In Fig. 2, the diagonal self-diffusion coefficients D_{ii} related to D_0 are plotted for the vibrational states $i = 0$ and $i = 4$. The ratios decrease monotonically with the temperature and increase significantly for the high vibrational levels. For $i = 0$, the maximum ratios are found for Cl_2 and the minimum for H_2 whereas for the high levels, the situation is turned to be opposite.

3.7 The thermal diffusion ratios

Other important transport coefficients are the thermal diffusion ratios k_{Ti} and the standard thermal conductivity λ [34]. A natural question is therefore how large is the influence of vibrationally excited molecule sizes on these coefficients.

Thermal diffusion ratios k_{Ti} for a single-component gas with excited vibrational states are introduced similarly to those defined for the gas-mixture:

$$\sum_j D_{ij} k_{Tj} = D_i^T, \qquad i = 0, \ldots, i_{\max}, \tag{76}$$

$$\sum_i k_{Ti} = 0. \tag{77}$$

Using this definition, the expression (8) for the heat flux can be written in the form

$$\mathbf{q} = -\lambda \nabla T + p \sum_{i=0}^{i_{\max}} \left(k_{Ti} + \left(\frac{7}{2} + \frac{\varepsilon_i}{kT} \right) x_i \right) \mathbf{V}_i \tag{78}$$

where the thermal conductivity coefficient λ

$$\lambda = \lambda' - nk \sum_i k_{Ti} D_i^T \tag{79}$$

can be measured experimentally in the stationary system. Note that the expression (78) differs from that introduced in [34] because it includes the energy and molar fractions of vibrationally excited states. It is also worth mentioning that for the case of constant molecular diameters, $k_{Ti} = 0$ in the same way as the thermal diffusion coefficients.

Once the diffusion and thermal diffusion coefficients are calculated, the thermal diffusion ratios and λ can be easily obtained. The difference between coefficients λ and λ' is found to be negligible which is not surprising since the correction is of the order of $(D_i^T)^2$. The thermal diffusion ratios are given in Table A.3 in Appendix. The role of thermal diffusion ratios in the heat transfer can be evaluated comparing the two terms in braces in Eq. (78). One can see that for low vibrational states, the contribution of thermal diffusion ratios is small ($k_{Ti} \sim 10^{-3}$ whereas $x_i \sim 10^{-1}$). However for high levels, when the molar fraction of vibrational states becomes small, $x_i \ll 1$, the terms in braces become of the same order or even $k_{Ti} \gg x_i$, and the role of the thermal diffusion ratios can be important.

3.8 The rate coefficients

To compute the rate coefficients of the VV and VT transitions, we utilize formulas given by the SSH (Schwartz-Slavsky-Herzfeld) theory [35], modified to account for the dependence of the molecular diameter on the vibrational state. Only single-quantum transitions are considered within the framework of the SSH theory.

By neglecting anharmonicity, the SSH theory gives the following expressions for the VV and VT rate coefficients [35, 36, 37]:

$$k_{i+1 \to i}^{k \to k+1} = \frac{\bar{Z}_{ik}}{n} P_{i+1 \to i}^{k \to k+1}, \qquad k_{i+1 \to i}^{k} = \frac{\bar{Z}_{ik}}{n} P_{i+1 \to i}^{k}, \tag{80}$$

where the probability transitions are given by

$$P_{i+1 \to i}^{k \to k+1} = (i+1)(k+1) P_{10}^{01}, \qquad P_{i+1 \to i}^{k} = (i+1) P_{10}. \tag{81}$$

Above $\bar{Z}_{ik}$ is the collision frequency of molecules with diameters d_i and d_k, defined by

$$\frac{\bar{Z}_{ik}}{n} = 4\pi \mathsf{d}_{i,k}^2 \sqrt{\frac{kT}{\pi m}}, \qquad \text{with} \qquad \mathsf{d}_{i,k} = \frac{(\mathsf{d}_i + \mathsf{d}_k)}{2}. \tag{82}$$

Furthermore, P_{10}^{01} is the averaged probability for the VV transition $M(1) + M(0) \to M(0) + M(1)$, while P_{10} is the averaged probability for the VT transition $M(1) + M \to M(0) + M$. Their expressions are given by [37]

$$P_{10} = 1.294 \left(\frac{r}{r_0} \right)^2 \frac{1}{Z_0} \left(1 + 1.1 \frac{\varepsilon}{kT} \right)^{-1} \frac{2\pi^2 m \omega}{\alpha^2 \hbar} \sqrt{\frac{4\pi}{3}} \chi^{1/2} \exp \left(-3\chi + \frac{\hbar \omega}{2kT} + \frac{\varepsilon}{kT} \right), \tag{83}$$

$$P_{10}^{01} = \lambda_1^2 \lambda_2^2 \frac{4kT}{\overline{m}} \frac{\alpha^2}{\omega^2}. \tag{84}$$

In the above equations $\overline{m}$ is the reduced oscillator mass, and for diatomic homonuclear molecules $\lambda_1 = \lambda_2 = 1/2$. Furthermore, ε is the depth of the potential well, r_0 is the distance at which the interparticle Lennard–Jones

potential is zero, r is the coordinate of the turning point, $\omega = 2\pi c \omega_e$ is the angular frequency of the oscillator and Z_0 is the steric factor defined by

$$Z_0 = (\alpha r_e)^2 \exp\left(-\frac{3}{8}\frac{\alpha r_e^2}{r}\right). \tag{85}$$

Here r_e is the internuclear distance of molecule, and

$$\alpha = \frac{17.5}{r_0}, \quad \chi = \left[\frac{\pi^2 m \omega^2}{4\alpha^2 kT}\right]^{1/3}, \quad \left(\frac{r}{r_0}\right)^2 = \left(\frac{1}{2}\sqrt{1 + \frac{\chi kT}{\varepsilon}} + \frac{1}{2}\right)^{-1/3}. \tag{86}$$

The values of r_0 and r_e for N_2, NO, O_2, H_2 are given in table 5, while the values of ε/k in table 2.

	N_2	NO	H_2	O_2	Cl_2
r_0, Å	3.621	3.47	2.92	3.458	4.262
r_e, Å	1.097	1.151	0.741	1.207	1.988

Table 5: Interaction parameters for N_2, NO, O_2, H_2 and Cl_2.

The rate coefficients of the reverse processes can be found by using the detailed balance principle:

$$k_{i'i}^k = k_{ii'}^k \exp\left(\frac{\varepsilon_{i'} - \varepsilon_i}{kT}\right), \qquad k_{i'i}^{k'k} = k_{ii'}^{kk'} \exp\left(\frac{\varepsilon_{i'} + \varepsilon_{k'} - \varepsilon_i - \varepsilon_k}{kT}\right). \tag{87}$$

For the transition probabilities, the detailed balance principle gives the following expressions:

$$P_{i' \to i}^k = P_{i \to i'}^k \exp\left(\frac{\varepsilon_{i'} - \varepsilon_i}{kT}\right) \frac{\mathsf{d}_{i,k}^2}{\mathsf{d}_{i',k}^2}, \qquad P_{i' \to i}^{k' \to k} = P_{i \to i'}^{k \to k'} \exp\left(\frac{\varepsilon_{i'} + \varepsilon_{k'} - \varepsilon_i - \varepsilon_k}{kT}\right) \frac{\mathsf{d}_{i,k}^2}{\mathsf{d}_{i',k'}^2}. \tag{88}$$

By taking into account for the fact that we have only single-quantum transitions and we consider a harmonic vibrational spectrum, the transition probabilities can be rewritten as

$$P_{i \to i+1}^k = P_{i+1 \to i}^k \exp\left(-\frac{hc\omega_e}{kT}\right) \frac{\mathsf{d}_{i+1,k}^2}{\mathsf{d}_{i,k}^2}, \qquad P_{i \to i+1}^{k+1 \to k} = P_{i+1 \to i}^{k \to k+1} \frac{\mathsf{d}_{i+1,k}^2}{\mathsf{d}_{i,k+1}^2}. \tag{89}$$

In tables 6 and 7 the calculated values for the probabilities for VT transitions $P_{1 \to 0}$ and for VV transitions $P_{1 \to 0}^{0 \to 1}$ are given for N_2, NO, O_2, H_2 and Cl_2 at different temperatures, respectively.

collision	T=2 500 K	T=5 000 K	T=10 000 K	T=15 000 K	$T = 20\,000$ K
N_2–N_2	$2.85 \cdot 10^{-6}$	$9.95 \cdot 10^{-5}$	$1.78 \cdot 10^{-3}$	$7.34 \cdot 10^{-3}$	$1.79 \cdot 10^{-2}$
NO–NO	$2.77 \cdot 10^{-5}$	$5.95 \cdot 10^{-4}$	$7.13 \cdot 10^{-3}$	$2.40 \cdot 10^{-2}$	$5.17 \cdot 10^{-2}$
H_2–H_2	$2.65 \cdot 10^{-3}$	$1.08 \cdot 10^{-2}$	$3.85 \cdot 10^{-2}$	$7.37 \cdot 10^{-2}$	0,112
O_2–O_2	$1.14 \cdot 10^{-4}$	$1.82 \cdot 10^{-3}$	$1.70 \cdot 10^{-2}$	$5.06 \cdot 10^{-2}$	0.101
Cl_2–Cl_2	$5.31 \cdot 10^{-3}$	$4.54 \cdot 10^{-2}$	0.251	0.572	0.961

Table 6: The probabilities for VT transitions $P_{1 \to 0}$.

4 Wave propagation

In this section we are interested in analyzing the influence of vibrational excitation in the wave propagation of a single-component diatomic gas. For that end we consider the system of equations (1)–(4) complemented with the constitutive equations (5)–(8), (80), (81) and the equations for the detailed balance (89). Furthermore, we take into account that the fields of the total particle number density n, particle number densities at the vibrational levels n_i,

collision	T=2 500 K	T=5 000 K	T=10 000 K	T=15 000 K	$T = 20\,000\,\text{K}$
N_2–N_2	$8.83 \cdot 10^{-3}$	$1.77 \cdot 10^{-2}$	$3.53 \cdot 10^{-2}$	$5.29 \cdot 10^{-2}$	$7.06 \cdot 10^{-2}$
NO–NO	$1.38 \cdot 10^{-2}$	$2.77 \cdot 10^{-2}$	$5.53 \cdot 10^{-2}$	$8.30 \cdot 10^{-2}$	0.111
H_2–H_2	$5.46 \cdot 10^{-2}$	0.109	0.218	0.328	0.437
O_2–O_2	$1.89 \cdot 10^{-2}$	$3.78 \cdot 10^{-2}$	$7.55 \cdot 10^{-2}$	0.113	0.151
Cl_2–Cl_2	$4.47 \cdot 10^{-2}$	$8.94 \cdot 10^{-2}$	0.179	0.268	0.358

Table 7: The probabilities for VV transitions $P_{1\to0}^{0\to1}$.

temperature T and velocity $\mathbf{v}$ are characterized by superpositions of constant values (which describe an equilibrium state) $n = n_0$, $n_i = n_i^0$, $T = T_0$ and vanishing velocity $\mathbf{v} = \mathbf{0}$ with longitudinal plane waves of small amplitudes with wavenumber $\mathsf{k} \in \mathbb{C}$ and frequency $\omega \in \mathbb{R}$ that are propagating in the positive x direction, namely

$$n = n_0 + \overline{n}\exp[i(\mathsf{k}x - \omega t)], \tag{90}$$

$$n_i = n_i^0 + \overline{n}_i\exp[i(\mathsf{k}x - \omega t)], \tag{91}$$

$$v_x = \overline{v}\exp[i(\mathsf{k}x - \omega t)], \tag{92}$$

$$T = T_0 + \overline{T}\exp[i(\mathsf{k}x - \omega t)]. \tag{93}$$

Here, $\overline{n}, \overline{n}_i, \overline{v}, \overline{T}$ are the amplitudes, which are considered to be small quantities.

The phase velocity v_{ph} and the attenuation coefficient α of the harmonic wave are given by

$$v_{\text{ph}} = \frac{\omega}{\Re\{\mathsf{k}\}}, \qquad \alpha = \Im\{\mathsf{k}\}, \tag{94}$$

where $\Re$ and $\Im$ represent the real and imaginary parts of the quantity within the braces.

From the substitution of (90)–(93) into (1)–(4) and linearization around the equilibrium state we obtain the following algebraic system of equations for the dimensionless amplitudes $\widehat{n} = \overline{n}/n_0$, $\widehat{n}_i = \overline{n}_i/n_i^0$, $\widehat{v} = v/v_0$, and $\widehat{T} = \overline{T}/T_0$:

$$\widehat{n} - \left(\frac{\mathsf{k}v_0}{\omega}\right)\widehat{v} = 0, \tag{95}$$

$$\widehat{n}_i - \left(\frac{\mathsf{k}v_0}{\omega}\right)\widehat{v} + i\frac{6\omega_*}{5}\left(\frac{\mathsf{k}v_0}{\omega}\right)^2\left[\sum_{k=0}^{i_{\max}-1}(\widetilde{D}_{ik} - \widetilde{D}_{ii_{\max}})x_k^0(\widehat{n}_k - \widehat{n}) + \widetilde{D}_i^T\widehat{T}\right]$$

$$= -\frac{5}{16}\sqrt{\frac{m}{\pi kT}}\frac{1}{\omega_* n_0 d_0^2}\sum_{ki'}\left[\left(\frac{n_k^0 n_{i'}^0}{n_i^0}\widehat{n}_{i'}k_{i'\to i}^k - n_k^0\widehat{n}_i k_{i\to i'}^k\right) + \left(\frac{n_k^0 n_{i'}^0}{n_i^0}\widehat{n}_k k_{i'\to i}^k - n_k^0\widehat{n}_k k_{i\to i'}^k\right)\right.$$

$$\left.+ \left(\frac{n_k^0 n_{i'}^0}{n_i^0}k_{i'\to i}^k - n_k^0 k_{i\to i'}^k\right)\right]$$

$$-\frac{5}{16}\sqrt{\frac{m}{\pi kT}}\frac{1}{\omega_* n_0 d_0^2}\sum_{ki'k'}\left[\left(\frac{n_{k'}^0 n_{i'}^0}{n_i^0}\widehat{n}_{i'}k_{i'\to i}^{k'\to k} - n_k^0\widehat{n}_i k_{i\to i'}^{k\to k'}\right) + \left(\frac{n_{k'}^0 n_{i'}^0}{n_i^0}\widehat{n}_{k'}k_{i'\to i}^{k'\to k} - n_k^0\widehat{n}_k k_{i\to i'}^{k\to k'}\right)\right.$$

$$\left.+ \left(\frac{n_{k'}^0 n_{i'}^0}{n_i^0}k_{i'\to i}^{k'\to k} - n_k^0 k_{i\to i'}^{k\to k'}\right)\right], \qquad i = 0,\ldots,i_{\max}-1, \tag{96}$$

$$\widehat{v} - \left(\frac{\mathsf{k}v_0}{\omega}\right)\left(\widehat{n} + \widehat{T}\right) + i\left(\frac{\mathsf{k}v_0}{\omega}\right)^2\omega_*\left(\frac{4}{3}\widetilde{\eta} + \widetilde{\zeta}\right)\widehat{v} = 0, \tag{97}$$

$$\frac{5}{2}\widehat{T} + \sum_{i=0}^{i_{\max}}\frac{\varepsilon_i}{kT_0}x_i^0(\widehat{n}_i - \widehat{n}) + i\frac{99\omega_*}{20}\left(\frac{\mathsf{k}v_0}{\omega}\right)^2\widetilde{\lambda}\widehat{T} + i\frac{6\omega_*}{5}\left(\frac{\mathsf{k}v_0}{\omega}\right)^2\sum_{i=0}^{i_{\max}-1}\left(\widetilde{D}_i^T - \widetilde{D}_{i_{\max}}^T\right)x_i^0(\widehat{n}_i - \widehat{n})$$

$$-\left(\frac{\mathsf{k}v_0}{\omega}\right)\widehat{v} + i\frac{6\omega_*}{5}\left(\frac{\mathsf{k}v_0}{\omega}\right)^2\sum_{i=0}^{i_{\max}}\left(\frac{7}{2} + \frac{\varepsilon_i}{kT_0}\right)x_i^0\left[\sum_{k=0}^{i_{\max}-1}\left(\widetilde{D}_{ik} - \widetilde{D}_{ii_{\max}}\right)x_k^0(\widehat{n}_k - \widehat{n}) + \widetilde{D}_i^T\widehat{T}\right] = 0. \tag{98}$$

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Here we have introduced the thermal velocity $v_0 = \sqrt{kT_0/m}$ and the dimensionless transport coefficients $\widetilde{\eta} = \eta/\eta_0$, $\widetilde{\lambda} = \lambda'/\lambda_0$, $\widetilde{\zeta} = \zeta/\eta_0$, $\widetilde{D}_i^T = D_i^T/D_0$, $\widetilde{D}_{ij} = D_{ij}/D_0$ where η_0, λ_0 and D_0 are given by (28), (45) and (47)$_2$, respectively. It has been shown in [38, 39] that the relaxation pressure p_{rel} due to vibrational transitions is small compared to the hydrostatic pressure $p = nkT$, so that in the above equations p_{rel} is neglected.

In the analysis of sound propagation in gases it is usual to introduce the dimensionless frequency ω_*, which is a measure of the ratio of the sound frequency to the collision frequency, namely $\omega_* = \eta_0\omega/p_0$. In the following we shall analyze the dependence of the phase velocity and attenuation coefficient on the dimensionless frequency ω_*.

Note that the equations (95)–(98) are written for an arbitrary initial state-to-state vibrational distribution and thus have a general form. This general form of the system of equations for the dimensionless amplitudes is inhomogeneous, since in the general case of a non-equilibrium initial distribution

$$\left(\frac{n_{k'}^0 n_{i'}^0}{n_i^0} k_{i'\to i}^{k'\to k} - n_k^0 k_{i\to i'}^{k\to k'} \right) \neq 0, \tag{99}$$

and thus, no dispersion relation can be obtained from this system of equations. In order to obtain the particular solution of Eqs. (95)–(98), the equilibrium level populations n_i^0 given by the Boltzmann distributions (19) can be used. Substituting the Boltzmann distribution to the Equations (96) and rewriting them for specific values of i – namely $i = 0$ and $i \neq 0$ – yield

$$\widehat{n}_0 - \left(\frac{\mathsf{k}v_0}{\omega}\right)\widehat{v} + i\frac{6\omega_*}{5}\left(\frac{\mathsf{k}v_0}{\omega}\right)^2\left[\sum_{k=0}^{i_{\max}-1}(\widetilde{D}_{0k} - \widetilde{D}_{0i_{\max}})x_k^0\,(\widehat{n}_k - \widehat{n}) + \widetilde{D}_0^T\widehat{T}\right]$$

$$= \frac{5}{4i\omega_*}\frac{1}{Z^{\mathrm{vibr}}(T_0)}\sum_{k=0}^{i_{\max}}\frac{\mathsf{d}_{1,k}^2}{\mathsf{d}_0^2}\exp\left(-\frac{\varepsilon_k}{kT_0}\right)\exp\left(-\frac{hc\omega_e}{kT_0}\right)(\widehat{n}_1 - \widehat{n}_0)\,P_{1\to 0}$$

$$+ \frac{5}{4i\omega_*}\frac{1}{Z^{\mathrm{vibr}}(T_0)}\sum_{k=1}^{i_{\max}}\frac{\mathsf{d}_{1,k-1}^2}{\mathsf{d}_0^2}\exp\left(-\frac{\varepsilon_k}{kT_0}\right)(\widehat{n}_1 + \widehat{n}_{k-1} - \widehat{n}_0 - \widehat{n}_k)\,P_{1\to 0}^{k-1\to k}, \tag{100}$$

$$\widehat{n}_i - \left(\frac{\mathsf{k}v_0}{\omega}\right)\widehat{v} + i\frac{6\omega_*}{5}\left(\frac{\mathsf{k}v_0}{\omega}\right)^2\left[\sum_{k=0}^{i_{\max}-1}(\widetilde{D}_{ik} - \widetilde{D}_{ii_{\max}})x_k^0\,(\widehat{n}_k - \widehat{n}) + \widetilde{D}_i^T\widehat{T}\right]$$

$$= -\frac{5}{4i\omega_*}\frac{1}{Z^{\mathrm{vibr}}(T_0)}\sum_{k=0}^{i_{\max}}\frac{\mathsf{d}_{i,k}^2}{\mathsf{d}_0^2}\exp\left(-\frac{\varepsilon_k}{kT_0}\right)(\widehat{n}_{i-1} - \widehat{n}_i)\,P_{i\to i-1}$$

$$- \frac{5}{4i\omega_*}\frac{1}{Z^{\mathrm{vibr}}(T_0)}\sum_{k=0}^{i_{\max}}\frac{\mathsf{d}_{i+1,k}^2}{\mathsf{d}_0^2}\exp\left(-\frac{\varepsilon_k}{kT_0}\right)\exp\left(-\frac{hc\omega_e}{kT_0}\right)(\widehat{n}_{i+1} - \widehat{n}_i)\,P_{i+1\to i}$$

$$- \frac{5}{4i\omega_*}\frac{1}{Z^{\mathrm{vibr}}(T_0)}\sum_{k=0}^{i_{\max}-1}\frac{\mathsf{d}_{i,k}^2}{\mathsf{d}_0^2}\exp\left(-\frac{\varepsilon_k}{kT_0}\right)(\widehat{n}_{i-1} + \widehat{n}_{k+1} - \widehat{n}_i - \widehat{n}_k)\,P_{i\to i-1}^{k\to k+1}$$

$$- \frac{5}{4i\omega_*}\frac{1}{Z^{\mathrm{vibr}}(T_0)}\sum_{k=1}^{i_{\max}}\frac{\mathsf{d}_{i+1,k-1}^2}{\mathsf{d}_0^2}\exp\left(-\frac{\varepsilon_k}{kT_0}\right)(\widehat{n}_{i+1} + \widehat{n}_{k-1} - \widehat{n}_i - \widehat{n}_k)\,P_{i+1\to i}^{k-1\to k}, \qquad i = 1, \ldots, i_{\max} - 1 \tag{101}$$

The homogeneous system of equations (95), (97)–(101) admits a solution for the dimensionless amplitudes $\widehat{n}, \widehat{n}_i, \widehat{v}, \widehat{T}$ if the determinant of the coefficients vanishes. Hence we get a dispersion relation which connects the ratio $\mathsf{k}v_0/\omega$ with the dimensionless frequency ω_*. The system of equations was solved numerically for $i = 0, \ldots, 4$ for the gases N_2, NO, O_2, H_2 and Cl_2 by taking into account the transport coefficients found in the last section. The dispersion relation for this system of equations is an algebraic equation of twelfth degree for $\mathsf{k}v_0/\omega$ as a function ω_*, which correspond to six waves that are propagating in the x direction and six waves that are propagating in the opposite direction. In the following we shall analyze only the wave which has the greatest velocity and smaller attenuation coefficient. This is the wave which can be observed by the experiments, since the others are heavily damped.

Here we introduce a dimensionless phase velocity and a dimensionless attenuation coefficient defined by

$$v_* = \frac{v_{\mathrm{ph}}}{v_0}, \qquad \alpha_* = \frac{\alpha}{v_0}. \tag{102}$$
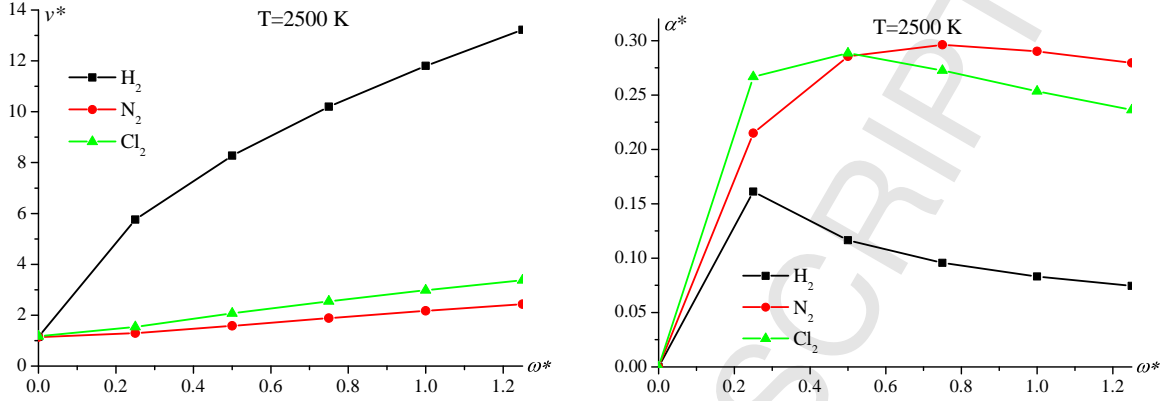
Figure 3: Phase velocity and attenuation coefficient for different gases at $T = 2500$ K.

In Figs. 3 and 4 we compare v_* and α_* for different gases. Due to the fact that the coefficients and molecular masses of O_2 and NO are close to those of N_2, the values of the dimensionless phase velocity and attenuation coefficient for O_2 and NO do not differ too much from the values for N_2, so that their values are not given here. One can see that the phase velocity increases with T and ω_* whereas the behaviour of the attenuation coefficient is non-monotonic: it achieves a maximum which for N_2 is shifted towards higher frequencies; for low frequencies α_* increases with the temperature while for $\omega_* > 0.5$ it decreases. In any case, the overall variation of α_* is rather weak. More data on v_*, α_* can be found in the Appendix, see Tables A.4, A.5 and A.6.

If we assume that all molecules are in the ground vibrational state, the system of equations (95)–(98) reduces to

$$\widehat{n} - \left(\frac{\mathsf{k}v_0}{\omega}\right)\widehat{v} = 0, \tag{103}$$

$$\widehat{v} - \left(\frac{\mathsf{k}v_0}{\omega}\right)\left(\widehat{n} + \widehat{T}\right) + i\left(\frac{\mathsf{k}v_0}{\omega}\right)^2 \omega_* \left(\frac{4}{3}\widetilde{\eta} + \widetilde{\zeta}\right)\widehat{v} = 0, \tag{104}$$

$$\frac{5}{2}\widehat{T} + i\frac{99\omega_*}{20}\left(\frac{\mathsf{k}v_0}{\omega}\right)^2 \widetilde{\lambda}\widehat{T} - \left(\frac{\mathsf{k}v_0}{\omega}\right)\widehat{v} = 0. \tag{105}$$

The above system of equations admits a solution for the amplitudes $\widehat{n}, \widehat{v}, \widehat{T}$, if the determinant of their coefficients vanishes. The dispersion relation for this system is an algebraic equation of fourth degree for $\mathsf{k}v_0/\omega$ as a function ω_*, which corresponds to two propagating waves in the positive x direction and two in the opposite direction. The value of the dimensionless phase velocity $v_* = \sqrt{7/5} \approx 1.1832$ corresponds to the adiabatic sound speed of a diatomic gas when the vibrational levels are totally excited, so that $U_{\mathrm{vibr}} = kT_0/m$. The analysis of results shows that the effect of vibrational energy redistribution between several low located states is weak; the difference in the phase velocity is about 2% to 3% for low temperatures and negligible for high temperatures (compare the values given in Tables A.5 and A.7 for N_2 molecules). The same behavior occurs for the other gases (H_2, O_2, NO and Cl_2).

A question that could be state is: what is the influence in the wave propagation when we take more vibrational states? In table 4 we gave the ratios for the bulk viscosity coefficient when more vibrational states are taken into account for the diatomic gases N_2, NO, O_2, H_2 and Cl_2. The influence of the vibrational states on the shear viscosity and thermal conductivity were reported in [26] and in the Table 8 we reproduce the results for the temperature $T = 20\,000$ K. In order to analyze the problem of wave propagation by considering more vibrational states we have to compute all other transport coefficients and to solve a large determinant for the evaluation of the dispersion relation. Instead of doing this, we will show only the influence of the vibrational states in the wave propagation by considering the system of equations (95)–(98), but with the bulk and shear viscosity and thermal conductivity coefficients taken from tables 4 and 8, respectively.

In Fig. 5, the dimensionless phase velocities v_* and attenuation coefficients α_* for Cl_2, N_2 and H_2 at $T_0 = 20\,000$ K are given as functions of the dimensionless frequencies ω_*, when we take into account 19 vibrational levels of the molecules and when we consider only the ground state. Note that now the influence is more sensitive, especially for H_2, since the phase velocity could be 15% smaller than the one without taking into account the vibrational levels.
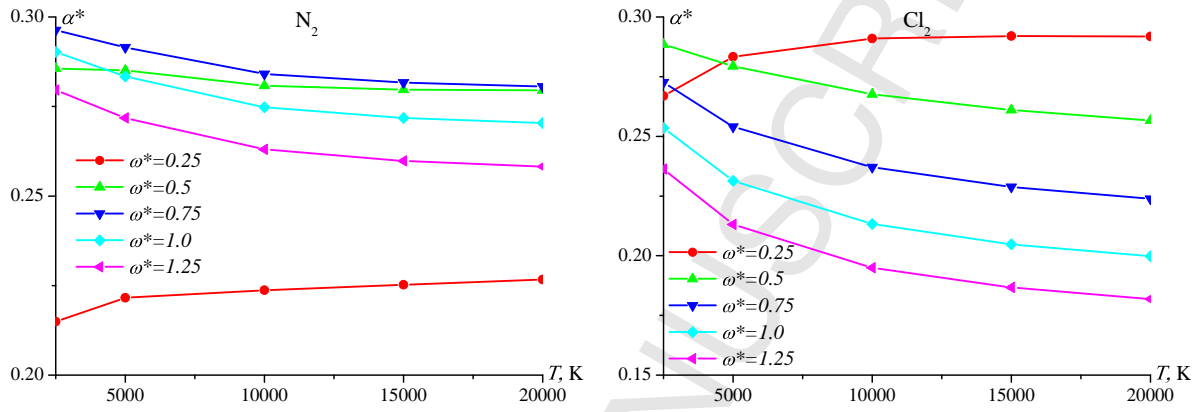
18

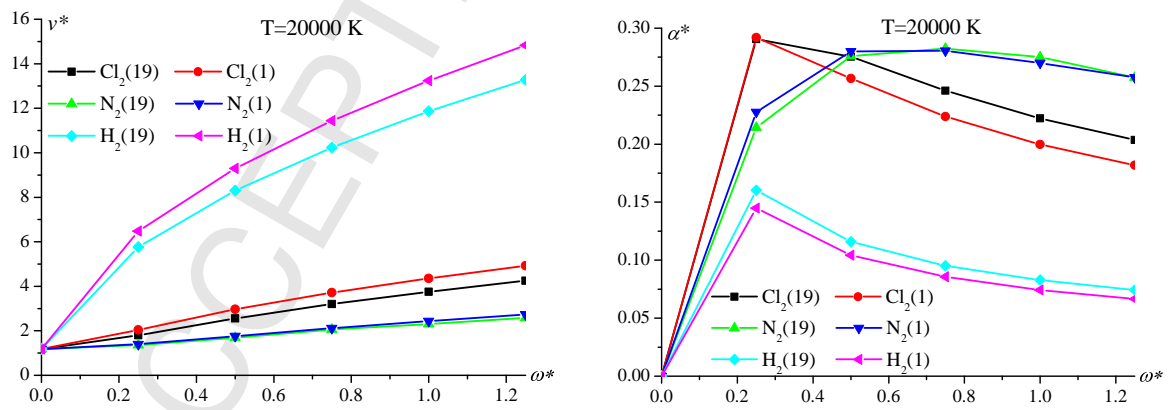Figure 4: Attenuation coefficients for N_2 and Cl_2 as functions of T.

Figure 5: Phase velocity and attenuation coefficient for different gases at $T = 20000$ K as functions of ω_*. Comparison of calculations with $i_{\max} = 19$ and $i_{\max} = 1$.

η_{19}/η_0 (N$_2$)	η_{11}/η_0 (H$_2$)	η_{18}/η_0 (O$_2$)	η_{18}/η_0 (NO)	η_{19}/η_0 (Cl$_2$)
0.8912	0.7915	0.7719	0.8325	0.7548
λ'_{19}/λ_0 (N$_2$)	λ'_{11}/λ_0 (H$_2$)	λ'_{18}/λ_0 (O$_2$)	λ'_{18}/λ_0 (NO)	λ'_{19}/λ_0 (Cl$_2$)
0.8891	0.7873	0.7672	0.8292	0.7511

Table 8: Ratios of the shear viscosity and thermal conductivity coefficients for $T = 20\,000$ K.
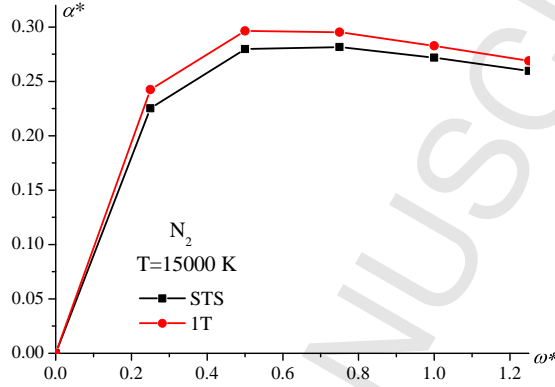
Figure 6: Attenuation coefficients for N$_2$ calculated in the state-to-state and one-temperature approach. $T = 15000$ K.

Finally, to complete the study we consider a one-temperature thermal equilibrium gas, in which the vibrational levels are populated according to the Boltzmann distribution. The system of linear equations for this case is similar to (103)–(105), however, in the one-temperature case, diffusion processes do not occur in a single-component gas, and the thermal conductivity coefficient accounts for the vibrational degrees of freedom. The equation (105) should be replaced by the following equation:

$$\widehat{c}_V \widehat{T} + i\frac{\lambda}{\eta}\frac{m}{k}\left(\frac{kv_0}{\omega}\right)^2 \widetilde{\lambda}\widehat{T} - \left(\frac{kv_0}{\omega}\right)\widehat{v} = 0, \tag{106}$$

where the dimensionless specific heat $\widehat{c_V}$ is defined as

$$\widehat{c}_V = \frac{c_V}{k/m} = \widehat{c}_{\text{tr}} + \widehat{c}_{\text{rot}} + \widehat{c}_{\text{vibr}} = \frac{5}{2} + \widehat{c}_{\text{vibr}}. \tag{107}$$

Here c_{vibr} is the specific heat of vibrational degrees of freedom

$$c_{\text{vibr}} = \frac{\partial U_{\text{vibr}}}{\partial T}. \tag{108}$$

The quantity $\frac{\lambda}{\eta}\frac{m}{k}$ is calculated via the Eucken formula, accounting for vibrational degrees of freedom [12], and utilizing expression (47) for the self-diffusion coefficient:

$$\frac{\lambda}{\eta}\frac{m}{k} = \frac{5}{2}\left(\frac{3}{2} + \frac{12}{25}\left(\widehat{c}_{\text{rot}} + \widehat{c}_{\text{vibr}}\right)\right). \tag{109}$$

A comparison of the attenuation coefficients in N$_2$ at $T = 15000$ K calculated using the state-to-state (STS) and one-temperature (1T) models is given in Fig. 6 (see also Table A.8). There is a discrepancy in α_* of about 6–8% at high temperature and low frequency; it practically disappears at high ω_*. The effect of vibrational relaxation on the phase velocity is negligible.

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5   Conclusions

A kinetic model for the vibrational state-dependent transport properties is developed for the case of a single-component diatomic gas with varying molecular diameters. Coefficients of shear and bulk viscosity, thermal conductivity, thermal diffusion and diffusion of vibrational states are calculated for five diatomic species in the temperature range 2500–20000 K. The contribution of increasing molecular size to the transport coefficients is small when the vibrational level populations follow the Boltzmann distribution; the effect of the number of accounted states on the bulk viscosity coefficient is more important. For a single-component gas, thermal diffusion coefficients of vibrational states vanish if molecular diameters are set constant. Diffusion coefficients increase significantly for highly located vibrational states; their behaviour is different for various species.

Linearized equations describing the propagation of longitudinal plane waves of small amplitudes are derived from the general set of fluid dynamic equations, and for the case of initial Boltzmann vibrational distribution, the dispersion relations are obtained numerically. The overall effect of vibrational relaxation and excitation of highly located states on the phase velocity and attenuation coefficient is weak; the solution is close to that obtained using the thermal equilibrium one-temperature model with the maximum discrepancy within 10%. Nevertheless under conditions of initial strong deviation of the vibrational distribution from the Boltzmann one, for instance for the case of optical pumping of some selected states, the effect of vibrational relaxation can be much more significant. The general equations derived in this study are suitable to describe initial non-equilibrium; however the method of small perturbations cannot be applied in this case since the resulting system is non-homogeneous. Studying the wave propagation through the initially strongly non-equilibrium media still remains a challenging problem.

6   Acknowledgements

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Appendix. Tables of transport coefficients, v_* and α_*

The appendix contains tables of computed values of transport coefficients (thermal diffusion, self-diffusion coefficients, thermal diffusion ratios) and dimensionless phase velocities and attenuation coefficients.

	T=2500 K	T=5000 K	T=10000 K	T=15000 K	$T = 20000$ K
$\widetilde{D}_0^T(N_2)$	8.288×10^{-4}	4.057×10^{-3}	6.470×10^{-3}	6.383×10^{-3}	5.835×10^{-3}
$\widetilde{D}_1^T(N_2)$	3.297×10^{-3}	8.058×10^{-3}	9.132×10^{-3}	8.040×10^{-3}	6.941×10^{-3}
$\widetilde{D}_2^T(N_2)$	1.238×10^{-2}	1.567×10^{-2}	1.274×10^{-2}	1.003×10^{-2}	8.187×10^{-3}
$\widetilde{D}_3^T(N_2)$	-1.812×10^{-1}	-1.187×10^{-1}	-6.863×10^{-2}	-4.810×10^{-2}	-3.701×10^{-3}
$\widetilde{D}_4^T(N_2)$	1.645×10^{-1}	5.499×10^{-2}	2.188×10^{-2}	1.336×10^{-2}	9.555×10^{-3}
$\widetilde{D}_0^T(H_2)$	1.401×10^{-5}	1.112×10^{-3}	4.149×10^{-3}	5.449×10^{-3}	5.786×10^{-3}
$\widetilde{D}_1^T(H_2)$	1.084×10^{-3}	4.786×10^{-3}	8.575×10^{-3}	8.943×10^{-3}	8.458×10^{-3}
$\widetilde{D}_2^T(H_2)$	7.763×10^{-3}	1.491×10^{-2}	1.548×10^{-2}	1.331×10^{-2}	1.338×10^{-2}
$\widetilde{D}_3^T(H_2)$	-2.154×10^{-1}	-1.564×10^{-1}	-9.654×10^{-2}	-6.929×10^{-2}	-5.399×10^{-2}
$\widetilde{D}_4^T(H_2)$	3.866×10^{-1}	1.031×10^{-1}	3.661×10^{-2}	2.101×10^{-2}	1.432×10^{-2}
$\widetilde{D}_0^T(O_2)$	2.503×10^{-3}	5.806×10^{-3}	6.339×10^{-3}	5.510×10^{-3}	4.731×10^{-3}
$\widetilde{D}_1^T(O_2)$	6.303×10^{-3}	9.224×10^{-3}	8.007×10^{-3}	6.442×10^{-3}	5.319×10^{-3}
$\widetilde{D}_2^T(O_2)$	1.528×10^{-2}	1.439×10^{-2}	9.993×10^{-3}	7.453×10^{-3}	5.917×10^{-3}
$\widetilde{D}_3^T(O_2)$	-1.434×10^{-1}	-8.654×10^{-2}	-4.775×10^{-2}	-3.293×10^{-2}	-2.513×10^{-2}
$\widetilde{D}_4^T(O_2)$	8.306×10^{-2}	3.125×10^{-2}	1.319×10^{-2}	8.224×10^{-3}	5.935×10^{-3}
$\widetilde{D}_0^T(NO)$	1.617×10^{-3}	5.101×10^{-3}	6.508×10^{-3}	5.958×10^{-3}	5.249×10^{-3}
$\widetilde{D}_1^T(NO)$	4.921×10^{-3}	8.892×10^{-3}	8.611×10^{-3}	7.188×10^{-3}	6.043×10^{-3}
$\widetilde{D}_2^T(NO)$	1.428×10^{-2}	1.519×10^{-2}	1.125×10^{-2}	8.581×10^{-3}	6.889×10^{-3}
$\widetilde{D}_3^T(NO)$	-1.607×10^{-1}	-1.004×10^{-1}	-5.646×10^{-2}	-3.919×10^{-2}	-3.001×10^{-3}
$\widetilde{D}_4^T(NO)$	1.119×10^{-1}	4.019×10^{-2}	1.655×10^{-2}	1.023×10^{-2}	7.359×10^{-3}
$\widetilde{D}_0^T(Cl_2)$	6.546×10^{-3}	5.752×10^{-3}	3.844×10^{-3}	2.840×10^{-3}	2.253×10^{-3}
$\widetilde{D}_1^T(Cl_2)$	9.085×10^{-3}	6.783×10^{-3}	4.170×10^{-3}	2.991×10^{-3}	2.334×10^{-3}
$\widetilde{D}_2^T(Cl_2)$	1.248×10^{-2}	7.939×10^{-3}	4.490×10^{-3}	3.123×10^{-3}	2.394×10^{-3}
$\widetilde{D}_3^T(Cl_2)$	-6.626×10^{-2}	-3.562×10^{-2}	-1.849×10^{-2}	-1.250×10^{-2}	-9.443×10^{-3}
$\widetilde{D}_4^T(Cl_2)$	2.079×10^{-2}	9.119×10^{-3}	4.203×10^{-3}	2.697×10^{-3}	1.969×10^{-3}

Table A.1: Ratios of the thermal-diffusion and self-diffusion coefficients for N_2, H_2, O_2, NO and Cl_2 at different temperatures by considering the first five vibrational levels.

	T=2 500 K	T=5 000 K	T=10 000 K	T=15 000 K	$T = 20\,000\,\text{K}$
$\widetilde{D}_{00}(\text{N}_2)$	0.3542	0.9822	1.8639	2.3686	2.6844
$\widetilde{D}_{11}(\text{N}_2)$	4.1837	2.8779	3.0054	3.2126	3.3569
$\widetilde{D}_{22}(\text{N}_2)$	18.5106	6.5220	4.5777	4.2528	4.1407
$\widetilde{D}_{33}(\text{N}_2)$	71.2157	13.4667	6.7332	5.5302	5.0517
$\widetilde{D}_{44}(\text{N}_2)$	261.8281	26.5834	9.6735	7.0931	6.1072
$\widetilde{D}_{00}(\text{H}_2)$	0.1016	0.4437	1.1488	1.6714	2.0428
$\widetilde{D}_{11}(\text{H}_2)$	11.0703	3.7768	2.9068	2.9777	3.1000
$\widetilde{D}_{22}(\text{H}_2)$	113.692	13.6928	5.8420	4.7744	4.4190
$\widetilde{D}_{33}(\text{H}_2)$	943.481	40.9883	10.5282	7.1618	6.0160
$\widetilde{D}_{44}(\text{H}_2)$	6720.40	110.202	17.6399	10.2036	7.8760
$\widetilde{D}_{00}(\text{O}_2)$	0.6769	1.4870	2.3687	2.8009	3.0530
$\widetilde{D}_{11}(\text{O}_2)$	3.1099	2.8931	3.2143	3.4125	3.5327
$\widetilde{D}_{22}(\text{O}_2)$	8.9306	5.0505	4.2528	4.1099	4.0595
$\widetilde{D}_{33}(\text{O}_2)$	22.6566	8.3349	5.5225	4.9021	4.6362
$\widetilde{D}_{44}(\text{O}_2)$	54.551	13.295	7.0671	5.7983	5.2651
$\widetilde{D}_{00}(\text{NO})$	0.5115	1.2465	2.1428	2.6124	2.8595
$\widetilde{D}_{11}(\text{NO})$	3.4542	2.8562	3.1172	3.3246	3.4570
$\widetilde{D}_{22}(\text{NO})$	11.9094	5.5636	4.3706	4.1624	4.0896
$\widetilde{D}_{33}(\text{NO})$	35.8004	10.0777	5.9750	5.1440	4.7986
$\widetilde{D}_{44}(\text{NO})$	102.169	17.5358	8.0178	6.2893	5.5903
$\widetilde{D}_{00}(\text{Cl}_2)$	1.9253	2.7321	3.2919	3.5078	3.6226
$\widetilde{D}_{11}(\text{Cl}_2)$	3.0255	3.3776	3.6471	3.7535	3.8100
$\widetilde{D}_{22}(\text{Cl}_2)$	4.5215	4.1263	4.0281	4.0094	4.0027
$\widetilde{D}_{33}(\text{Cl}_2)$	6.5483	4.9925	4.4352	4.2756	4.2002
$\widetilde{D}_{44}(\text{Cl}_2)$	9.2838	5.9922	4.8693	4.5517	4.4022

Table A.2: Ratios of the diffusion and self-diffusion coefficients for N_2, H_2, O_2, NO and Cl_2 at different temperatures by considering the first five vibrational levels.

	T=2 500 K	T=5 000 K	T=10 000 K	T=15 000 K	$T = 20\,000$ K
$k_{T0}(N_2)$	6.120×10^{-4}	2.047×10^{-3}	2.259×10^{-3}	1.895×10^{-3}	1.584×10^{-3}
$k_{T1}(N_2)$	6.360×10^{-4}	2.078×10^{-3}	2.280×10^{-3}	1.909×10^{-3}	1.593×10^{-3}
$k_{T2}(N_2)$	6.345×10^{-4}	2.083×10^{-3}	2.284×10^{-3}	1.909×10^{-3}	1.593×10^{-3}
$k_{T3}(N_2)$	-2.509×10^{-3}	-8.205×10^{-3}	-8.875×10^{-3}	-7.366×10^{-3}	-6.116×10^{-4}
$k_{T4}(N_2)$	6.266×10^{-4}	1.997×10^{-3}	2.051×10^{-3}	1.653×10^{-3}	-4.158×10^{-3}
$k_{T0}(H_2)$	1.27×10^{-5}	7.702×10^{-4}	1.931×10^{-3}	2.040×10^{-3}	1.902×10^{-3}
$k_{T1}(H_2)$	8.98×10^{-5}	1.002×10^{-3}	2.195×10^{-3}	2.248×10^{-3}	2.063×10^{-3}
$k_{T2}(H_2)$	6.77×10^{-5}	1.015×10^{-3}	2.262×10^{-3}	2.305×10^{-3}	2.469×10^{-3}
$k_{T3}(H_2)$	-2.281×10^{-4}	-3.725×10^{-3}	-8.374×10^{-3}	-8.490×10^{-3}	-7.695×10^{-3}
$k_{T4}(H_2)$	5.79×10^{-5}	9.379×10^{-4}	1.986×10^{-3}	1.897×10^{-3}	1.262×10^{-3}
$k_{T0}(O_2)$	1.493×10^{-3}	2.335×10^{-3}	1.882×10^{-3}	1.450×10^{-3}	1.167×10^{-3}
$k_{T1}(O_2)$	1.534×10^{-3}	2.369×10^{-3}	1.899×10^{-3}	1.460×10^{-3}	1.173×10^{-3}
$k_{T2}(O_2)$	1.539×10^{-3}	2.378×10^{-3}	1.902×10^{-3}	1.459×10^{-3}	1.169×10^{-3}
$k_{T3}(O_2)$	-6.062×10^{-3}	-9.271×10^{-3}	-7.321×10^{-3}	-5.579×10^{-3}	-4.459×10^{-3}
$k_{T4}(O_2)$	1.497×10^{-3}	2.188×10^{-3}	1.637×10^{-3}	1.211×10^{-3}	9.484×10^{-4}
$k_{T0}(NO)$	1.070×10^{-3}	2.271×10^{-3}	2.071×10^{-3}	1.649×10^{-3}	1.360×10^{-3}
$k_{T1}(NO)$	1.105×10^{-3}	2.306×10^{-3}	2.091×10^{-3}	1.662×10^{-3}	1.356×10^{-3}
$k_{T2}(NO)$	1.106×10^{-3}	2.314×10^{-3}	2.095×10^{-3}	1.662×10^{-3}	1.354×10^{-3}
$k_{T3}(NO)$	-4.367×10^{-3}	-9.063×10^{-3}	-8.095×10^{-3}	-6.379×10^{-3}	-5.175×10^{-4}
$k_{T4}(NO)$	1.086×10^{-3}	2.172×10^{-3}	1.838×10^{-3}	1.405×10^{-3}	-3.552×10^{-3}
$k_{T0}(Cl_2)$	2.238×10^{-3}	1.541×10^{-3}	8.956×10^{-4}	6.300×10^{-4}	4.874×10^{-4}
$k_{T1}(Cl_2)$	2.257×10^{-3}	1.549×10^{-3}	8.973×10^{-4}	6.292×10^{-4}	4.852×10^{-4}
$k_{T2}(Cl_2)$	2.260×10^{-3}	1.549×10^{-3}	8.930×10^{-4}	6.234×10^{-4}	4.785×10^{-4}
$k_{T3}(Cl_2)$	-8.778×10^{-3}	-5.944×10^{-3}	-3.402×10^{-3}	-2.369×10^{-3}	-1.816×10^{-3}
$k_{T4}(Cl_2)$	2.023×10^{-3}	1.305×10^{-3}	7.159×10^{-4}	4.867×10^{-4}	3.647×10^{-4}

Table A.3: Thermal diffusion ratios for N_2, H_2, O_2, NO and Cl_2 at different temperatures by considering the first five vibrational levels.

ω_*	$T_0 = 2\,500$ K		$T_0 = 5\,000$ K		$T_0 = 10\,000$ K		$T_0 = 15\,000$ K		$T_0 = 20\,000$ K	
	v_*	α_*	v_*	α_*	v_*	α_*	v_*	α_*	v_*	α_*
0	1.1500	0	1.1413	0	1.1544	0	1.1657	0	1.1720	0
0.25	5.7559	0.1612	6.0730	0.1541	6.2859	0.1492	6.3773	0.1472	6.4324	0.1460
0.50	8.2762	0.1164	8.7181	0.1109	9.0188	0.1074	9.1489	0.1059	9.2272	0.1050
0.75	10.1957	0.0957	10.7335	0.0911	11.1015	0.0882	11.2612	0.0869	11.3572	0.0862
1.00	11.8082	0.0831	12.4272	0.0791	12.8518	0.0766	13.0364	0.0755	13.1474	0.0749
1.25	13.2258	0.0745	13.9165	0.0709	14.3910	0.0686	14.5976	0.0676	14.7217	0.0671

Table A.4: Dimensionless phase velocity v_* and attenuation coefficient α_* for H_2 as a function of the dimensionless frequency ω_* for different temperatures T_0.

ω_*	$T_0 = 2\,500$ K		$T_0 = 5\,000$ K		$T_0 = 10\,000$ K		$T_0 = 15\,000$ K		$T_0 = 20\,000$ K	
	v_*	α_*	v_*	α_*	v_*	α_*	v_*	α_*	v_*	α_*
0	1.1412	0	1.1524	0	1.1706	0	1.1769	0	1.1795	0
0.25	1.2923	0.2149	1.3296	0.2216	1.3702	0.2237	1.3866	0.2252	1.3960	0.2267
0.50	1.5848	0.2856	1.6511	0.2851	1.7151	0.2808	1.7423	0.2797	1.7577	0.2795
0.75	1.8857	0.2963	1.9739	0.2915	2.0537	0.2841	2.0888	0.2817	2.1092	0.2806
1.00	2.1682	0.2902	2.2742	0.2834	2.3659	0.2748	2.4072	0.2718	2.4317	0.2704
1.25	2.4307	0.2796	2.5522	0.2718	2.6537	0.2630	2.7001	0.2598	2.7281	0.2582

Table A.5: Dimensionless phase velocity v_* and attenuation coefficient α_* for N_2 as a function of the dimensionless frequency ω_* for different temperatures T_0.

ω_*	$T_0 = 2\,500\,\text{K}$		$T_0 = 5\,000\,\text{K}$		$T_0 = 10\,000\,\text{K}$		$T_0 = 15\,000\,\text{K}$		$T_0 = 20\,000\,\text{K}$	
	v_*	α_*	v_*	α_*	v_*	α_*	v_*	α_*	v_*	α_*
0	1.1717	0	1.1799	0	1.1823	0	1.1828	0	1.1830	0
0.25	1.5408	0.2669	1.7170	0.2833	1.8912	0.2910	1.9837	0.2920	2.0442	0.2918
0.50	2.0693	0.2885	2.3954	0.2794	2.7055	0.2676	2.8645	0.2610	2.9653	0.2566
0.75	2.5516	0.2726	2.9873	0.2540	3.3871	0.2371	3.5891	0.2288	3.7163	0.2238
1.00	2.9834	0.2535	3.5044	0.0.2314	3.9731	0.2133	4.2080	0.2048	4.3556	0.1998
1.25	3.3741	0.2363	3.9653	0.2131	4.4917	0.1949	4.7542	0.1867	4.9190	0.1819

Table A.6: Dimensionless phase velocity v_* and attenuation coefficient α_* for Cl_2 as a function of the dimensionless frequency ω_* for different temperatures T_0.

ω_*	$T_0 = 2\,500\,\text{K}$		$T_0 = 5\,000\,\text{K}$		$T_0 = 10\,000\,\text{K}$		$T_0 = 15\,000\,\text{K}$		$T_0 = 20\,000\,\text{K}$	
	v_*	α_*	v_*	α_*	v_*	α_*	v_*	α_*	v_*	α_*
0	$\sqrt{7/5}$	0	$\sqrt{7/5}$	0	$\sqrt{7/5}$	0	$\sqrt{7/5}$	0	$\sqrt{7/5}$	0
0.25	1.3392	0.2055	1.3617	0.2152	1.3803	0.2224	1.3893	0.2256	1.3950	0.2276
0.50	1.6386	0.2718	1.6891	0.2757	1.7299	0.2783	1.7494	0.2794	1.7614	0.2800
0.75	1.9421	0.2814	2.0131	0.2813	2.0705	0.2809	2.0979	0.2807	2.1149	0.2805
1.00	2.2235	0.2755	2.3113	0.2733	2.3827	0.2715	2.4169	0.2706	2.4381	0.2700
1.25	2.4825	0.2657	2.5854	0.2624	2.6693	0.2597	2.7096	0.2584	2.7346	0.2576

Table A.7: Dimensionless phase velocity v_* and attenuation coefficient α_* for N_2 as a function of the dimensionless frequency ω_* for different temperatures T_0, when the vibrational levels are not taken into account.

ω_*	$T_0 = 2\,500\,\text{K}$		$T_0 = 5\,000\,\text{K}$		$T_0 = 10\,000\,\text{K}$		$T_0 = 15\,000\,\text{K}$		$T_0 = 20\,000\,\text{K}$	
	v_*	α_*	v_*	α_*	v_*	α_*	v_*	α_*	v_*	α_*
0	1.1392	0	1.1353	0	1.1343	0	1.1352	0	1.1383	0
0.25	1.2960	0.2187	1.3161	0.2310	1.3350	0.2391	1.3454	0.2424	1.3512	0.2423
0.50	1.5976	0.2871	1.6482	0.2927	1.6913	0.2957	1.7130	0.2964	1.7216	0.2955
0.75	1.9040	0.2955	1.9778	0.2965	2.0394	0.2960	2.0700	0.2953	2.0802	0.2941
1.00	2.1886	0.2882	2.2818	0.2866	2.3590	0.2843	2.3965	0.2828	2.4088	0.2817
1.25	2.4512	0.2771	2.5617	0.2740	2.6528	0.2707	2.6966	0.2688	2.7103	0.2676

Table A.8: Dimensionless phase velocity v_* and attenuation coefficient α_* for N_2 in a one-temperature approximation.