

Effect of strong excitation of the CO₂ asymmetric mode on transport properties

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Abstract

Transport properties of carbon dioxide with strongly excited asymmetric vibrational mode are studied on the basis of kinetic theory treatment. The kinetic model takes into account anharmonism of molecular vibrations and different rates of various energy exchanges. The method of transport coefficients derivation is proposed. The calculation of nonequilibrium specific heats is carried out using a non-Boltzmann distribution of the molecules over vibrational energy levels. The effect of strong vibrational excitation and anharmonicity on thermal conductivity, shear and bulk viscosity coefficients is estimated.

1. Introduction

Development of laser physics, plasma chemistry, atmosphere physics, dynamics of expanding flows and other fields of modern sciences requires the prediction of nonequilibrium transport properties in polyatomic gases. The first attempt of description of thermal conductivity in molecular gases was done by Eucken [1]. He derived an empirical model which connects thermal conductivity with heat capacity of internal degrees of freedom. More rigorous models were developed for weak-nonequilibrium conditions [2–5] on the basis of kinetic theory. Thermal conductivity coefficients of CO₂ under strong vibrational nonequilibrium conditions were considered in Refs. [6,7]. However, in all these works the complex structure of the molecule CO₂ was neglected, and various vibrational modes were not distinguished. Actually, a precise description of internal modes and their interaction remains complicated. Real gas effects such as anharmonism of molecular vibrations, different rates of various energy exchange inside and between modes can disturb the equilibrium distribution functions and impact essentially on transport terms. The vibrational kinetics of polyatomic gases taking into account these peculiarities was studied in Refs. [8–10]. The kinetic model of dissipative processes in polyatomic gases considering the vibrational energy exchange within and between modes was proposed in Ref. [11]. Transport properties of CO₂ simulated by a set of harmonic oscillators were investigated in Ref. [12].

Strong excitation of asymmetric vibrations occurs in many cases such as flows in nozzles and gasdynamic lasers [13,14], experiments on laser fluorescence [15] or nonequilibrium plasmas and discharges [10]. In

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the present paper transport coefficients in carbon dioxide with strongly excited asymmetric vibrational mode are studied on the basis of the kinetic theory treatment taking into account anharmonic effects. The linear tri-atomic molecule CO₂ is simulated by a rigid rotator and a set of three anharmonic oscillators. The modified Chapman–Enskog method is used for the determination of distribution functions and evaluation of transport terms. It is shown that anharmonism of molecular vibrations and non-Boltzmann distribution of molecules over vibrational levels can influence significantly the specific heats and thermal conductivity coefficients.

2. Kinetic equations

The carbon dioxide molecule is a linear triatomic molecule which, in the ground electronic state, has three vibrational degrees of freedom. The first mode is the symmetric stretching mode with frequency ν_1 , the second is the doubly degenerate bending mode with frequency ν_2 , and the third is the asymmetric stretching mode with frequency ν_3 .

Vibrational energy of linear tri-atomic molecules is defined as follows [16]:

$$\begin{aligned} \varepsilon_{i_1 i_2 i_3}^e = & \sum_{k=1}^3 \omega_k^e \left(i_k + \frac{d_k}{2} \right) + \sum_{k=1}^3 \sum_{j \geq k}^3 x_{kj}^e \left(i_k + \frac{d_k}{2} \right) \left(i_j + \frac{d_j}{2} \right) \\ & + \sum_{k=1}^3 \sum_{j \geq k}^3 \sum_{l \geq j \geq k}^3 y_{kjl}^e \left(i_k + \frac{d_k}{2} \right) \left(i_j + \frac{d_j}{2} \right) \left(i_l + \frac{d_l}{2} \right) + x_{il}^e l^2 + \sum_{k=1}^3 y_{kll}^e i_k l^2 \dots \end{aligned} \quad (1)$$

Here i_1, i_2, i_3 are the vibrational quantum numbers corresponding to the symmetric, bending and asymmetric modes, d_k is the degree of degeneracy of the k th mode, l is the additional quantum number describing the projection of the angular momentum of the bending vibrations onto the axis of the molecule, ω_k^e is the wave number of k th mode, x_{kj}^e and y_{kjl}^e are the constants of anharmonicity.

Rotational energy levels are described by the rigid rotator model. Vibrational and rotational energy levels are assumed to be independent, i.e.

$$\varepsilon_{ij} = \varepsilon_i + \varepsilon_j, \quad (2)$$

with j the rotational quantum number and ε_{ij} the total internal energy of the molecule.

The system of Boltzmann kinetic equations for the distribution functions $f_{ij}(\mathbf{r}, \mathbf{u}, t)$ of each vibrational $i = (i_1, i_2, i_3)$ and rotational j species over velocities \mathbf{u} and spatial and temporal co-ordinates \mathbf{r} and t can be written in the form of Wang Chang and Uhlenbeck [3]:

$$\frac{\partial f_{ij}}{\partial t} + \mathbf{u} \cdot \frac{\partial f_{ij}}{\partial \mathbf{r}} = J_{ij}, \quad (3)$$

where the collisional operator J_{ij} has the form:

$$J_{ij} = \frac{1}{2} \sum_{klj'k'l'} \int \left(f_{i'j'} f_{k'l'} \frac{s_{ij} s_{kl}}{s_{i'j'} s_{k'l'}} - f_{ij} f_{kl} \right) g \sigma_{ijkl}^{i'j'k'l'} d^2 \Omega d^3 \mathbf{u}_{kl}, \quad (4)$$

in which $\sigma_{ijkl}^{i'j'k'l'}$ is the differential cross section for inelastic scattering into a solid angle $d^2 \Omega$ of the molecules at the i th and k th vibrational levels and j th and l th rotational ones, g is the relative velocity, while $s_{ij} = s_i s_j$, s_i and s_j are the vibrational and rotational statistical weights. The collisional operator represents the sum of several terms which describe collisions of different types:

$$J_{ij} = J_{ij}^{TT} + J_{ij}^{RR} + J_{ij}^{RT} + J_{ij}^{W'} + J_{ij}^{W''} + J_{ij}^{VT} + J_{ij}^{VRT}. \quad (5)$$

The term J_{ij}^{TT} is concerned with elastic collisions, J_{ij}^{RR} and J_{ij}^{RT} represent collisions with rotational and rotational-translational energy exchanges, J_{ij}^{VRT} corresponds to collisions with exchange of all kinds of energy. The collision integrals $J_{ij}^{W'}$ and $J_{ij}^{W''}$ describe collisions with vibrational energy transfer within and between vibrational modes, and can be written as a sum of terms:

$$J_{ij}^{W'} = J_{ij}^{W'_1} + J_{ij}^{W'_2} + J_{ij}^{W'_3}, \quad (6)$$

$$J_{ij}^{W''} = J_{ij}^{W''_1} + J_{ij}^{W''_2} + J_{ij}^{W''_3}. \quad (7)$$

Collisions with vibrational–translational energy exchange are characterized by the operator J_{ij}^{VT} which can also be expressed as a sum of three terms.

It is known that in real gas flows the rates of various processes can differ significantly. Thus, for the equilibration of the translational degrees of freedom, only a few collisions are needed, whereas vibrational relaxation requires several thousand collisions [9,17]. The macroscopic kinetic model depends essentially on the relations between characteristic times of different processes. Strong nonequilibrium conditions appear when some of characteristic relaxation times become comparable with the macroscopic time θ , and hence the right-hand side of the kinetic equation (3) can be written as a sum of terms of different orders [7,18]:

$$\frac{\partial f_{ij}}{\partial t} + \mathbf{u} \frac{\partial f_{ij}}{\partial \mathbf{r}} = \frac{1}{\varepsilon} J_{ij}^{\text{rap}} + J_{ij}^{\text{sl}}, \quad (8)$$

where $\varepsilon = \tau_{\text{rap}}/\tau_{\text{sl}}$ is a small parameter, τ_{rap} and τ_{sl} are the mean times between frequent and rare collisions, J_{ij}^{rap} and J_{ij}^{sl} are the collision operators for rapid and slow processes. The structure of these operators is determined by the specific flow conditions. Thus, in the general case, for a linear triatomic molecule with strongly excited vibrational degrees of freedom, nonresonant W' -exchange within modes is much more probable than exchange of vibrational energy between different modes and VT exchange [9]. In the particular case of the CO_2 molecule, Fermi resonance [16] results in increasing the probability of near-resonant exchange between the symmetric and bending modes. Strong coupling of the symmetric and bending modes is typical for flows behind shock waves, in nozzles and discharges [14,15]. Under conditions of essential excitation of the third mode the equilibration of the combined Fermi-resonance mode is found to be more rapid when compared to the relaxation of the asymmetric vibrations [15]. A number of experiments on laser fluorescence [13,15] and measurements of vibrational temperatures in laser mixtures containing CO_2 [14] show that the symmetric and bending modes can often be considered to be in equilibrium with the rotational and translational degrees of freedom. In this case the hierarchy between relaxation times is the following:

$$\tau_{TT} < \tau_{RT} \sim \tau_{RR} < \tau_{W'_{1,2,3}} \sim \tau_{W''_{1,2}} \sim \tau_{VT_{1,2}} \ll \tau_{VT_3} \sim \tau_{W'_3} \sim \tau_{VRT} \sim \theta. \quad (9)$$

This relation is also valid for flow behind a strong shock wave, except for the zone of relaxation of the combined mode, which is rather short when compared to the length of the relaxation zone for the vibrational energy.

3. Zeroth-order approximation

For the solution of Eq. (8) the generalized Chapman–Enskog method is used. Distribution functions $f_{ij}(\mathbf{r}, \mathbf{u}_c, t)$ are expanded in power series of the parameter ε ($\varepsilon \ll 1$). The zeroth approach gives the following relation [18]:

$$J_{ij}^{\text{rap}}(f^{(0)}, f^{(0)}) = 0. \quad (10)$$

Under conditions (9) integral operators of rapid and slow processes can be written as:

$$J_{ij}^{\text{rap}} = J_{ij}^{\text{TT}} + J_{ij}^{\text{RR}} + J_{ij}^{\text{RT}} + J_{ij}^{\text{W}'_{1,2,3}} + J_{ij}^{\text{VT}_{1,2}} + J_{ij}^{\text{W}''_{1,2}}, \quad (11)$$

$$J_{ij}^{\text{sl}} = J_{ij}^{\text{VT}_3} + J_{ij}^{\text{W}'_3} + J_{ij}^{\text{VRT}}. \quad (12)$$

The logarithm of the zeroth order distribution function $\ln f_{ij}^{(0)}/s_{ij}$ is found to be a linear combination of the summational invariants $\psi_{ij}^{(\lambda)}$ ($\lambda = 1, 2, \dots$) of the most frequent collisions (eigenfunctions of the linearized collisional integral of rapid processes J_{ij}^{rap}). The invariants for all collisions are the number of particles ($\psi_{ij}^{(1)} = 1$), the momentum ($\psi_{ij}^{(2)} = m\mathbf{u}$, m is the molecular mass), and the total energy of the molecule ($\psi_{ij}^{(3)} = mu^2/2 + \varepsilon_i + \varepsilon_j$). In strong nonequilibrium conditions there exist also additional invariants of the rapid process. For the harmonic oscillator model W exchange is resonant, and the vibrational energy of the molecule is conserved in rapid processes. For the anharmonic oscillator models this quantity is not conserved due to the nonequidistant separation of the vibrational levels. The number of vibrational quanta was found to be an additional collisional invariant for diatomic gases [19]. For polyatomic molecules under conditions (9), the number of vibrational quanta of the asymmetric mode is conserved in nonresonant W'_3 exchange ($\psi_{ij}^{(4)} = i_3$).

Actually, this last invariant exists only for the lower vibrational levels, when the most frequent collisions do not include resonant exchange between the neighboring levels in each mode. In addition, the probability of VT exchange increases rapidly with vibrational quantum number for the anharmonic oscillator, and for the upper levels becomes comparable with the probability of W transfers [19]. Taking these features into account leads to a complex form for the distribution function. Such a distribution has been derived for diatomic gases in Refs. [20,21]. It is also known that for a high degree of vibrational excitation, a strong interaction occurs between vibrational modes, and that in the quasi-continuum region they cannot be distinguished. The vibrational kinetics of the CO_2 molecule with mixed modes in the upper levels has been studied in Ref. [10]. The present work is restricted to those levels of the asymmetric mode for which nonresonant processes are more probable. Vibrational modes are assumed to be separable.

The normalizing conditions for the distribution function are written using the system of collision invariants:

$$n = \sum_{ij} \int f_{ij} \, d\mathbf{u} = \sum_{ij} \int f_{ij}^{(0)} \, d\mathbf{u}, \quad (13)$$

$$\rho\mathbf{v} = \sum_{ij} \int m\mathbf{u} f_{ij} \, d\mathbf{u} = \sum_{ij} \int m\mathbf{u} f_{ij}^{(0)} \, d\mathbf{u}, \quad (14)$$

$$\rho U = \sum_{ij} \int \left(\frac{mu^2}{2} + \varepsilon_i + \varepsilon_j \right) f_{ij} \, d\mathbf{u} = \sum_{ij} \int \left(\frac{mu^2}{2} + \varepsilon_i + \varepsilon_j \right) f_{ij}^{(0)} \, d\mathbf{u}, \quad (15)$$

$$\rho W_3 = \sum_{ij} i_3 \int f_{ij} \, d\mathbf{u} = \sum_{ij} i_3 \int f_{ij}^{(0)} \, d\mathbf{u}. \quad (16)$$

Here n is the total number of particles, \mathbf{v} is the macroscopic velocity, ρ is the density, W_3 is the average number of vibrational quanta in the asymmetric mode per unit mass, U is the total energy per unit mass:

$$\rho U = \frac{3}{2}nkT + \rho E_r + \rho E_v, \quad (17)$$

where k is the Boltzmann constant, T is the gas temperature, and E_r , E_v , are respectively the rotational, vibrational energy per unit mass.

Starting from the system of collisional invariants and using the normalizing conditions (13)–(16), the distribution function in the zeroth Chapman–Enskog approximation method is found to be

$$f_{ij}^{(0)} = \frac{ns_{ij}}{Z_r Z_v} \exp \left(-\frac{mc^2}{2kT} - \frac{\varepsilon_j}{kT} - \frac{\varepsilon_i}{kT} \right) X_i. \quad (18)$$

Here $\mathbf{c} = \mathbf{u} - \mathbf{v}$ is the peculiar velocity. Partition functions are defined as follows:

$$Z_t = \left(\frac{2\pi kT}{m} \right)^{3/2}, \quad Z_r = \sum_j s_j \exp\left(-\frac{\varepsilon_j}{kT}\right), \quad Z_v = \sum_i s_i \exp\left(-\frac{\varepsilon_i}{kT}\right) X_i. \quad (19)$$

The term X_i describes the deviation of the zeroth-order distribution function from the equilibrium Maxwell-Boltzmann distribution, and is due to the conservation of some additional quantities in the most frequent collisions [18]. In the present case X_i is determined by the conservation of the number of vibrational quanta in the asymmetric mode i_3 :

$$X_i = \exp(\gamma_3 i_3). \quad (20)$$

The parameter γ_3 is defined from the normalizing condition (16) and can be expressed in terms of the “effective” temperature of the first level of the asymmetric vibrational mode:

$$\gamma_3 = \frac{\varepsilon_{13}}{k} \left(\frac{1}{T} - \frac{1}{T_3} \right), \quad \varepsilon_{13} = \varepsilon_{0,0^0,1}. \quad (21)$$

Thus the distribution function (18) takes a form

$$f_{ij}^{(0)} = \frac{ns_{ij}}{Z_t Z_r Z_v} \exp\left(-\frac{mc^2}{2kT} - \frac{\varepsilon_j}{kT} - \frac{\varepsilon_i - i_3 \varepsilon_{13}}{kT} - \frac{i_3 \varepsilon_{13}}{kT_3}\right). \quad (22)$$

Nonequilibrium populations of vibrational levels $n_i = n_{i_1, i_2, i_3}$ are obtained from Eq. (22) as follows:

$$n_i = \frac{ns_i}{Z_v} \exp\left(-\frac{\varepsilon_i - i_3 \varepsilon_{13}}{kT} - \frac{i_3 \varepsilon_{13}}{kT_3}\right). \quad (23)$$

One can see that the distribution (23) represents a Boltzmann distribution of the molecules over the vibrational levels in the symmetric and bending modes and an analogue of the Treanor distribution in the asymmetric mode. For vibrational equilibrium, with $T_3 = T$, it reduces to the equilibrium Boltzmann distribution with temperature T . If the anharmonism of the vibrations is negligible, then Eq. (23) reduces to the nonequilibrium multi-temperature Boltzmann distribution, with the vibrational temperature of the asymmetric mode $T_v^3 = T_3$.

Fig. 1 represents reduced level populations of asymmetric mode $n_{0,0^0,i_3}/n$ as functions of i_3 at $T = 1000$ K for different T_3 as well as the corresponding Boltzmann distributions for the harmonic oscillator model. One can conclude that for $T_3 < T$ the deviation of (23) from the Boltzmann distribution is negligible. The discrepancy becomes noticeable for equilibrium conditions (i.e. $T_3 = T$), and increases essentially with the nonequilibrium factor T_3/T . Populating the more energetic higher levels will therefore have a significant effect on nonequilibrium specific heats.

4. Macroscopic equations

The macroparameters ρ , \mathbf{v} , U and W_3 are found from the following system of equations.

Equation of mass conservation:

$$\frac{d\rho}{dt} + \rho \nabla \mathbf{v} = 0; \quad (24)$$

Equation of momentum conservation:

$$\rho \frac{d\mathbf{v}}{dt} + \nabla \mathbf{P} = 0; \quad (25)$$

Equation of total energy conservation:

$$\rho \frac{dU}{dt} + \nabla \mathbf{q} + \mathbf{P} : \nabla \mathbf{v} = 0; \quad (26)$$

Relaxation equation for the mean number of vibrational quanta in the third mode (it is written in the dimension of energy):

$$\rho \frac{d(\varepsilon_{13} W_3)}{dt} + \nabla \mathbf{q}_3 = \sum_{ij} i_3 \varepsilon_{13} \int J_{ij}^{sl} d\mathbf{u}. \quad (27)$$

Here \mathbf{P} is the pressure tensor:

$$\mathbf{P} = \sum_{ij} \int m \mathbf{c} \mathbf{c} f_{ij} d\mathbf{u}; \quad (28)$$

\mathbf{q} is the heat flux:

$$\mathbf{q} = \sum_{ij} \int \left(\frac{m\mathbf{c}^2}{2} + \varepsilon_i + \varepsilon_j \right) \mathbf{c} f_{ij} d\mathbf{u}; \quad (29)$$

and \mathbf{q}_3 is the flux of vibrational quanta in the third mode:

$$\mathbf{q}_3 = \sum_{ij} i_3 \varepsilon_{13} \int \mathbf{c} f_{ij} d\mathbf{u}. \quad (30)$$

In the zeroth approximation $\mathbf{q}^{(0)} = \mathbf{q}_3^{(0)} = 0$, $\mathbf{P}^{(0)} = p\mathbf{I}$, $p = nkT$, \mathbf{I} is the unit tensor. For the derivation of the first-order distribution functions and transport terms nonequilibrium specific heats must first be defined.

5. Nonequilibrium specific heats

On the basis of zeroth-order distribution functions (22) the nonequilibrium specific heats at constant volume are introduced, as follows:

$$c_t = \frac{\partial E_t}{\partial T} = \frac{3}{2} \frac{k}{m}, \quad c_r = \frac{\partial E_r}{\partial T}, \quad (31)$$

$$c_v^T = \frac{\partial E_v(T, T_3)}{\partial T}, \quad c_v^{T_3} = \frac{\partial E_v(T, T_3)}{\partial T_3}. \quad (32)$$

Here translational, rotational and vibrational energy per unit mass E_t , E_r , E_v are defined as:

$$\rho E_t(T) = \frac{3}{2} nkT,$$

$$\rho E_r(T) = \sum_{ij} \int \varepsilon_j f_{ij}^{(0)} d\mathbf{u} = \frac{n}{Z_r} \sum_j \varepsilon_j \exp\left(-\frac{\varepsilon_j}{kT}\right),$$

$$\rho E_v(T, T_3) = \sum_{ij} \int \varepsilon_i f_{ij}^{(0)} d\mathbf{u} = \sum_i \varepsilon_i n_i = \frac{n}{Z_v} \sum_i \varepsilon_i \exp\left(-\frac{\varepsilon_i - i_3 \varepsilon_{13}}{kT} - \frac{i_3 \varepsilon_{13}}{kT_3}\right). \quad (33)$$

For gas temperatures higher than room temperature the rotational specific heat can be defined classically: $c_r = k/m$ (except for the light molecules H_2 , D_2). Vibrational specific heats depend on both gas temperature

and the temperature T_3 ; they differ from the equilibrium specific heats and those calculated with the harmonic oscillator model. Thus, for the harmonic oscillator $c_v^T = c_v^T(T)$ and $c_v^{T_3} = c_v^{T_3}(T_3)$.

It is conventional to introduce the definition of the averaged value $\langle \xi \rangle_v$ of ξ_i over the vibrational spectrum:

$$\langle \xi \rangle_v = \frac{1}{n} \sum_i \xi_i n_i = \frac{1}{Z_v} \sum_i \xi_i \exp \left(-\frac{\varepsilon_i - i_3 \varepsilon_{13}}{kT} - \frac{i_3 \varepsilon_{13}}{kT_3} \right), \quad (34)$$

and $\langle \xi \rangle_r$, the averaged value of ξ_j over the rotational spectrum:

$$\langle \xi \rangle_r = \frac{1}{Z_r} \sum_j \xi_j \exp \left(-\frac{\varepsilon_j}{kT} \right). \quad (35)$$

After carrying out differentiation one can obtain the following expressions for the vibrational specific heats:

$$c_v^T = \frac{k}{m} \left(\left\langle \frac{\varepsilon_i}{kT} \frac{\varepsilon_i - i_3 \varepsilon_{13}}{kT} \right\rangle_v - \left\langle \frac{\varepsilon_i}{kT} \right\rangle_v \left\langle \frac{\varepsilon_i - i_3 \varepsilon_{13}}{kT} \right\rangle_v \right), \quad (36)$$

$$c_v^{T_3} = \frac{k}{m} \left(\left\langle \frac{\varepsilon_i}{kT} \frac{i_3 \varepsilon_{13}}{kT_3} \right\rangle_v - \left\langle \frac{\varepsilon_i}{kT} \right\rangle_v \left\langle \frac{i_3 \varepsilon_{13}}{kT_3} \right\rangle_v \right). \quad (37)$$

For a clearer understanding of further developments, it is necessary to introduce additional modified specific heats:

$$c_w^T = \frac{\partial (\varepsilon_{13} W_3(T, T_3))}{\partial T}, \quad c_w^{T_3} = \frac{\partial (\varepsilon_{13} W_3(T, T_3))}{\partial T_3}, \quad (38)$$

and total specific heat:

$$c_u = \frac{\partial U}{\partial T} = c_t + c_r + c_v^T. \quad (39)$$

The expressions for c_w^T and $c_w^{T_3}$ have the forms:

$$c_w^T = \frac{k}{m} \frac{T_3}{T} \left(\left\langle \frac{i_3 \varepsilon_{13}}{kT_3} \frac{\varepsilon_i - i_3 \varepsilon_{13}}{kT} \right\rangle_v - \left\langle \frac{i_3 \varepsilon_{13}}{kT_3} \right\rangle_v \left\langle \frac{\varepsilon_i - i_3 \varepsilon_{13}}{kT} \right\rangle_v \right), \quad (40)$$

$$c_w^{T_3} = \frac{k}{m} \left(\left\langle \left(\frac{i_3 \varepsilon_{13}}{kT_3} \right)^2 \right\rangle_v - \left\langle \frac{i_3 \varepsilon_{13}}{kT_3} \right\rangle_v^2 \right). \quad (41)$$

For thermal equilibrium ($T_3 = T$) the total vibrational specific heat is $c_v = c_v^T + c_v^{T_3}$. This value has been calculated for CO₂ in the temperature range 300–4500 K for varying numbers of vibrational energy levels. The results are plotted in Fig. 2. Furthermore, the dimensionless specific heats (divided by k/m) are considered with the same notation. One can see that by increasing the gas temperature the upper levels become populated significantly, and consideration of only the lower levels leads to irregular behavior of c_v , with a consequent underestimation of its values. Thus, consideration of the 10 first levels in each mode gives reasonable values for c_v up to temperatures of 1000 K. Then, for temperatures up to 2500 K 30 levels are sufficient for a good estimation of c_v . Finally, for higher temperatures ($T < 6000$ K) 60 vibrational levels in each mode need to be taken into account. The influence of anharmonism on the equilibrium specific heat reaches 5% at $T = 4500$ K, and increases with temperature.

The effect of strong excitation of the asymmetric mode on specific heats is presented in Figs. 3 and 4 where their dependence on T_3 is plotted at different T . Both c_v^T and $c_v^{T_3}$ increase with T_3 and T . The comparison with

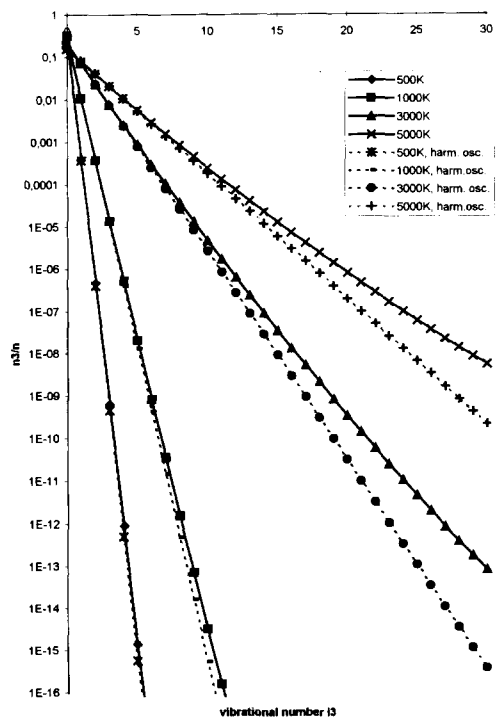


Fig. 1. Level populations of the CO₂ asymmetric mode $n_{0,1^0, i_3} / n$ for different values of T_3 for $T = 1000$ K. Comparison with the harmonic oscillator model.

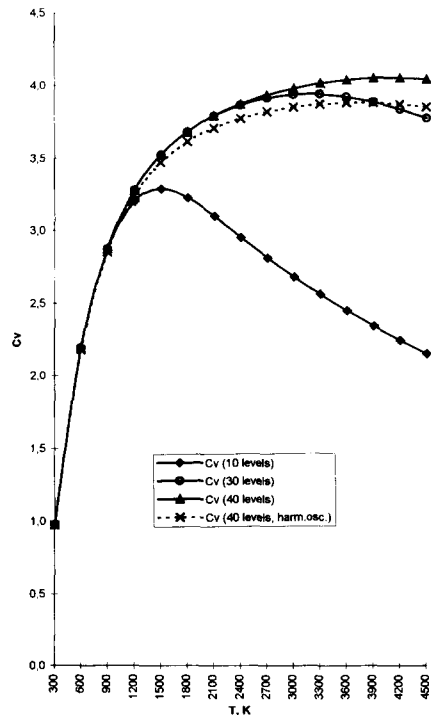


Fig. 2. Thermal equilibrium CO₂ specific heat c_v as a function of T calculated with different numbers of vibrational levels. Comparison with the harmonic oscillator model.

specific heats calculated for the harmonic oscillator model shows the essential discrepancy for large values of the nonequilibrium factor $\gamma = T_3/T$. This deviation is related to the increased populations of the upper vibrational levels in the case of the anharmonic oscillator (see Fig. 1). The surprising behavior of the specific heat $c_v^{T_3}$ at $T = 500$ K is explained by the strong influence of the non-Boltzmann vibrational distribution at high values of the nonequilibrium factor, $\gamma > 5-6$. It is interesting to note that peaks, corresponding to $\gamma \sim 6-8$, are achieved at the maximum vibrational energy store at several lower levels. Further decreasing of the specific heat $c_v^{T_3}$ with increasing γ is due to the re-distribution of vibrational energy over vibrational levels and the shift of its maximum towards the higher levels. A similar behavior of the specific heat in excited diatomic gases was obtained in Ref. [21].

6. First-order approximation

The first-order distribution functions are found from the following linear integral equation:

$$J_{ij}^{\text{rap}}(f^{(0)}, f^{(0)})\phi = \frac{df_{ij}^{(0)}}{dt} - J_{ij}^{\text{sl}}(f^{(0)}, f^{(0)}). \quad (42)$$

Here ϕ_{ij} is the perturbation term, $f_{ij}^{(1)} = \phi_{ij} f_{ij}^{(0)}$.

Upon converting to the peculiar velocity \mathbf{c} and taking into account the zeroth-order distribution functions (22) and macroscopic equations (24)–(27) in zeroth-approach, one can express $df_{ij}^{(0)}/dt$ in the form:

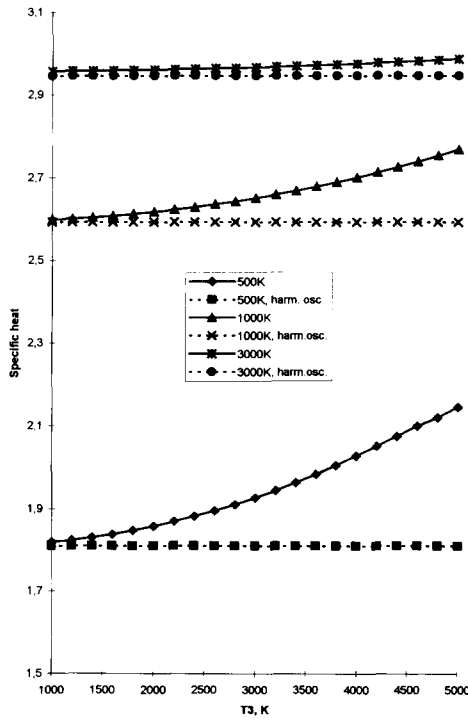


Fig. 3. Specific heat c_v^T as a function of T_3 for different T . Comparison with the harmonic oscillator model.

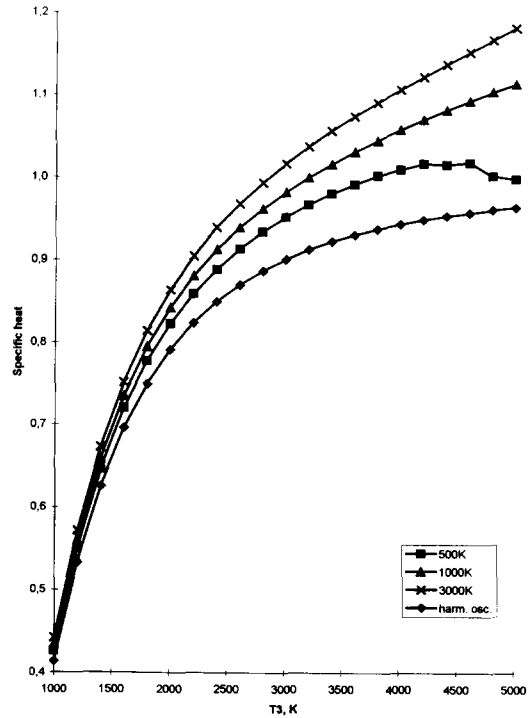


Fig. 4. Specific heat $c_v^{T_3}$ as a function of T_3 for different T . Comparison with the harmonic oscillator model.

$$\begin{aligned}
 \frac{df_{ij}^{(0)}}{dt} = f_{ij}^{(0)} & \left\{ \left(\frac{mc^2}{2kT} - \frac{5}{2} + \left[\frac{\epsilon_j}{kT} \right]'_r + \left[\frac{\epsilon_i - i_3 \epsilon_{13}}{kT} \right]'_v \right) \mathbf{c} \nabla \ln T \right. \\
 & + \left[\frac{i_3 \epsilon_{13}}{kT_3} \right]'_v \mathbf{c} \nabla \ln T_3 + \left(\frac{m}{2kT} \mathbf{c} \mathbf{c} - \frac{1}{3} \frac{mc^2}{2kT} \mathbf{I} \right) : \nabla \mathbf{v} \\
 & + \left(\frac{-nkT}{\rho(c_u c_w^{T_3} - c_w^T c_v^{T_3})} \left(\left(\frac{mc^2}{2kT} - \frac{3}{2} + \left[\frac{\epsilon_i - i_3 \epsilon_{13}}{kT} \right]'_v \right) \right. \right. \\
 & + \left. \left. \left[\frac{\epsilon_j}{kT} \right]'_r \right) \frac{c_w^{T_3}}{T} - \left[\frac{i_3 \epsilon_{13}}{kT_3} \right]'_v \frac{c_w^T}{T_3} + \frac{mc^2}{3kT} - 1 \right) \cdot \nabla \mathbf{v} \\
 & - \frac{R}{\rho(c_u c_w^{T_3} - c_w^T c_v^{T_3})} \left(\left(\frac{mc^2}{2kT} - \frac{3}{2} + \left[\frac{\epsilon_i - i_3 \epsilon_{13}}{kT} \right]'_v \right) \right. \\
 & \left. \left. + \left[\frac{\epsilon_j}{kT} \right]'_r \right) \frac{c_v^{T_3}}{T} - \left[\frac{i_3 \epsilon_{13}}{kT_3} \right]'_v \frac{c_u}{T_3} \right) \left. \right\}, \tag{43}
 \end{aligned}$$

where

$$\left[\xi_i \right]'_v = \xi_i - \langle \xi \rangle_v, \quad \left[\xi_j \right]'_r = \xi_j - \langle \xi \rangle_r, \tag{44}$$

with average values defined by Eqs. (34) and (35), and R given by:

$$R = \sum_{ij} \varepsilon_{13} \int J_{ij}^{sl}(f^{(0)}, f^{(0)}) d\mathbf{u}. \quad (45)$$

Proceeding from Eq. (43), the solution of Eq. (42) can be found to have the form

$$f_{ij}^{(1)} = f_{ij}^{(0)} \left(-\frac{1}{n} A_{ij} \nabla \ln T - \frac{1}{n} A_{ij}^{(3)} \nabla \ln T_3 - \frac{1}{n} \mathbf{B}_{ij} : \nabla \mathbf{v} - \frac{1}{n} F_{ij} \nabla \mathbf{v} - \frac{1}{n} G_{ij} \right), \quad (46)$$

in which functions A_{ij} , $A_{ij}^{(3)}$, \mathbf{B}_{ij} , F_{ij} , G_{ij} depend on the microscopic velocities \mathbf{u} and the macroparameters $n(\mathbf{r}, t)$, $\mathbf{v}(\mathbf{r}, t)$, $T(\mathbf{r}, t)$, $T_3(\mathbf{r}, t)$, and can be obtained from the linear integral equations which follow from Eq. (42) after substituting Eq. (43) into Eq. (42) and equating the coefficients of the gradients of the same macroparameters. Finally, these integral equations take the forms:

$$nI_{ij}(A) = f_{ij}^{(0)} c \left(C^2 - \frac{5}{2} + \left[\frac{\varepsilon_j}{kT} \right]'_r + \left[\frac{\varepsilon_i - i_3 \varepsilon_{13}}{kT} \right]'_v \right), \quad (47)$$

$$nI_{ij}(A^{(3)}) = f_{ij}^{(0)} c \left[\frac{i_3 \varepsilon_{13}}{kT_3} \right]'_v, \quad (48)$$

$$nI_{ij}(B) = 2f_{ij}^{(0)} (CC - \frac{1}{3}C^2I), \quad (49)$$

$$nI_{ij}(F) = f_{ij}^{(0)} \left(\frac{-nkT}{\rho(c_u c_w^{T_3} - c_w^T c_v^{T_3})} \left(\left(C^2 - \frac{3}{2} + \left[\frac{\varepsilon_i - i_3 \varepsilon_{13}}{kT} \right]'_v \right. \right. \right. \\ \left. \left. \left. + \left[\frac{\varepsilon_j}{kT} \right]'_r \right) \frac{c_w^{T_3}}{T} - \left[\frac{i_3 \varepsilon_{13}}{kT_3} \right]'_v \frac{c_w^T}{T_3} \right) + \frac{2}{3}C^2 - 1 \right), \quad (50)$$

$$nI_{ij}(G) = -f_{ij}^{(0)} \left(\frac{R}{\rho(c_u c_w^{T_3} - c_w^T c_v^{T_3})} \left(\left(C^2 - \frac{3}{2} + \left[\frac{\varepsilon_i - i_3 \varepsilon_{13}}{kT} \right]'_v \right. \right. \right. \\ \left. \left. \left. + \left[\frac{\varepsilon_j}{kT} \right]'_r \right) \frac{c_v^{T_3}}{T} - \left[\frac{i_3 \varepsilon_{13}}{kT_3} \right]'_v \frac{c_u}{T_3} \right) - J_{ij}^{sl}(f^{(0)}, f^{(0)}) \right), \quad (51)$$

where

$$C = \sqrt{\frac{m}{2kT}} c$$

is the reduced peculiar velocity, and I_{ij} is a linearized operator of rapid processes:

$$I_{ij}(\phi) = \frac{1}{n^2} \sum_{k,l,i',j',k',l'} \int f_{ij}^{(0)} f_{kl}^{(0)} (\phi_{ij} + \phi_{kl} - \phi'_{i'j'} - \phi'_{k'l'}) g \sigma_{ijkl}^{i'j'k'l'(0)} d\mathbf{u}_{ij} d^2\Omega. \quad (52)$$

From the normalizing conditions (13)–(16) additional constraints for the functions $A = A(\mathbf{c})c$, $A^{(3)} = A^{(3)}(\mathbf{c})c$, F , G are derived:

$$\sum_{ij} m \int f_{ij}^{(0)} A c^2 d\mathbf{u} = 0, \quad \sum_{ij} m \int f_{ij}^{(0)} A^{(3)} c^2 d\mathbf{u} = 0, \quad (53)$$

$$\sum_{ij} \int f_{ij}^{(0)} F d\mathbf{u} = 0, \quad \sum_{ij} \int f_{ij}^{(0)} G d\mathbf{u} = 0, \quad (54)$$

$$\sum_{ij} \int f_{ij}^{(0)} \left(\frac{mc^2}{2} + \varepsilon_j + \varepsilon_i \right) F \, d\mathbf{u} = 0, \quad (55)$$

$$\sum_{ij} \int f_{ij}^{(0)} \left(\frac{mc^2}{2} + \varepsilon_j + \varepsilon_i \right) G \, d\mathbf{u} = 0. \quad (56)$$

These constraints should be taken into account for the solution of the integral equations (47)–(50).

7. Transport terms

First-order distribution functions provide the following expression for the pressure tensor \mathbf{P} :

$$\mathbf{P} = (p - p_{\text{rel}})\mathbf{I} - 2\mu\mathbf{S} - \eta\nabla \cdot \mathbf{v}\mathbf{I}. \quad (57)$$

Here μ , η are the shear and bulk viscosity coefficients, p_{rel} is the relaxation pressure:

$$\mu = \frac{kT}{10} [\mathbf{B}, \mathbf{B}], \quad \eta = kT [F, F], \quad p_{\text{rel}} = kT [F, G]. \quad (58)$$

The bracket integrals are as defined in Ref. [22]:

$$[A, B] = \sum_{ij} \int I_{ij}(A) B_{ij} \, d\mathbf{u},$$

while the functions \mathbf{B} , F and G are determined from the linear integral equations (49)–(51).

The bulk viscosity appears in the expression for the pressure tensor as part of viscous dissipation. In a flow field, $\nabla \cdot \mathbf{v} \neq 0$ corresponds to pure expansion or compression of the gas. This process involves directly only the translational degrees of freedom. A certain time is needed to equilibrate translational and internal degrees of freedom through inelastic collisions. This time is determined by nonresonant and inelastic rapid processes: RT exchange, W' and W'' transfers and VT exchange in the symmetric and bending modes. The appearance of the relaxation pressure p_{rel} is connected with the existence of slow VT_3 and VRT processes, together with rapid inelastic ones.

The expression for the total heat flux \mathbf{q} is:

$$\mathbf{q} = -\lambda\nabla T - \lambda_v^{(3)}\nabla T_3. \quad (59)$$

It contains the gradients of two temperatures ∇T and ∇T_3 . The thermal conductivity λ is a sum of three terms $\lambda = \lambda_t + \lambda_r + \lambda_{vt}$, where λ_t and λ_r are translational and rotational thermal conductivity coefficients. The coefficient $\lambda_{vt} = \lambda_v^{(1)} + \lambda_v^{(2)} + \lambda_v^{(3)}$, in which the first and second terms are connected to the transfer of vibrational energy in the first and second vibrational modes, which are in equilibrium with the rotational and translational modes, and the third term appears due to the rapid nonresonant W' vibrational energy exchanges in the asymmetric mode, and vanishes for the harmonic oscillator. For the λ -coefficients the following equations are obtained:

$$\lambda = \frac{k}{3} [A, A] + \frac{kT_3}{3T} [A^{(3)}, A], \quad (60)$$

$$\lambda_v^{(3)} = \frac{kT}{3T_3} [A, A^{(3)}] + \frac{k}{3} [A^{(3)}, A^{(3)}], \quad (61)$$

in which the functions A and $A^{(3)}$ are solutions of Eqs. (47)–(48).

One can notice that shear and bulk viscosity coefficients and all thermal conductivity coefficients are determined by cross sections for the rapid processes. On the other hand, the expression of the relaxation pressure includes in addition cross sections for the slow processes.

8. Transport coefficients

For the solution of the integral equations (47)–(51) the functions A , $A^{(3)}$, B , F and G are expanded into triple series of orthogonal Sonine polynomials [22] and polynomials used by Wang Chang and Uhlenbeck [3] and by Waldmann and Trübenbacher [23]:

$$A_{ij} = \frac{m}{2kT} c \sum_{rpq} a_{rpq} S_{3/2}^{(r)}(C^2) P_j^{(p)} \left(\frac{\epsilon_j}{kT} \right) P_i^{(q)} \left(\frac{\epsilon_i - i_3 \epsilon_{13}}{kT} \right), \quad (62)$$

$$A_{ij}^{(3)} = \frac{m}{2kT} c \sum_r a_r^{(3)} P_i^{(r)} \left(\frac{i_3 \epsilon_{13}}{kT_3} \right), \quad (63)$$

$$B_{ij} = \sum_p b_p S_{5/2}^{(r)}(C^2) \left(CC - \frac{1}{3} C^2 I \right), \quad (64)$$

$$F_{ij} = \sum_{rpq} d_{rpq} S_{1/2}^{(r)}(C^2) P_j^{(p)} \left(\frac{\epsilon_j}{kT} \right) P_i^{(q)} \left(\frac{\epsilon_i - i_3 \epsilon_{13}}{kT} - \frac{c_w^T}{c_v^T} \frac{T}{T_3} \frac{i_3 \epsilon_{13}}{kT_3} \right), \quad (65)$$

$$G_{ij} = \sum_{rpq} g_{rpq} S_{1/2}^{(r)}(C^2) P_j^{(p)} \left(\frac{\epsilon_j}{kT} \right) P_i^{(q)} \left(\frac{\epsilon_i - i_3 \epsilon_{13}}{kT} - \frac{c_u^T}{c_v^T} \frac{T}{T_3} \frac{i_3 \epsilon_{13}}{kT_3} \right). \quad (66)$$

Basic functions of the Waldmann–Trübenbacher polynomials differ from those usually applied for the derivation of transport coefficients [2]. They are chosen in accordance with the right-hand sides of equations (47)–(51), so that the system of algebraic equations for the coefficients of expansion can be simplified and then the transport coefficients can be expressed in terms of the first non-vanishing members of the series (62)–(66).

Using a procedure similar to that elaborated in Refs. [20,21] for diatomic gases, systems of linear algebraic equations for the coefficients of expansions (62)–(66) are obtained. The coefficients of these systems are the bracket integrals depending on cross sections of the rapid processes.

Solution of the systems for a_{rpq} and $a_r^{(3)}$ provides the following expressions for the heat conductivity coefficients:

$$\lambda_t = \frac{5k}{4} \frac{\Delta_1}{\Delta}, \quad \lambda_r = \frac{k}{2} \frac{\Delta_3}{\Delta} c_r, \quad (67)$$

$$\lambda_{vt} = \frac{k}{2} \frac{\Delta_2}{\Delta} c_v^T, \quad \lambda_v^{(3)} = \frac{3k^2 T}{8m} \frac{c_v^T}{\alpha_{22}}. \quad (68)$$

Determinants Δ_i ($i = 1, 2, 3$) and Δ are composed of bracket integrals $\Lambda_{rr'pp'qq'}$ [20]:

$$\Lambda_{rr'pp'qq'} = \left[S_{3/2}^{(r)} P_j^{(p)} P_i^{(q)} \left(\frac{\epsilon_i - i_3 \epsilon_{13}}{kT} \right) C, S_{3/2}^{(r')} P_j^{(p')} P_i^{(q')} \left(\frac{\epsilon_i - i_3 \epsilon_{13}}{kT} \right) C \right]. \quad (69)$$

The integral α_{22} is also a bracket integral defined as:

$$\alpha_{22} = \left[P_i^{(1)} \left(\frac{i_3 \epsilon_{13}}{kT_3} \right) C, P_i^{(1)} \left(\frac{i_3 \epsilon_{13}}{kT_3} \right) C \right]. \quad (70)$$

Once the simplifications based on the assumptions of Mason and Monchick [2] have been made, the bracket integrals $\Lambda_{rr'pp'qq'}$ and α_{22} can be expressed in terms of the nonequilibrium specific heats, the elastic $\Omega^{(l,r)}$ -integrals [22]:

$$\Omega^{(l,r)} = \left(\frac{kT}{\pi m}\right)^{1/2} \int_0^\infty \exp(-g_0^2) g_0^{2r+3} Q^{(l)} dg_0,$$

$$Q^{(l)} \equiv Q^{(l)}(g) = 2\pi \int \{1 - \cos^l \chi(b, g)\} b db, \quad (71)$$

and the inelastic collision integral β containing the inelastic cross sections of all frequent collisions:

$$\beta = \frac{2}{Z_r^2 Z_v^2} \left(\frac{kT}{\pi m}\right)^{1/2} \sum_{\substack{i j k l \\ i' j' k' l'}} s_{ij} s_{kl} \exp\left(-\frac{\varepsilon_i - i_3 \varepsilon_{13}}{kT} - \frac{i_3 \varepsilon_{13}}{kT_3} - \frac{\varepsilon_j}{kT} - \frac{\varepsilon_k - k_3 \varepsilon_{13}}{kT} - \frac{k_3 \varepsilon_{13}}{kT_3} - \frac{\varepsilon_l}{kT}\right) \iint \exp(-g^2) g^3 (\Delta\varepsilon)^2 \sigma_{i j k l}^{i' j' k' l'} d^2 \Omega dg. \quad (72)$$

Here $\Delta\varepsilon$ is the defect of resonance in nonresonant inelastic collisions:

$$\Delta\varepsilon = \frac{1}{kT} (\varepsilon_{i'} + \varepsilon_{j'} + \varepsilon_{k'} + \varepsilon_{l'} - \varepsilon_i - \varepsilon_j - \varepsilon_k - \varepsilon_l). \quad (73)$$

Since vibrational and rotational energy have been assumed to be independent, $\Delta\varepsilon$ can be represented as a sum of resonance defects of the rotational and vibrational energy, $\Delta\varepsilon = \Delta\varepsilon^r + \Delta\varepsilon^v$. Then, as far as VRT exchange is considered to be a slow process, one can neglect the product of $\Delta\varepsilon^r$ and $\Delta\varepsilon^v$. Therefore integral β also can be divided into two parts, β_r and β_v , containing, respectively, the cross sections of RT exchanges and all frequent vibrational transfers (W' , W'' , VT_1 , VT_2).

Thus we obtain the following expressions for $\Lambda_{rr'pp'qq'}$ and α_{22} :

$$\alpha_{22} = 4\Omega^{(1,1)} c_w^T + \frac{3}{4} \beta_v, \quad (74)$$

$$\begin{aligned} \Lambda_{110000} &= 4\Omega^{(2,2)} + \frac{25}{12} \beta_r + \frac{25}{12} \beta_v, & \Lambda_{001001} &= \Lambda_{000110} = 0, \\ \Lambda_{001100} &= 4\Omega^{(1,1)} c_r + \frac{3}{4} \beta_r, & \Lambda_{100100} &= \Lambda_{011000} = -\frac{5}{4} \beta_r, \\ \Lambda_{000011} &= 4\Omega^{(1,1)} c_a^T + \frac{3}{4} \beta_v, & \Lambda_{100001} &= \Lambda_{010010} = -\frac{5}{4} \beta_v. \end{aligned} \quad (75)$$

By using the theory of Parker [24] for the rotational relaxation time τ_r , the integral β_r can be written in terms of the time τ_r as

$$\beta_r = \frac{3}{2n} \frac{c_r}{c_u} \frac{1}{\tau_r}. \quad (76)$$

Calculation of the integral β_v is rather complicated. Theoretically, it can also be expressed in terms of relaxation times of each vibrational exchange: W' , W'' , VT_1 , VT_2 . Nevertheless, there are no experimental data available for relaxation times of the different modes in CO_2 . For the calculation of β_v the generalized SSH theory [9,25] has been used to obtain an analytical expression for β_v . This approach is not quite rigorous, but it can be applied to estimate the order of magnitude. In this way β_v is found to be one to three orders of magnitude smaller than β_r .

At this step all λ -coefficients have been obtained as functions of the nonequilibrium specific heats, elastic collisional integrals, the rotational relaxation time and the probability of different vibrational energy transfers.

Table 1

Comparison between the thermal conductivity coefficients (λ , 10^{-3} W/Km) calculated on the basis of exact (Eqs. (67)–(68)) and approximate (Eq. (77)) models for CO₂ at $T_3 = 2000$ K

$T(K)$	Eqs. (67)–(68)				Eq. (77)			
	$\lambda_v^{(3)}$	λ_{vt}	λ_r	λ_t	$\lambda_v^{(3)}$	λ_{vt}	λ_r	λ_t
1000	8.5388	26.600	10.063	29.133	8.5561	26.600	10.168	28.933
1200	9.8035	31.638	11.495	33.223	9.8241	31.639	11.611	33.002
1400	10.989	36.220	12.834	37.036	11.013	36.221	12.961	36.794
1600	12.110	40.452	14.098	40.626	12.137	40.454	14.235	40.365
1800	13.177	44.412	15.301	44.034	13.207	44.413	15.448	43.753
2000	14.198	48.150	16.450	47.286	14.231	48.152	16.607	46.987
2200	15.180	51.708	17.555	50.406	15.216	51.710	17.722	50.089
2400	16.127	55.113	18.621	53.411	16.165	55.115	18.798	53.075
2600	17.043	58.388	19.652	56.314	17.085	58.390	19.838	55.960
2800	17.933	61.549	20.653	59.127	17.977	61.552	20.848	58.756
3000	18.798	64.610	21.626	61.859	18.844	64.612	21.830	61.470

The expressions for the thermal conductivity can be further simplified under the assumption that $\Delta\varepsilon = 0$ (in this case the integrals $\beta_r = \beta_v = 0$). The validity of this assumption for diatomic gases, except for light molecules with large rotational cross sections, is proved in Refs. [20,21]. In the present consideration, it is obvious that the term β_r contributes much more in the expressions (74)–(75) than does β_v . Moreover the cross sections of RT exchange for CO₂ are similar in magnitude to those for N₂ and O₂. Thus, one can expect that the influence of the defect of resonance on the thermal conductivity of CO₂ is rather small. Under the assumption $\Delta\varepsilon = 0$ formulas (67)–(68) retain only nonequilibrium specific heats and elastic Ω -integrals:

$$\lambda_t = \frac{75k^2T}{32m\Omega^{(2,2)}}, \quad \lambda_r = \frac{3k^2T}{8m\Omega^{(1,1)}}c_r, \quad (77)$$

$$\lambda_{vt} = \frac{3k^2T}{8m\Omega^{(1,1)}}c_v^T, \quad \lambda_v^{(3)} = \frac{3k^2T}{8m\Omega^{(1,1)}}c_v^{T_3}.$$

Thermal conductivity coefficients have been calculated on the basis of both exact formulas of the kinetic theory (67)–(68) and approximate expressions (77). A comparison of the results is given in Table 1. Again, as in the case of diatomic gases, good agreement between the two approaches is shown, the maximum discrepancy of 1% is found in the rotational thermal conductivity coefficient λ_r . However, the influence of inelastic collision integrals on the total thermal conductivity coefficient λ , in the expression of the total heat flux (59), does not exceed 0.5%. Therefore, approximate formulas (77) give a good accuracy, and inelastic collision integrals can be neglected in the calculation of the thermal conductivity in CO₂ with strong vibrational excitation. Nonequilibrium effects are taken into account in the expressions for the specific heats. It is obvious that the assumption $\Delta\varepsilon = 0$ cannot be applied for the calculation of the bulk viscosity and relaxation pressure.

The following expression is obtained for shear viscosity coefficient:

$$\mu = \frac{5kT}{8\Omega^{(2,2)}}. \quad (78)$$

The bulk viscosity and relaxation pressure depend upon $\Delta\varepsilon$, and can be divided into two terms:

$$\eta = \eta_r + \eta_v, \quad p_{rel} = p_{rel}^r + p_{rel}^v. \quad (79)$$

Finally, the bulk viscosity coefficients can be obtained in the next form:

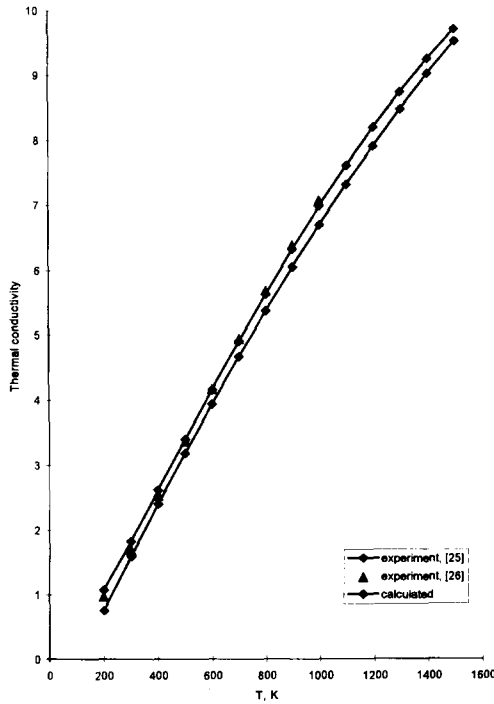


Fig. 5. Thermal equilibrium CO_2 heat conductivity coefficient λ , $10^{-2} \cdot \text{W/m} \cdot \text{K}$ as a function of T . Comparison with experiment.

$$\eta_r = \frac{kT}{\beta_r} \left(\frac{c_r^T c_w^{T_3}}{c_u^T c_w^{T_3} - c_w^T c_v^{T_3}} \right)^2, \quad \eta_v = \frac{kT}{\beta_v} \left(\frac{c_a^T c_w^{T_3} - c_w^T c_a^{T_3}}{c_u^T c_w^{T_3} - c_w^T c_v^{T_3}} \right)^2. \quad (80)$$

The expression obtained for the relaxation pressure is rather complex. Nevertheless, an estimation of its value shows that the contribution of p_{rel} to the pressure tensor is negligible.

9. Results and discussion

The transport coefficients for gaseous CO_2 have been calculated for various temperatures. In order to validate the model, a comparison of the total equilibrium thermal conductivity coefficient $\lambda_{\text{tot}} = \lambda + \lambda_v^{(3)}$ with experimental values [26,27] is presented in the temperature range 300–1500 K (Fig. 5). The following semi-empirical formula fitting the experimental data in this temperature range has been given in Ref. [26]:

$$10^5 \lambda_{\text{exp}} = -2400 + 2.16 \times 10^{-2} T - 3.244 \times 10^{-6} T^2, \quad (81)$$

where λ_{exp} is given in $\text{cal cm}^{-1} \text{s}^{-1} \text{K}^{-1}$, T in K. The overall uncertainty in λ_{exp} is $\pm 2\%$. The parameters of a Lennard-Jones potential taken from Ref. [28] were used for the calculation of the elastic collision integrals. One observes good agreement between the calculated values of the thermal conductivity coefficients and their experimental values. The mean deviation does not exceed 2.5%.

The shear viscosity coefficient does not depend on the vibrational temperature, and hence also not on the degree of nonequilibrium. Its comparison with the experimental data given in Ref. [29] for temperatures

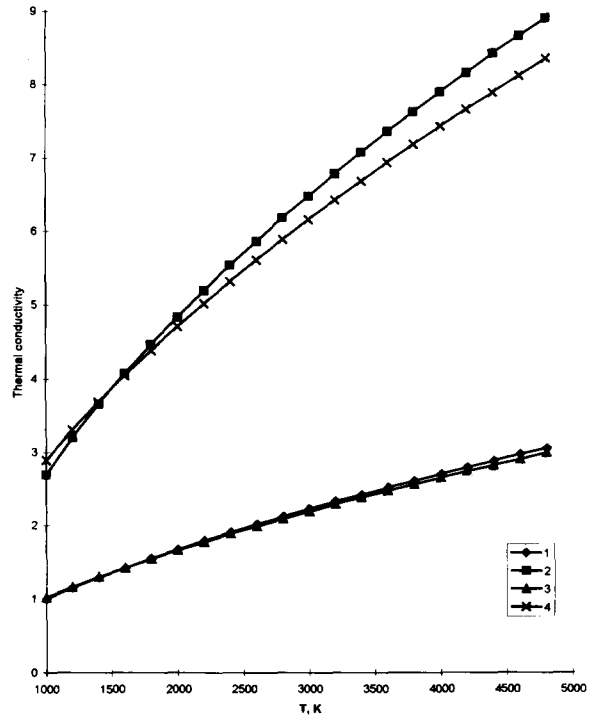


Fig. 6. Thermal conductivity coefficients $\lambda_v^{(3)}$, λ_{vt} , λ_r , λ_t ($10^{-2} \cdot \text{W/m} \cdot \text{K}$) as functions of T at $T_3 = 3000 \text{ K}$ (curves 1–4, respectively).

Table 2

Shear viscosity coefficient μ , $10^{-6} \cdot \text{kg/m} \cdot \text{s}$, experimental (μ_{exp} [28]) and calculated (μ_{calc}), σ is the deviation from experiment in %

$T(K)$	μ_{exp}	μ_{calc}	σ
300	15.03	15.186	-1.03792
400	19.77	19.712	0.293374
500	24.13	23.841	1.197679
600	28.1	27.659	1.569395
700	31.74	31.228	1.613106
800	35.1	34.595	1.438746
900	38.23	37.792	1.145697
1000	41.18	40.843	0.818358
1100	43.99	43.77	0.500114
1200	46.69	46.587	0.220604
1300	49.32	49.308	0.024331
1400	51.89	51.941	-0.09828
1500	54.43	54.497	-0.12309

300–1300 K is shown in Table 2. Again good agreement is obtained between the calculated values and the experimental data. The mean deviation is less than 0.6%.

Thermal conductivity coefficients for nonequilibrium conditions are presented in Figs. 6–8. In Fig. 6 the temperature dependence for each λ -coefficient for $T_3 = 3000$ K is shown. All thermal conductivity coefficients rise with the temperature. It should be pointed out that for CO_2 the contribution of the vibrational degrees of freedom to the thermal conductivity is much greater than it is for diatomic gases. Thus, for N_2 , with moderately excited vibrations, the vibrational thermal conductivity coefficient is of the same order as λ_r and smaller than λ_t . For CO_2 the coefficient λ_{vt} exceeds λ_t , and the coefficient $\lambda_v^{(3)}$ is close to λ_r .

Fig. 7 gives the temperature dependence of the vibrational thermal conductivity coefficient $\lambda_v^{(3)}$ for different values of the vibrational temperature T_3 . Equilibrium values of this coefficient are also shown. One can see that for $T_3 < T$, the values of $\lambda_v^{(3)}$ are less than the corresponding equilibrium ones and at $T_3 > T$ the opposite is true. The thermal conductivity coefficients $\lambda_v^{(3)}$ and λ_{vt} are shown as functions of the vibrational temperature T_3 in Fig. 8. Both $\lambda_v^{(3)}$ and λ_{vt} increase with T_3 . Coefficients calculated for the harmonic and anharmonic oscillator models are compared. The effect of anharmonicity on λ_{vt} does not exceed 4–5%, and reaches 10–12% for $\lambda_v^{(3)}$.

The shear and bulk viscosity coefficients as functions of T for $T_3 = 3000$ K are given in Fig. 9. Both the shear and rotational bulk viscosity coefficients increase with temperature. The vibrational bulk viscosity coefficient η_v is much larger than η_r and μ , and decreases rapidly with temperature. Such a behaviour arises from the temperature dependence of the relaxation times. It is known that at high gas temperatures vibrational relaxation becomes more and more rapid, in contrast to rotational relaxation [9,17]. In this context note the large values of η_v compared to those for the other viscosity coefficients. It has been shown for diatomic gases [30] that at $T \sim 500$ K the vibrational part of the bulk viscosity far outweighs the rotational part: $\eta_v/\eta_r \sim 10^6$. Paradoxically, in many experiments on sound absorption it is not noticeable unless quite low frequencies are employed. In this case sound absorption is rather difficult to measure. Ultrasonic absorption, which is the predominant means for measuring bulk viscosity, reveals only the rotational part of η [30]. However, the contribution of the vibrational bulk viscosity to the pressure tensor can be significant.

10. Conclusions

Strong excitation of the asymmetric vibrational mode of CO_2 , as simulated by an anharmonic oscillator model, leads to a non-Boltzmannian distribution of molecules over the vibrational energy levels. This influences

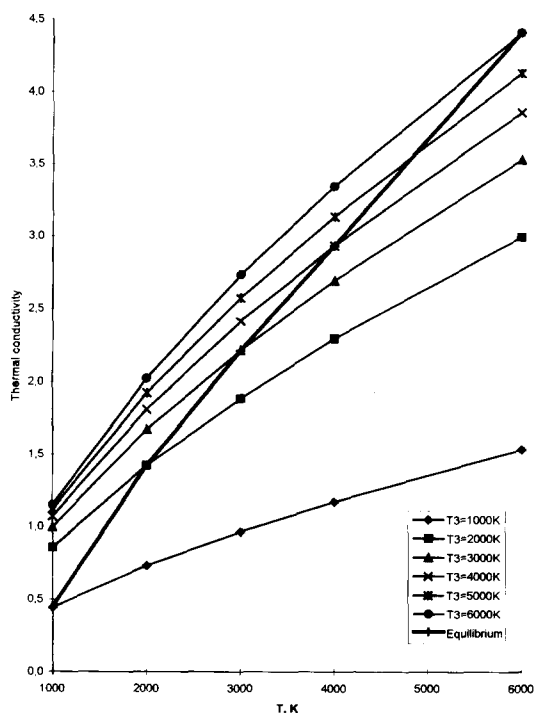


Fig. 7. The vibrational thermal conductivity coefficient $\lambda_v^{(3)}$, $10^{-2} \cdot \text{W/m} \cdot \text{K}$ as a function of T for different values of T_3 . Comparison with the equilibrium values of $\lambda_v^{(3)}$.

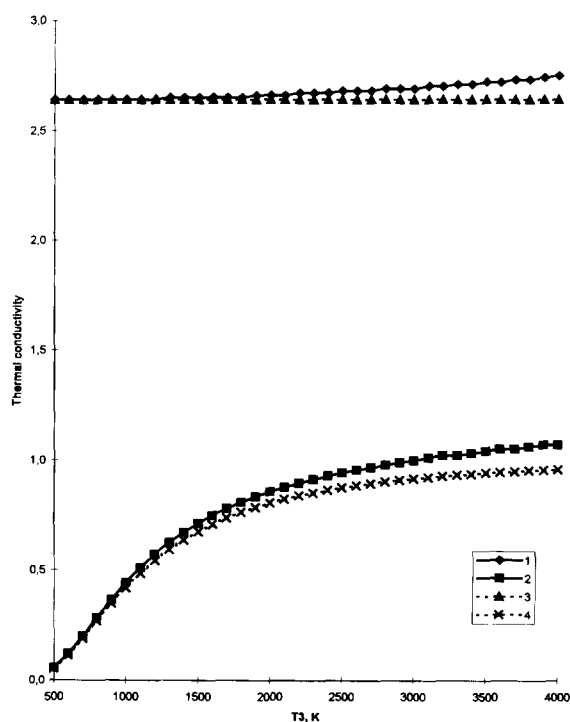


Fig. 8. The thermal conductivity coefficients $\lambda_v^{(3)}$, λ_{vt} ($10^{-2} \cdot \text{W/m} \cdot \text{K}$) as functions of T_3 for $T = 1000 \text{ K}$ (curves 1 and 2) and the corresponding coefficients calculated for the harmonic oscillator model (curves 3 and 4).

directly the essentially nonequilibrium specific heats. They differ both from the equilibrium ones and specific heats calculated using the harmonic oscillator model. The system of macroparameters contains the average number of vibrational quanta in the third mode W_3 (or the temperature T_3 associated with the first vibrational level of the asymmetric mode), and the system of macroscopic equations has to be supplemented by a relaxation equation for W_3 . Transport terms contain additional coefficients, such as bulk viscosity, relaxation pressure, and several additional thermal conductivity coefficients. The contribution of inelastic collision integrals to the thermal conductivity of CO_2 is negligible, nonequilibrium effects can be taken into account through nonequilibrium specific heats. The energy storage in the asymmetric mode has no essential effect either on the shear and rotational bulk viscosity coefficients or on the thermal conductivity coefficients associated with the gas temperature gradient ∇T (i.e. λ_t , λ_r and λ_{vt}), whereas its impact on the coefficients $\lambda_v^{(3)}$ and η_v is important. The effect of anharmonicity increases with the temperature, even at equilibrium and increases significantly for nonequilibrium conditions.

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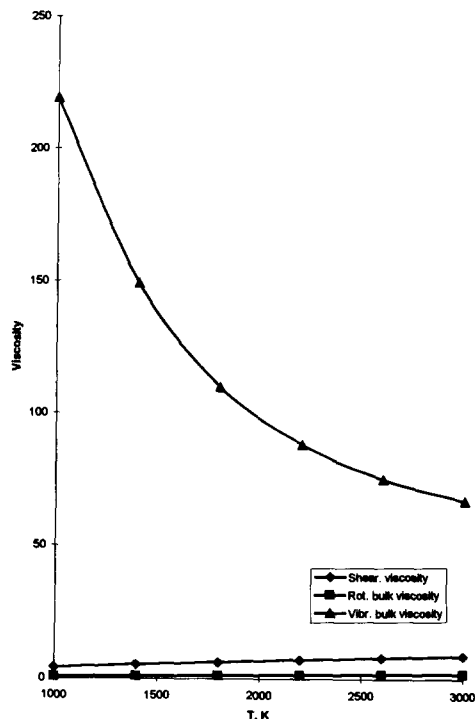


Fig. 9. Shear and bulk viscosity coefficients μ , η_r and η_v ($10^{-5} \cdot \text{kg/m} \cdot \text{s}$) as functions of T at $T_3 = 3000$ K.

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