

Strong nonequilibrium effects on specific heats and thermal conductivity of diatomic gas

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Abstract

The specific heats and thermal conductivity in a diatomic gas with a strong vibrational nonequilibrium are studied starting from the kinetic equations for the distribution functions. Three models for the heat conductivity coefficients are considered. The first one is based on a rigorous kinetic theory treatment. In the second model the inelastic collision integrals are neglected and the thermal conductivity coefficients are expressed only in terms of standard elastic collision integrals and nonequilibrium specific heats. The third model uses the Eucken empirical formula with real gas specific heats. The results are compared with experimental data and with the results of other authors. The limits of the validity of the Eucken formula are estimated and a refinement for strong nonequilibrium is given. A simplified formula for the heat conductivity coefficient is proposed which closely agrees with the experimental data and with the exact kinetic model.

Keywords: Distribution function; Kinetic equations; Specific heats; Heat conductivity

1. Introduction

The thermal conductivity of a nonequilibrium gas with internal degrees of freedom has been studied extensively starting from Eucken [1]. He introduced an empirical correction factor which establishes the relationship between the thermal conductivity of a molecular gas and the internal heat capacity. Hirschfelder [2] expressed the Eucken factor in terms of a diffusion coefficient considering a gas with internal degrees of freedom as a mixture of different components. Mason and Monchick [3] used a kinetic theory method for the calculation of the structural gas thermal conductivity under the conditions of weak deviations from equilibrium and considered the effects of inelastic collisions. From an analysis of the different approaches Ferziger and Kaper [4] supposed a weak influence of the inelastic collisions on the thermal conductivity in the case of a weakly nonequilibrium gas.

The strong nonequilibrium conditions in a diatomic gas were considered in Refs. [5,6] where the heat flux was obtained as a sum of the gradients of both the translational and vibrational temperatures and the vibrational heat conductivity was calculated for a system of harmonic oscillators. The heat conductivity of a strongly nonequilibrium polyatomic gas with different vibrational temperatures of various vibrational modes was investigated in Ref. [7].

If the vibrational temperature appears to be higher than the translational and rotational ones, anharmonic effects may be important and, strictly speaking, a multi-temperature distribution is not valid. A kinetic model of the transport processes in a gas consisting of anharmonic oscillators was put forward in Refs. [8,9].

All these models based on the kinetic theory contain both elastic and inelastic collision integrals. The question arises under what conditions the influence of the inelastic integrals on the thermal conductivity is essential and whether a simple formula like the Eucken one with real gas specific heats may be used for the heat conductivity determination in a strongly nonequilibrium gas.

In this paper the asymptotic solution of the generalized Boltzmann equation is obtained taking into account the strong deviations from the equilibrium and anharmonic effects. Starting from this distribution function a rigorous treatment of the heat conductivity of a diatomic gas with rotational and vibrational degrees of freedom is presented. It is shown that in this case there exist several heat conductivity coefficients and all of them are expressed in terms of the elastic and inelastic collision integrals and the real gas specific heats. The collision integrals, the specific heats and the heat conductivity coefficients are calculated for N_2 in a wide range of temperatures. A comparison with the two-temperature approximation for the harmonic oscillator and with the one-temperature approach for the weakly nonequilibrium gas is carried out.

Moreover, a heat conductivity approximate formula containing only the real gas specific heats and the elastic collision integrals neglecting the inelastic ones is derived. The results obtained on the basis of this expression are compared both with rigorous ones and with those deduced from the Eucken formula with the real gas specific heats. The limits of the validity of these two approaches are given. The role of the specific heats is shown to be very important for the heat conductivity of the strongly excited gas.

2. The kinetic equations. The zero order solution

We consider a diatomic gas with rotational and vibrational degrees of freedom. In the case of weak translational–rotational nonequilibrium and a strong vibrational one the kinetic equations for the distribution functions $f_{ij}(\mathbf{r}, \mathbf{u}, t)$ over velocities \mathbf{u} , space and time coordinates \mathbf{r} , t for every vibrational i and rotational j energy level may be written in the form

$$\frac{\partial f_{ij}}{\partial t} + \mathbf{u} \cdot \frac{\partial f_{ij}}{\partial \mathbf{r}} = \frac{1}{\varepsilon} J_{ij}^{(0)} + J_{ij}^{(1)}. \quad (1)$$

Here $J_{ij}^{(0)}$, $J_{ij}^{(1)}$ are collision operators of rapid and slow processes, $\varepsilon = \tau_0/\tau_1$ is a small parameter, τ_0 , τ_1 are average times between the frequent and rare collisions.

Under the conditions under consideration the most frequent collisions are those with TT, RR, RT translational and rotational energy exchanges. The vibrational energy transfers are known to have different characteristic rates at different energy levels [10]. In particular at the lower levels of an anharmonic oscillator nonresonant VV' exchanges of vibrational quanta,

$$k + l = (k \pm m) + (l \mp m),$$

(k , l , are vibrational species, m is the number of exchanging quanta) may also be assigned to the most frequent collisions [11]. At the intermediate levels the most frequent collisions include the resonant VV'' exchanges between neighbouring levels

$$k + (k \pm 1) = (k \pm 1) + k.$$

At the upper levels all the vibrational transfers have the same frequency as the other collisions. Therefore the operators $J_{ij}^{(0)}$, $J_{ij}^{(1)}$ appear to be different in three groups of levels:

$$J_{ij}^{(0)} = \begin{cases} J_{ij}^{TT} + J_{ij}^{TR} + J_{ij}^{RR} + J_{ij}^{VV}, & 0 \leq i < i_* \\ J_{ij}^{TT} + J_{ij}^{TR} + J_{ij}^{RR} + J_{ij}^{VV}, & i_* \leq i < i_{**} \\ J_{ij}, & i \geq i_{**}, \end{cases} \quad (2)$$

$$J_{ij}^{(1)} = \begin{cases} J_{ij}^{VT} + J_{ij}^{VRT}, & 0 \leq i < i_{**} \\ 0, & i \geq i_{**}. \end{cases} \quad (3)$$

J_{ij} is the total collision operator.

In order to find a solution of Eq. (1) we use the Chapman–Enskog method generalization for rapid and slow processes representing $f_{ij}(\mathbf{r}, \mathbf{u}, t)$ as a power series of ε .

In the zero order approach we obtain

$$J_{ij}^{(0)} = \sum_{k,l,i',j',k',l'} \int \left(\frac{f_{k'l'}^{(0)} f_{i'j'}^{(0)}}{s_{k'l'} s_{i'j'}} - \frac{f_{kl}^{(0)} f_{ij}^{(0)}}{s_{kl} s_{ij}} \right) g \sigma_{ijkl}^{i'j'k'l'}(g, \omega) s_{ij} s_{kl} d\mathbf{u}_{ij} d^2\Omega = 0. \quad (4)$$

Here $\sigma_{ijkl}^{i'j'k'l'} d^2\Omega$ is the differential cross-section of the scattering into a solid angle $d^2\Omega$, g is the relative velocity of particles, $s_{ij} = s_i s_j$, s_i, s_j are the statistical weights.

It traditionally follows from Eq. (4) that $\ln(f_{ij}^{(0)}/s_{ij})$ has to be a linear combination of the additive invariants $\psi_{ij}^{(\lambda)}$, ($\lambda = 1, 2, \dots$) of the most frequent collisions. At any collisions these invariants are the following: the number of particles $\psi_{ij}^{(1)} = 1$, the momentum $\psi_{ij}^{(2)} = m\mathbf{u}$, the total energy $\psi_{ij}^{(3)} = \frac{1}{2}m\mathbf{u}^2 + \varepsilon_i + \varepsilon_j$. As a matter of fact there exist additional invariants in a system of anharmonic oscillators, which are different at the lower and intermediate levels. The first one is the number of quanta $\psi_{ij}^{(4)} = i$, the second one is any value independent of velocity and the rotational energy level j and depending arbitrarily on i : $\psi_{ij}^{(5)} = a_{ij}$. Hence $f_{ij}^{(0)}$ may be obtained in the form

$$f_{ij}^{(0)} = \begin{cases} \alpha_1 s_{ij} \exp\left(-\frac{mc^2}{2kT} - \frac{\varepsilon_i + \varepsilon_j}{kT} - \vartheta i\right), & 0 \leq i < i_*, \\ \frac{n_i}{Z_t Z_r} s_{ij} \exp\left(-\frac{mc^2}{2kT} - \frac{\varepsilon_j}{kT}\right), & i_* \leq i < i_{**}, \\ \alpha_2 s_{ij} \exp\left(-\frac{mc^2}{2kT} - \frac{\varepsilon_i + \varepsilon_j}{kT}\right), & i \geq i_{**}. \end{cases} \quad (5)$$

$$\alpha_k = \frac{n_k}{Z_t Z_r Z_{v_k}}, \quad k = 1, 2.$$

Here the rotational ε_j and the vibrational ε_i energy spectra are simulated as a rigid rotator and an anharmonic oscillator,

$$\varepsilon_j = (\hbar^2/2I_a)j(j+1), \quad \varepsilon_i = \hbar\nu(1-\alpha)i - \alpha\hbar\nu i^2,$$

\hbar is the Planck constant, ν is a frequency of molecular vibrations, α is an anharmonicity parameter, I_a is the inertia momentum, k is the Boltzmann constant, m is a molecular mass, $\mathbf{c} = \mathbf{u} - \mathbf{v}$, $\mathbf{v}(\mathbf{r}, t)$ is the macroscopic gas velocity, T is the gas temperature, Z_t, Z_r, Z_{v_k} are the statistical sums, and n_i are the level populations at the intermediate levels. They may be found from the master equations in the form of a sloping plateau [10]:

$$n_i = \frac{\Gamma}{i+1}, \quad i_* \leq i < i_{**}.$$

The parameter Γ as well as n_1, n_2 are determined from the continuity conditions for $f_{ij}^{(0)}$ at $i = i_*$ and $i = i_{**}$ and from the normalization conditions.

The parameter ϑ is defined in terms of the total number of vibrational quanta at the lower levels W ,

$$\rho W = \sum_{i=0}^{i_*} \sum_j i \int f_{ij}^{(0)} du, \quad (6)$$

($\rho = mn$ is the density, n is the total number of particles) and may be presented traditionally as follows:

$$\vartheta = \frac{\varepsilon_1}{k} \left(\frac{1}{T_1} - \frac{1}{T} \right).$$

Here T_1 is introduced as the temperature of the first vibrational level and $\varepsilon_1 = \hbar\nu(1 - 2\alpha)$. The distribution (5) may be written in the unified form [8]

$$f_{ij}^{(0)} = \frac{ns_{ij}}{Z} \exp \left(-\frac{mc^2}{2kT} - \frac{\varepsilon_j}{kT} - \frac{\varepsilon_\alpha + \varepsilon_\beta - \beta\varepsilon_1}{kT} - \frac{\beta\varepsilon_1}{kT_1} + \ln \frac{i_* + 1}{\gamma + 1} \right), \quad (7)$$

$$\alpha(i) = \begin{cases} i_{**}, & 0 \leq i < i_{**}, \\ i, & i_{**} \leq i < L, \end{cases} \quad \beta(i) = \begin{cases} i, & 0 \leq i < i_*, \\ i_*, & i_* \leq i < L, \end{cases} \quad \gamma(i) = \begin{cases} i_*, & 0 \leq i < i_*, \\ i, & i_* \leq i < i_{**}, \\ i_{**}, & i_{**} \leq i < L. \end{cases}$$

Here Z is the total statistical sum.

The nonequilibrium distribution functions (5) and (7) are defined in terms of the macroscopic parameters $n(\mathbf{r}, t)$, $c(\mathbf{r}, t)$, $T(\mathbf{r}, t)$, $T_1(\mathbf{r}, t)$.

In the equilibrium state ($T = T_1$) Eq. (7) transforms into the Maxwell–Boltzmann distribution. If the anharmonicity of the vibrations is negligible ($\alpha = 0$, $\varepsilon_i = \hbar\nu i$) then we have a two-temperature distribution. The length of the plateau becomes small with decreasing T_1/T , and may be neglected for $T_1/T < 4$.

3. The nonequilibrium specific heats

Let us introduce translational, rotational and two vibrational specific heats at constant volume on the basis of the distribution functions (5) and (7):

$$c_t = \frac{\partial E_t}{\partial T} = \frac{3}{2} \frac{k}{m}, \quad c_r = \frac{\partial E_r}{\partial T}, \quad c_v^T = \frac{\partial E_v(T, T_1)}{\partial T}, \quad c_v^{T_1} = \frac{\partial E_v(T, T_1)}{\partial T_1}. \quad (8)$$

Here E_t , E_r , E_v are the translational, rotational and vibrational energies per unit mass:

$$\rho E_t = \frac{3}{2} nkT, \quad \rho E_r = \sum_{ij} \int \varepsilon_j f_{ij}^{(0)} du = \frac{n}{Z} \sum_j \varepsilon_j \exp \left(-\frac{\varepsilon_j}{kT} \right),$$

$$\rho E_v = \sum_{ij} \int \varepsilon_i f_{ij}^{(0)} du = \sum_i \varepsilon_i n_i^{(0)} = \frac{n}{Z} \sum_i \varepsilon_i \exp \left(-\frac{\varepsilon_\alpha + \varepsilon_\beta - \beta\varepsilon_1}{kT} - \frac{\beta\varepsilon_1}{kT_1} + \ln \frac{i_* + 1}{\gamma + 1} \right).$$

If the gas temperature is not very low ($\hbar^2/2kI_a \ll T$) then $c_r = k/m$. The vibrational specific heats c_v^T and $c_v^{T_1}$ depend on the two temperatures T and T_1 and differ from the equilibrium specific heats (when $T = T_1$) and from the specific heats obtained on the basis of a harmonic oscillator model (when $c_v^T = 0$, $c_v^{T_1} = c_v^{T_1}(T_v)$, $T_1 = T_v$).

Hereafter we will use dimensionless values for all specific heats (divided by k/m) with the same designations.

In Figs. 1 and 2 the dimensionless vibrational specific heats c_v^T and $c_v^{T_1}$ versus T and T_1 calculated on the

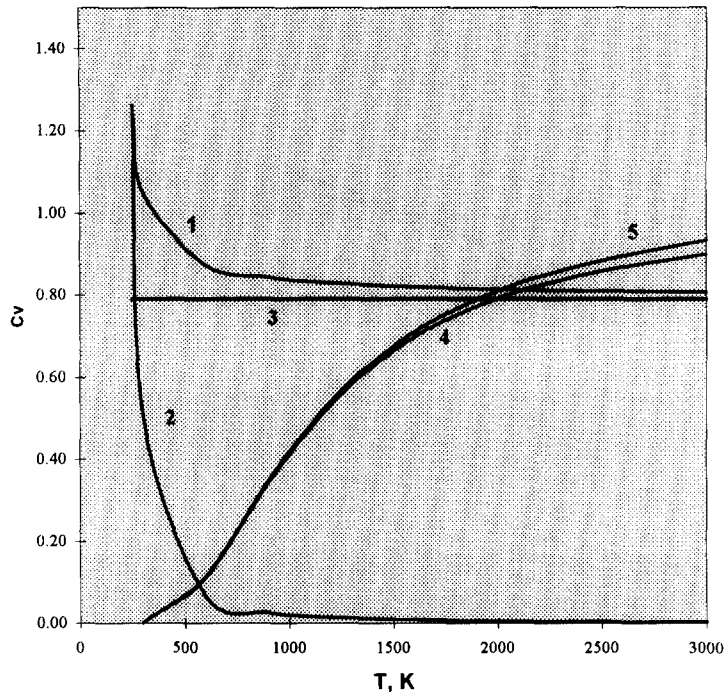


Fig. 1. Dimensionless specific heats: (1) $c_v^{T_1}$, (2) $-c_v^T$, (3) $c_v^{T_1}$ (h.o.), (4) c_v^{eq} (h.o.) and (5) c_v^{eq} (a.o.) (5) as function of T for N_2 at $T_1 = 2000$ K.

basis of Eq. (7) are given for molecular nitrogen. The comparison with the vibrational specific heat $c_v^{T_1}$ (h.o.) calculated for a harmonic oscillator model is shown. Fig. 1 depicts also the equilibrium specific heat $c_v^{eq}(T)$ versus T for both harmonic and anharmonic oscillators (they are denoted respectively c_v^{eq} (h.o.) and c_v^{eq} (a.o.)).

One can see that the magnitude of c_v^T is growing in importance with the nonequilibrium factor T_1/T rising, c_v^T can play an essential role for $T_1/T > 4$ and becomes negligible as compared to $c_v^{T_1}$ for $T_1/T < 3$. It will be revealed in Section 5 that the negative sign of c_v^T determines the unusual behaviour of the thermal conductivity under strong nonequilibrium conditions. The coefficient $c_v^{T_1}$ exceeds that calculated for a harmonic oscillator and approaches $c_v^{T_1}$ (h.o.) with reduction in T_1/T down to 0.5. For $T_1/T > 2$ the difference between $c_v^{T_1}$ and $c_v^{T_1}$ (h.o.) becomes noticeable and increases with T_1/T rising. It may be pointed out that $c_v^{eq} < c_v^{T_1}$ for $T_1 > T$ and $c_v^{eq} > c_v^{T_1}$ for $T_1 < T$. This fact explains the similar character of the vibrational thermal conductivity coefficients shown in Ref. [6].

The anharmonic effects are found to be most important for $T_1 \gg T$ and also for high temperatures in the equilibrium case ($T_1 = T$), on the other hand they may be neglected for $T_1 \ll T$. Fig. 3 depicts the constant pressure equilibrium internal specific heats at high temperature. Here c_p (a.o.) is that obtained for the anharmonic oscillator, c_p (h.o.) are those for the harmonic oscillator and c_p ([12]) has been calculated in Ref. [12] with the inclusion of the electronic degrees of freedom. It is evident that for $T > 7000$ K the electronic excitation impact on c_p becomes very significant and must be taken into account in the transport process investigation. The distinctions between c_p (h.o.) and c_p (a.o.) also increase progressively with rising T .

From the formulas given above it is apparent that the coefficients c_v^T and $c_v^{T_1}$ depend crucially on the vibrational level populations. Strictly speaking the vibrational energy distribution over vibrational levels plays a dominant role in the c_v^T and $c_v^{T_1}$ behaviour. In particular the curves $c_v^T(T_1)$ and $c_v^{T_1}(T_1)$ have peaks (Fig. 2b) which correspond to the maximum store of the vibrational energy on the three lower energy levels. It will be shown in Section 5 that c_v^T and $c_v^{T_1}$ influence very strongly the heat conductivity coefficients of a nonequilibrium gas.

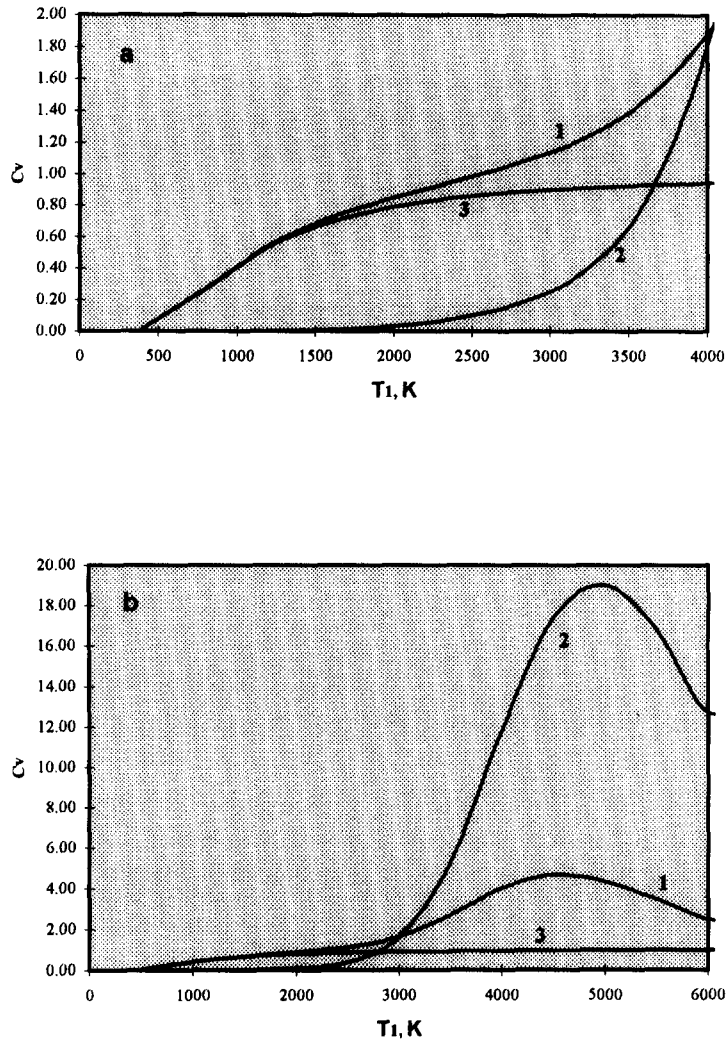


Fig. 2. Dimensionless specific heats: (1) $c_v^{T_1}$, (2) $-c_v^T$, (3) $c_v^{T_1}$ (h.o.) as function of T_1 for N_2 at (a) $T = 800$ K and (b) $T = 500$ K.

4. The first-order distribution functions

For the first order distribution functions we have the following linear integral equations:

$$J_{ij}^{(0)}(f^{(0)}, f^{(0)}\phi) = \frac{df_{ij}^{(0)}}{dt} - J_{ij}^{(1)}(f^{(0)}, f^{(0)}), \quad (9)$$

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

Taking into account Eq. (7), the expression $df_{ij}^{(0)}/dt$ may be written in the form

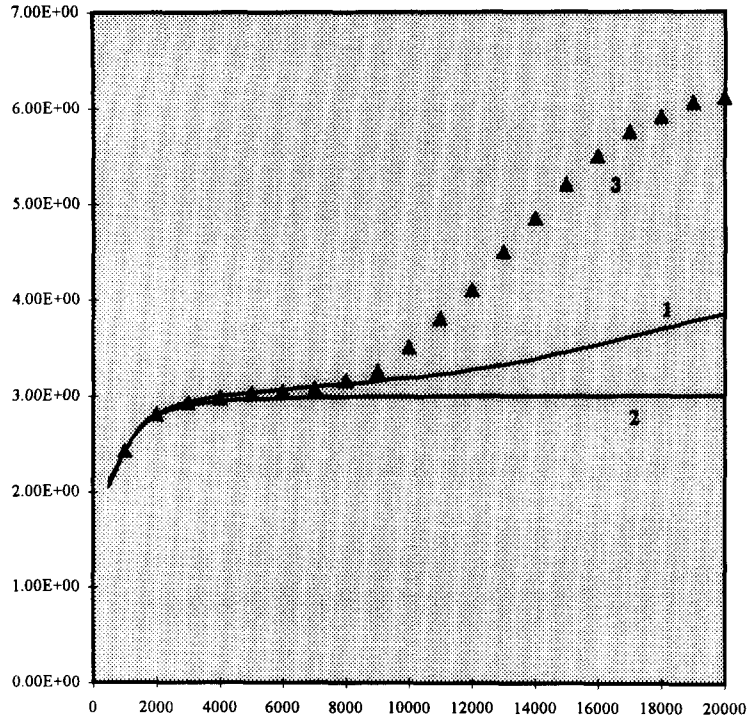


Fig. 3. Dimensionless internal constant pressure specific heats: (1) c_p (a.o.), (2) c_p (h.o.) and (3) c_p from Ref. [12] as function of T for N_2 at equilibrium ($T_1 = T$).

$$\begin{aligned}
 \frac{df_{ij}^{(0)}}{dt} = & f_{ij}^{(0)} \left\{ \left(\frac{mc^2}{2kT} - \frac{5}{2} + \left[\frac{\epsilon_j}{kT} \right]' + \left[\frac{\epsilon_\alpha + \epsilon_\beta - \beta\epsilon_1}{kT} \right]' \right) c \nabla \ln T \right. \\
 & + \left[\frac{\beta\epsilon_1}{kT_1} \right]' c \nabla \ln T_1 + \left(\frac{m}{2kT} c c - \frac{1}{3} \frac{mc^2}{2kT} I \right) : \nabla v \\
 & + \left(\frac{-nkT}{\rho(c_u c_w^{T_1} - c_w^T c_v^{T_1})} \left(\left(\frac{mc^2}{2kT} - \frac{3}{2} + \left[\frac{\epsilon_\alpha + \epsilon_\beta - \beta\epsilon_1}{kT} \right]' \right) \right. \right. \\
 & + \left. \left. \left[\frac{\epsilon_j}{kT} \right]' \right) \frac{c_w^{T_1}}{T} - \left[\frac{\beta\epsilon_1}{kT_1} \right]' \frac{c_w^T}{T_1} + \frac{mc^2}{3kT} - 1 \right) \nabla \cdot v \\
 & - \frac{\sum_j \sum_{i=0}^{i_*} i \epsilon_1 \int J_{ij}^{(1)}(f^{(0)}, f^{(0)}) du}{\rho(c_u c_w^{T_1} - c_w^T c_v^{T_1})} \left(\left(\frac{mc^2}{2kT} - \frac{3}{2} \right) \right. \\
 & \left. + \left[\frac{\epsilon_\alpha + \epsilon_\beta - \beta\epsilon_1}{kT} \right]' + \left[\frac{\epsilon_j}{kT} \right]' \right) \frac{c_v^{T_1}}{T} - \left[\frac{i \xi_i \epsilon_1}{kT_1} \right]' \frac{c_u}{T_1} \left. \right\}, \tag{10}
 \end{aligned}$$

where

$$[\xi_i]' = \xi_i - \langle \xi \rangle_v, \quad [\zeta_j]' = \zeta_j - \langle \zeta \rangle_r,$$

$\langle \xi \rangle_v$, $\langle \zeta \rangle_r$ are the values of ξ_i and ζ_j averaged over a vibrational and rotational spectrum, respectively:

$$\langle \xi \rangle_v = \frac{\sum_i \xi_i \exp\left(-\frac{\varepsilon_\alpha + \varepsilon_\beta - \beta\varepsilon_1}{kT} - \frac{\beta\varepsilon_1}{kT_1} + \ln \frac{i_* + 1}{\gamma + 1}\right)}{\sum_i \exp\left(-\frac{\varepsilon_\alpha + \varepsilon_\beta - \beta\varepsilon_1}{kT} - \frac{\beta\varepsilon_1}{kT_1} + \ln \frac{i_* + 1}{\gamma + 1}\right)},$$

$$\langle \zeta \rangle_r = \frac{\sum_j \zeta_j \exp(-\varepsilon_j/kT)}{\sum_j \exp(-\varepsilon_j/kT)},$$

c_u denotes the total specific heat at constant volume:

$$c_u = \frac{\partial U}{\partial T} = c_t + c_r + c_v^T, \quad U = E_t + E_r + E_v, \quad (11)$$

U is the total energy per unit mass, c_w^T , $c_w^{T_1}$ are additional coefficients:

$$c_w^T = \frac{\partial (\varepsilon_1 W)}{\partial T}, \quad c_w^{T_1} = \frac{\partial (\varepsilon_1 W)}{\partial T_1}.$$

Proceeding from Eq. (10) the solution of Eq. (9) may be found in the form

$$f_{ij}^{(1)} = f_{ij}^{(0)} \left(-\frac{1}{n} A_{ij}^{(1)} \nabla \ln T - \frac{1}{n} A_{ij}^{(2)} \nabla \ln T_1 - \frac{1}{n} B_{ij} : \nabla v - \frac{1}{n} F_{ij} \nabla \cdot v - \frac{1}{n} G_{ij} \right). \quad (12)$$

The functions $A_{ij}^{(\gamma)}$ ($\gamma = 1, 2$), B_{ij} , F_{ij} , G_{ij} depend on the microscopic velocities \mathbf{u} and the macroscopic parameters $n(\mathbf{r}, t)$, $\mathbf{v}(\mathbf{r}, t)$, $T(\mathbf{r}, t)$, $T_1(\mathbf{r}, t)$ and can be obtained from the linear integral equations which follow from Eq. (9) after substitution of Eq. (10) in (9) and equating the coefficients at the gradients of the same macroparameters. In particular for $A_{ij}^{(1)}$ and $A_{ij}^{(2)}$ we have [8]

$$nI_{ij}(A^{(1)}) = f_{ij}^{(0)} c \left(\frac{mc^2}{2kT} - \frac{5}{2} + \left[\frac{\varepsilon_j}{kT} \right]' + \left[\frac{\varepsilon_\alpha + \varepsilon_\beta - \beta\varepsilon_1}{kT} \right]' \right),$$

$$nI_{ij}(A^{(2)}) = f_{ij}^{(0)} c \left[\frac{\beta\varepsilon_1}{kT_1} \right]'. \quad (13)$$

Here I_{ij} is a linearized operator of the rapid processes

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

5. The thermal conductivity coefficients

The first order distribution function (12) provides the following expression for the total energy flux:

$$\mathbf{q} = -\lambda \nabla T - \lambda_v \nabla T_1, \quad (14)$$

containing the gradients of the two temperatures ∇T and ∇T_1 . The thermal conductivity λ is the sum of the three terms $\lambda = \lambda_t + \lambda_r + \lambda_v$, where λ_t and λ_r are the translational and rotational thermal conductivity

coefficients and the coefficient λ_{vr} appears due to nonresonant W' vibrational energy exchanges on lower levels and equals zero for harmonic oscillators. For all λ -coefficients we have

$$\begin{aligned}\lambda_r &= \frac{k}{3} \left[(C^2 - \frac{5}{2}) C, A_{ij}^{(1)} \right], & \lambda_r &= \frac{k}{3} \left[\left(\frac{\varepsilon_j}{kT} - \left\langle \frac{\varepsilon_j}{kT} \right\rangle_r \right) C, A_{ij}^{(1)} \right], \\ \lambda_{vr} &= \frac{k}{3} \left[\left(\frac{\varepsilon_i}{kT} - \left\langle \frac{\varepsilon_i}{kT} \right\rangle_v \right) C, A_{ij}^{(1)} \right], & \lambda_v &= \frac{k}{3} \left[\left(\frac{\varepsilon_i}{kT} - \left\langle \frac{\varepsilon_i}{kT} \right\rangle_v \right) C, A_{ij}^{(2)} \right].\end{aligned}\quad (15)$$

Here

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

the integral bracket $[R, D]$ is defined as

$$[R, D] = \sum_{ij} \int I_{ij}(R) D_{ij} du.$$

The functions $A_{ij}^{(1)}$, $A_{ij}^{(2)}$ are obtained from the linear integral equations using the Waldmann and Sonine polynomials:

$$A_{ij}^{(1)} = \frac{mc}{2kT} \sum_{rpq} a_{rpq}^{(1)} b_{rpq}, \quad A_{ij}^{(2)} = \frac{mc}{2kT} \sum_r a_r^{(2)} b_r, \quad (16)$$

$$b_{rpq} = S_{3/2}^{(r)} \left(\frac{mc^2}{2kT} \right) P_i^{(p)} \left(\frac{\varepsilon_\alpha + \varepsilon_\beta - \beta\varepsilon_1}{kT} \right) P_j^{(q)} \left(\frac{\varepsilon_j}{kT} \right), \quad b_r = P_i^{(r)} \left(\frac{\beta\varepsilon_1}{kT_1} \right).$$

The system of the linear algebraic equations for the coefficients $a_{rpq}^{(1)}$ and $a_r^{(2)}$ is obtained after multiplying Eq. (13) by b_{rpq} and b_r , integration over velocity and summation over i and j . If we restrict the consideration to the first non-vanishing terms in the series (16), the equations for $a_{rpq}^{(1)}$ and $a_r^{(2)}$ may be written

$$\begin{cases} A_{110000} a_{100}^{(1)} + A_{100100} a_{010}^{(1)} + A_{100001} a_{001}^{(1)} = \frac{15kT}{2m}, \\ A_{011000} a_{100}^{(1)} + A_{001100} a_{010}^{(1)} + A_{001001} a_{001}^{(1)} = \frac{3kT}{m} c_a^T, \\ A_{010010} a_{100}^{(1)} + A_{000110} a_{010}^{(1)} + A_{000011} a_{001}^{(1)} = \frac{3kT}{m} c_r, \end{cases} \quad (17)$$

$$a_1^{(2)} = \frac{3kT}{m} \frac{c_w^T}{\alpha_{22}}, \quad (18)$$

where $c_a^T = c_r^T - c_w^T$, $c_a^{T_1} = c_v^{T_1} - c_w^{T_1}$, $A_{rr'pp'qq'}$ and α_{22} are the integral brackets:

$$\begin{aligned}A_{110000} &= \left[S_{3/2}^{(1)}(C^2) C, S_{3/2}^{(1)}(C^2) C \right], \\ A_{001100} &= \left[P_i^{(1)} \left(\frac{\varepsilon_\alpha + \varepsilon_\beta - \beta\varepsilon_1}{kT} \right) C, P_i^{(1)} \left(\frac{\varepsilon_\alpha + \varepsilon_\beta - \beta\varepsilon_1}{kT} \right) C \right], \\ A_{000011} &= \left[P_j^{(1)} \left(\frac{\varepsilon_j}{kT} \right) C, P_j^{(1)} \left(\frac{\varepsilon_j}{kT} \right) C \right],\end{aligned}$$

$$\Lambda_{100100} = \Lambda_{011000} = \left[S_{3/2}^{(1)}(C^2) C, P_i^{(1)} \left(\frac{\varepsilon_\alpha + \varepsilon_\beta - \beta \varepsilon_1}{kT} \right) C \right],$$

$$\Lambda_{100001} = \Lambda_{010010} = \left[S_{3/2}^{(1)}(C^2) C, P_j^{(1)} \left(\frac{\varepsilon_j}{kT} \right) C \right],$$

$$\Lambda_{001001} = \Lambda_{000110} = \left[P_i^{(1)} \left(\frac{\varepsilon_\alpha + \varepsilon_\beta - \beta \varepsilon_1}{kT} \right) C, P_j^{(1)} \left(\frac{\varepsilon_j}{kT} \right) C \right],$$

$$\alpha_{22} = \left[P_i^{(1)} \left(\frac{\beta \varepsilon_1}{kT_1} \right) C, P_i^{(1)} \left(\frac{\beta \varepsilon_1}{kT_1} \right) C \right].$$

The solution of Eqs. (17) and (18) provides the following expressions for the heat conductivity coefficients:

$$\lambda_t = \frac{5k}{4} \frac{\Delta_1}{\Delta},$$

$$\lambda_r = \frac{k}{2} \frac{\Delta_3}{\Delta} c_r,$$

$$\lambda_{vt} = \frac{k}{2} \frac{\Delta_2}{\Delta} c_w^T + \frac{k}{2} \frac{\Delta_2}{\Delta} c_a^T = \frac{k}{2} \frac{\Delta_2}{\Delta} c_v^T,$$

$$\lambda_v = \frac{3k^2 T}{8m} \frac{c_a^T}{\alpha_{22}} + \frac{3k^2 T}{8m} \frac{c_w^T}{\alpha_{22}} = \frac{3k^2 T}{8m} \frac{c_v^T}{\alpha_{22}}.$$

(19)

Here Δ , Δ_1 , Δ_2 , Δ_3 are the determinant of the system (17) and the corresponding minors.

In order to simplify the integral brackets as well as in Ref. [3] we suppose that

$$(\varepsilon_{i'} + \varepsilon_{j'} - \varepsilon_{k'} - \varepsilon_{l'}) g' = (\varepsilon_i + \varepsilon_j - \varepsilon_k - \varepsilon_l) g$$

and replace the expression $\sin^2 \chi$ in the inelastic collision integrals by its mean value obtained after averaging over a unit sphere and equal to $2/3$. As a result all integral brackets $\Lambda_{rr'pp'qq'}$ and α_{22} may be expressed in terms of the specific heats, the standard elastic $\Omega^{(l,r)}$ -integrals:

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

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

and the two integrals β_r and β_v containing the inelastic cross-sections $\sigma_{ijkl}^{i'j'k'l'}$,

$$\begin{aligned} \beta_r = & \frac{2}{Z_r^2 Z_v^2} \left(\frac{kT}{\pi m} \right)^{1/2} \sum_{i j k l i' j' k' l'} s_{ij} s_{kl} \exp \left(-\frac{\varepsilon_{\alpha(i)} + \varepsilon_{\beta(i)} - \beta(i) \varepsilon_1}{kT} - \frac{\beta(i) \varepsilon_1}{kT_1} \right) \\ & + \ln \frac{i_* + 1}{\gamma(i) + 1} - \frac{\varepsilon_j}{kT} - \frac{\varepsilon_{\alpha(k)} + \varepsilon_{\beta(k)} - \beta(k) \varepsilon_1}{kT} - \frac{\beta(k) \varepsilon_1}{kT_1} + \ln \frac{i_* + 1}{\gamma(k) + 1} - \frac{\varepsilon_l}{kT} \\ & \times \int \int \exp(-g^2) g^3 (\Delta \varepsilon^r)^2 \sigma_{ijkl}^{i'j'k'l'} d^2 \Omega dg, \end{aligned}$$

$$\beta_v = \frac{2}{Z_r^2 Z_v^2} \left(\frac{kT}{\pi m} \right)^{1/2} \sum_{\substack{i j k l \\ i' j' k' l'}} s_{ij} s_{kl} \exp \left(-\frac{\varepsilon_{\alpha(i)} + \varepsilon_{\beta(i)} - \beta(i) \varepsilon_1}{kT} - \frac{\beta(i) \varepsilon_1}{kT_1} \right) \\ + \ln \frac{i_* + 1}{\gamma(i) + 1} - \frac{\varepsilon_j}{kT} - \frac{\varepsilon_{\alpha(k)} + \varepsilon_{\beta(k)} - \beta(k) \varepsilon_1}{kT} - \frac{\beta(k) \varepsilon_1}{kT_1} + \ln \frac{i_* + 1}{\gamma(k) + 1} - \frac{\varepsilon_l}{kT} \\ \times \int \int \exp(-g^2) g^3 (\Delta \varepsilon^v)^2 \sigma_{i j k l}^{i' j' k' l'} d^2 \Omega dg,$$

Here for $\alpha(i)$, $\beta(i)$ and $\gamma(i)$ the notations from Eq. (7) are used,

$$\Delta \varepsilon = \frac{1}{kT} (\varepsilon_{i'} + \varepsilon_{j'} + \varepsilon_{k'} + \varepsilon_{l'} - \varepsilon_i - \varepsilon_j - \varepsilon_k - \varepsilon_l) = \Delta \varepsilon^r + \Delta \varepsilon^v,$$

$\Delta \varepsilon^r$ and $\Delta \varepsilon^v$ are the resonance defects of the rotational and vibrational energy at the inelastic collisions.

Thus we have the following expressions for $A_{rr'pp'qq'}$ and α_{22} :

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

$$A_{111000} = 4\Omega^{(2,2)} + \frac{25}{12} \beta_r + \frac{25}{12} \beta_v, \quad A_{001001} = A_{000110} = 0,$$

$$A_{001100} = 4\Omega^{(1,1)} c_a^T + \frac{3}{4} \beta_v, \quad A_{100100} = A_{011000} = -\frac{5}{4} \beta_v,$$

$$A_{000011} = 4\Omega^{(1,1)} c_r + \frac{3}{4} \beta_r, \quad A_{100001} = A_{010010} = -\frac{5}{4} \beta_r.$$

The integral β_r was written in terms of the rotational relaxation time τ_r :

$$\beta_r = \frac{3}{2n} \frac{c_r}{c_u} \frac{1}{\tau_r},$$

using the Parker theory for τ_r . For the calculation of β_v the generalized SSH-theory was applied taking into account anharmonic effects [10]. Finally all λ -coefficients were obtained as functions of T and T_1 .

Simultaneously with the rigorous kinetic theory code, approximate formulas for the heat conductivity coefficients were found in the limit case supposing $\Delta \varepsilon = \Delta \varepsilon^r + \Delta \varepsilon^v = 0$. It is reasonable to expect that $\Delta \varepsilon$ is close to zero because in molecular collisions the inelastic energy exchange is generally small [3,4]. The assumption $\Delta \varepsilon^r = 0$ is validated for rotating molecules by the fact that the rotational quantum for gases at ordinary temperatures is much smaller than the relative kinetic energy of a colliding pair, and in collisions between rotating molecules generally only one or a few quanta of rotational energy are exchanged. For the vibrational energy one-quantum exchange prevails excluding the upper levels with small vibrational quanta. Under the conditions of one-quantum exchange $\Delta \varepsilon^v = 0$ for harmonic oscillator, and it is proportional to the anharmonicity parameter for anharmonic oscillators and has the form

$$\Delta \varepsilon^v = \frac{\varepsilon_{i+1} + \varepsilon_{k-1} - \varepsilon_i - \varepsilon_k}{kT} = \frac{2\alpha \hbar \nu}{kt} (k - i - 1).$$

One can see that $\Delta \varepsilon^v$ is negligible for neighbouring levels and increases with $k - i$ rising. However, the probabilities of the nonresonant exchange of vibrational quanta have a maximum at small $k - i$ values [11]. Furthermore, the value $\Delta \varepsilon^v$ is considered small in Ref. [4] because the collisions with vibrational energy transfer are known to be rare in comparison to elastic ones and collisions with rotational energy exchange.

Table 1

Comparison between the thermal conductivity coefficients (λ , 10^{-3} W/K m) calculated on the basis of exact (Eq. (19)) and approximate (Eq. (20)) models for N_2 at $T_1 = 2000$ K

T (K)	Eq. (19)				Eq. (20)			
	λ_t	λ_r	λ_{vt}	λ_v	λ_t	λ_r	λ_{vt}	λ_v
400	24.251	8.364	2.034	10.768	24.070	8.459	2.034	10.768
600	32.335	11.187	0.014	9.982	32.095	11.314	0.014	9.981
800	39.344	13.649	0.0082	11.821	39.050	13.805	0.0082	11.821
1000	45.655	15.874	0.0056	13.526	45.309	16.058	0.0056	13.526
1200	51.464	17.930	0.0042	15.120	51.069	18.140	0.0042	15.120
1400	56.890	19.854	0.0033	16.624	56.448	20.091	0.0033	16.624
1600	62.013	21.675	0.0027	18.055	61.524	21.937	0.0027	18.055
1800	66.886	23.410	0.0022	19.423	66.352	23.696	0.0022	19.423
2000	71.550	25.073	0.0019	20.739	70.972	25.384	0.0019	20.739

Under the condition $\Delta\varepsilon^v = 0$, integrals $\beta_r = \beta_v = 0$ and formulas (19) appear to be much simplified:

$$\lambda_t = \frac{75k^2T}{32m\Omega^{(2,2)}}, \quad \lambda_r = \frac{3k^2T}{8m\Omega^{(1,1)}}c_r, \quad (20)$$

$$\lambda_{vt} = \frac{3k^2T}{8m\Omega^{(1,1)}}c_v^T, \quad \lambda_v = \frac{3k^2T}{8m\Omega^{(1,1)}}c_v^{T_1},$$

and keep only specific heats and elastic Ω -integrals.

A comparison of the λ -coefficients obtained on the basis of the explicit (Eq. (19)) and approximate (Eq. (20)) models is given in Table 1. One can see that the difference does not exceed 1.5%. The strongest discrepancy is observed in the rotational thermal conductivity coefficients λ_r (up to 1.5%) but the differences in the total coefficients λ at ∇T are no more than 0.3%. It leads to the conclusion that in order to predict the thermal conductivity coefficients it is sufficient to take into account real gas effects such as vibrational nonequilibrium and anharmonicity of vibrations only in the specific heats. The neglecting of the inelastic integrals for $\Delta\varepsilon \rightarrow 0$ does not influence noticeably on the thermal conductivity. Previously Mason and Monchik [3] came to the similar conclusion that the inelastic collision integrals may be eliminated in the kinetic theory code for the thermal conductivity in the weakly nonequilibrium gas.

Now let us consider the formulas for the thermal conductivity coefficient λ at the gas temperature gradient. In the limit case $\Delta\varepsilon = 0$ from Eq. (20) we obtain

$$\lambda = \frac{5}{2} \frac{k}{m} \left(\frac{c_t}{c_u} + \frac{2}{5} \frac{\rho D}{\eta} \frac{c_r + c_v^T}{c_u} \right) \eta c_u, \quad (21)$$

where

$$D = \frac{3}{8} \frac{kT}{\rho\Omega^{(1,1)}}$$

is the self-diffusion coefficient and η is the shear viscosity coefficient. In Ref. [8] it was shown that the strong vibrational nonequilibrium does not affect the shear viscosity and therefore this coefficient may be written only in terms of elastic collision integrals:

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

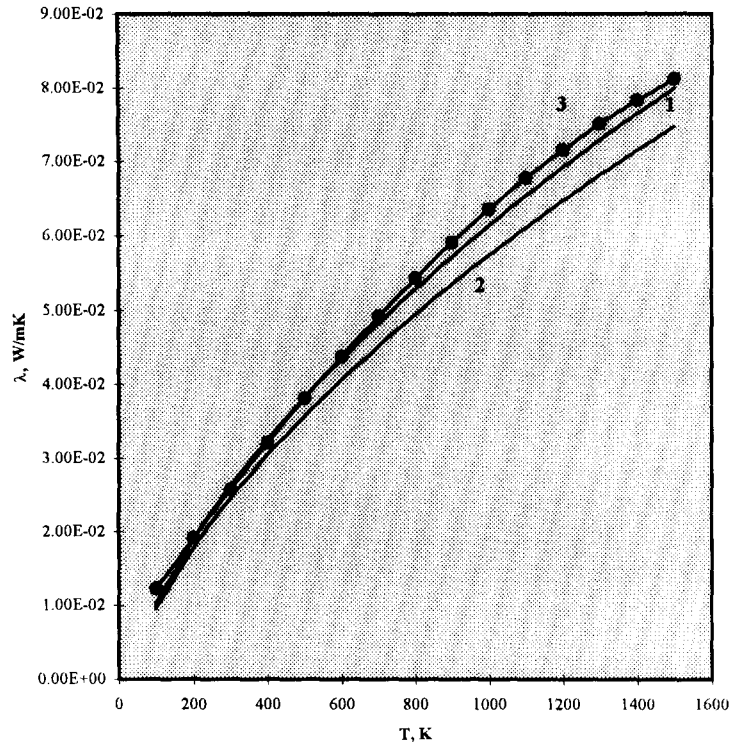


Fig. 4. Thermal conductivity coefficient $\lambda = \lambda_t + \lambda_r + \lambda_{vt}$ versus T calculated for N_2 on the basis of present model: (1) Eq. (20), (2) λ_{ME} , Eq. (22), and (3) λ_{exp} , Ref. [13]. Equilibrium case ($T_1 = T$).

Eq. (21) corresponds to the correction obtained previously by Hirschfelder [2] for slightly nonequilibrium gas. Under strong nonequilibrium conditions the specific heats in Eq. (21) are defined by Eqs. (8) and (11).

If one sets $\rho D/\eta = 1$ then Eq. (21) transforms into

$$\lambda = \frac{5}{2} \frac{k}{m} \left(1 - \frac{3}{5} \frac{c_r + c_v^T}{c_u} \right) \eta c_u. \quad (22)$$

In fact Eq. (22) represents the Eucken formula with real gas specific heats. The results of the λ -coefficients calculation in molecular nitrogen on the basis of different models are given in Figs. 4–6. Fig. 4 depicts the thermal conductivity λ dependence on T deduced from our model (Eq. (20)), from the Eucken formula (22) with the nonequilibrium specific heats (λ_{ME}), and from experiment (λ_{exp}) [13]. It is evident that the percentage deviation of the thermal conductivity coefficient defined by Eq. (20) from experimental data does not exceed 3.5% whereas the Eucken correction (22) gives a deviation up to 9.8%.

Fig. 5 gives the dependence of λ -coefficient on T_1 calculated on the basis of the kinetic theory (λ), the modified Eucken formula with the real gas specific heats (λ_{ME}), the Eucken formula with the equilibrium specific heats (λ_E). Taking into account the nonequilibrium specific heats in the empirical Eucken formula results in its refinement which appears to be important under the condition $T_1/T > 3$. For $T_1/T < 3$ the distinction between λ obtained from the kinetic model and λ_{ME} does not exceed 6–7% and both of them are close to λ_E . One can see a considerable discrepancy with vibrational temperature rising. The increase of the difference between λ and λ_{ME} at $2500 \text{ K} < T_1 < 4000 \text{ K}$ is connected with the rising of specific heat values. Under these conditions the deviation of the factor $\rho D/\eta$ from unit must be taken into account in (21). Hirschfelder [2] has calculated this factor for Lennard-Jones and Buckingham (6-exp) potentials and deduced

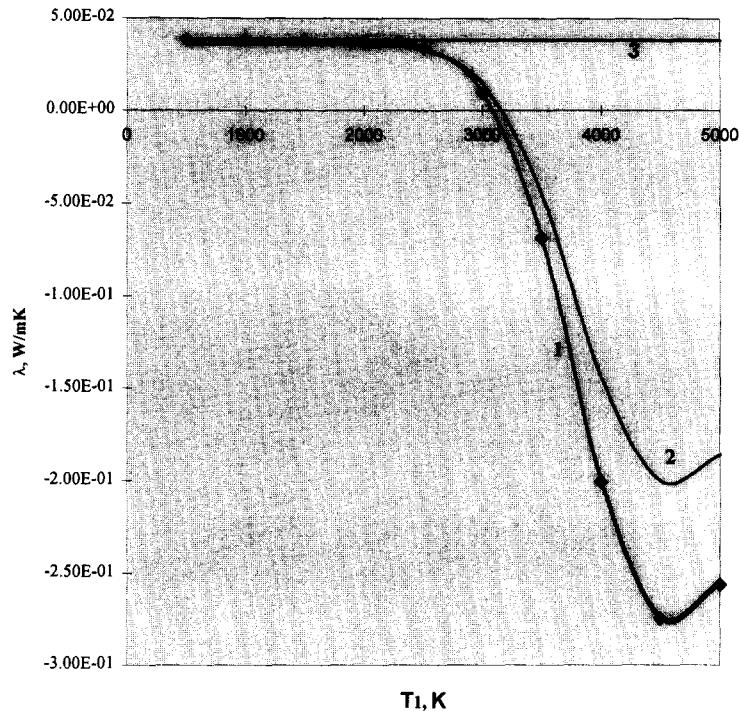


Fig. 5. Thermal conductivity coefficient $\lambda = \lambda_t + \lambda_r + \lambda_{vt}$ versus T_1 calculated for N_2 on the basis of the present model: (1) Eq. (20), (2) λ_{ME} , Eq. (22), with the real specific heats, (3) λ_E , Eq. (22), with the equilibrium specific heats, and (♦) λ_{MH} , Eq. (23), with the nonequilibrium specific heats. $T = 500$ K.

that its dependence on temperature is very weak. Then he suggested to replace $\rho D/\eta$ by its average value 1.328. In so doing the expressions for the thermal conductivity can be further simplified:

$$\lambda = \frac{5}{2} \frac{k}{m} \left(\frac{c_t}{c_u} + 0.5312 \frac{c_r + c_v^T}{c_u} \right) \eta c_u, \quad \lambda_v = 1.328 \frac{k}{m} \eta c_v^T. \quad (23)$$

The difference between λ values coming from (21) and (23) is not more than 1.5%. In Fig. 5 λ values taken from (23) are also shown and denoted by λ_{MH} .

Formulas (23) present λ and λ_v in terms of only nonequilibrium specific heats and a shear viscosity coefficient and are suitable for calculations. It is seen that this approximate model gives a good agreement with a rigorous kinetic theory results in a wide range of temperatures.

The unusual behaviour of λ at high vibrational temperatures $T_1 > T$ is explained by the strong impact of non-Boltzmann distribution (7). Anharmonic effects lead to the negative c_v^T and λ_{vt} , and λ_{vt} magnitude becomes much more than λ_t and λ_r [8,9]. It can be noticed that the peaks of λ_{ME} , λ_{MH} and λ correspond to the maximum absolute value of c_v^T . Under close examination of the vibrational energy distribution over vibrational levels it is shown that these peaks are achieved at the maximum vibrational energy store at several lower levels.

Fig. 6 shows the vibrational thermal conductivity coefficient λ_v versus T for anharmonic oscillators (Eq. (20)), for the harmonic oscillator (λ_v (h.o.)) and λ_v from Ref. [6], obtained for a N_2 - O_2 mixture (λ_v ([6])). The difference between λ_v values calculated for harmonic and anharmonic oscillator decreases with T_1/T reduction and practically disappears for $T_1/T < 0.5$. At high temperature the anharmonic effects are of the importance for λ_v corresponding to the equilibrium case ($T = T_1$) like that for c_v^{eq} .

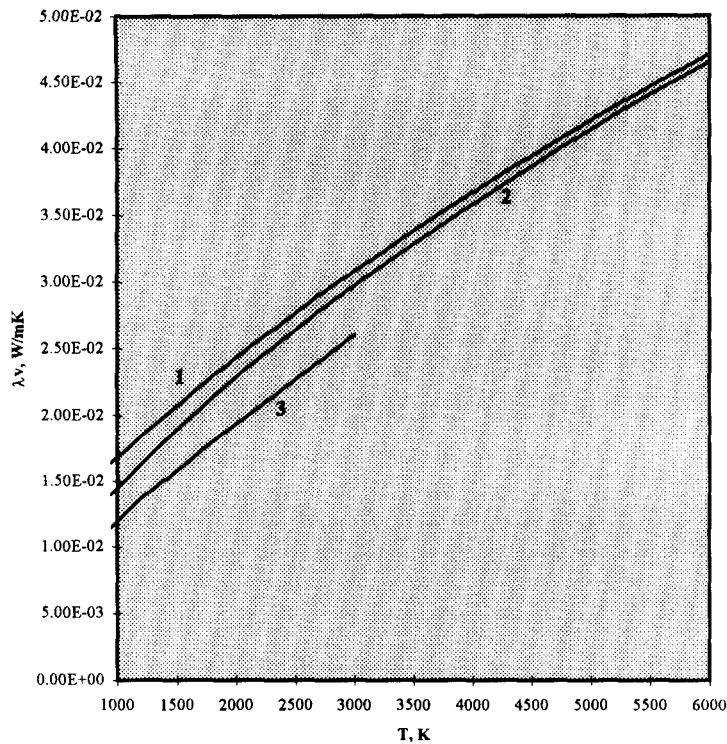


Fig. 6. Vibrational thermal conductivity coefficient λ_v versus T calculated for N_2 using (1) the anharmonic oscillator model, (2) the harmonic oscillator model and (3) taken from Ref. [6]. $T_1 = 3000$ K.

Proceeding from the distribution function (7) one can obtain the Prandtl number in a nonequilibrium gas:

$$Pr = \frac{c_p \eta}{\lambda} \frac{k}{m}, \quad (24)$$

where $c_p = 1 + c_u$ is the dimensionless specific heat at the constant pressure, c_u is defined from Eq. (11). Fig. 7 gives the Pr calculated on the basis of the different models. Curve 1 depicts Pr obtained from Eq. (24) with c_u and λ found under the condition $T_1 = T$, curve 2 is taken from Ref. [14], curve 3 is from Ref. [15] and curve 4 corresponds to the results of Ref. [6] for N_2 – O_2 mixture. It is seen that taking into account real gas effects in the specific heats and the thermal conductivity coefficient leads to the Prandtl number decreasing in comparison to near-equilibrium approach. Prandtl number in a mixture appears to be less than that in a monocomponent gas.

6. Conclusions

In the strongly nonequilibrium gas the anharmonicity of vibrations leads to the distribution (7) and to the heat flux depending on the gradients of two temperatures: T (translational–rotational) and T_1 (the vibrational temperature of the first vibrational level). The anharmonic effects become particularly important at $T < T_1$. Two vibrational thermal conductivity coefficients λ_{vt} and λ_v appear at ∇T and ∇T_1 respectively.

The kinetic theory gives the validation of different models of the heat conductivity coefficients in the nonequilibrium gas. The vibrational thermal conductivity coefficients λ_{vt} and λ_v are expressed in terms of the

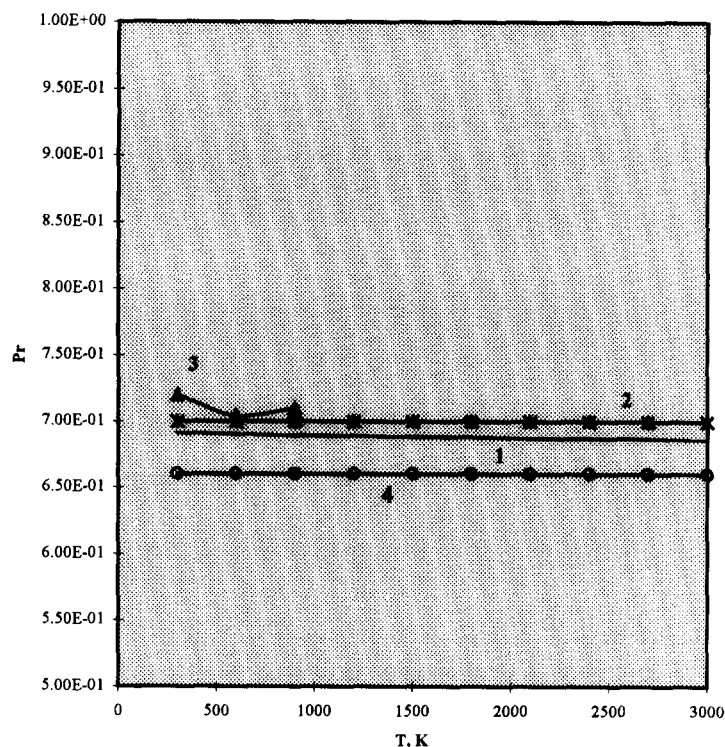


Fig. 7. Prandtl number for N_2 at equilibrium ($T_1 = T$) as function of T . (1) Present model, Eq. (24), (2) taken from Ref. [14], (3) from Ref. [15], (4) from Ref. [6].

nonequilibrium specific heats and do not depend noticeably on the inelastic vibrational collision integrals. This conclusion seems to be important because the existing models of inelastic scattering cross sections are not sufficiently rigorous. The approximate formulas (21) and (23) obtained above for $\lambda = \lambda_t + \lambda_r + \lambda_{vt}$ give the refinement of the Eucken and Hirschfelder factors respectively due to the real gas specific heats. The minimum deviation from the kinetic theory results is achieved with use of Eq. (23) with nonequilibrium specific heats and Hirschfelder suggestion about replacing the factor $\rho D/\eta$ by 1.328. The difference between λ deduced from exact and approximate expressions does not exceed 1.5%. Eq. (23) with real specific heats (8) may be recommended as a usable formula for the calculation of heat conductivity coefficients in a nonequilibrium gas.

The evaluation of the real gas specific heats and the thermal conductivity coefficients under the strong nonequilibrium conditions requires an adequate model of the vibrational level populations. More exactly the vibrational energy distribution over the vibrational levels becomes particularly important. The dominant role of the vibrational energy store at the lower levels is shown. The maximum energy store at three lower levels for $T_1/T \sim 6-7$ corresponds to the peaks of the λ_{vt} and λ_v which are found on the basis of both exact and approximate model.

The solution of the master equations for level populations is known to be more sensitive to transition probabilities. It means that the inelastic cross sections are very important in the code of calculation of the level populations. The results obtained in this paper are based on the asymptotic solution (5) of the kinetic equations with use of the suggestion only about the characteristic rates between elastic and different kinds of inelastic collisions.

For $T_1/T < 1$ anharmonic effects on the thermal conductivity are not very important, λ_{vt} is small and λ_v is close to one calculated on the basis of two-temperature harmonic oscillator model. By contrast, anharmonicity

of vibrations affects significantly by λ_{vt} and λ_v for $T_1/T \gg 1$. Also the anharmonic effects become noticeable at high gas temperatures even with $T_1 = T$ (in the case of equilibrium level populations), and result in increasing of c_r^{eq} and λ with T rising.

In conclusion it has to be said that the results obtained are valid at gas temperatures when electronic excitation is not very important, for molecular nitrogen it is about 7000–8000 K. The transport properties of partially ionized gases and the role of different collisions were considered in Refs. [4,16]. In particular the increasing of collision integrals with the rising of principle quantum number of atoms is shown in Ref. [16]. These peculiarities should be taken into account in the development of the simplified models of transport coefficients in ionized gases.

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