Transport Properties of Non-Equilibrium Vibrational Reacting Flows

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Introduction

Renewed interest to the transport processes in non-equilibrium media is connected to the development of

- Chemical technology
- Hypersonic applications
- Planetary atmosphere reentry problems
  - Earth reentry → diatomic gas mixtures
  - Mars reentry → particular interest to polyatomic gas mixtures containing CO₂
Transport kinetic theory

- **Maxwell, 1859**: transport equations, statistical approach
- **Boltzmann, 1872**: Boltzmann equations
- **Chapman, Enskog, 1916–1917**: 
  - closed system of macroscopic equations; transport coefficients are expressed in terms of $\rho, T$; structure-less gases; elastic collisions only; chemical reactions are frozen
- **Chapman, Cowling, 1939; Hirschfelder, Curtiss, Bird, 1954**, development of transport theory of structure-less gas mixtures
Internal degrees of freedom

- Eucken, 1913: phenomenological theory
  - First attempt to take into account internal degrees of freedom in the heat conductivity coefficient:
    \[
    \lambda = \lambda_{tr} + \lambda_{int}
    \]
    \(\lambda_{int}\) is found using phenomenological mean free path approach
- Taxman, 1950th: classical treatment
- Waldmann, 1950–60: quantum-mechanics treatment
  - Advantage: correct description of rotational degrees of freedom
  - Disadvantage: very complicated expressions for transport coefficients
  - Advantage: simplicity of final expressions for transport coefficients
Modern state of the art

• Thermal equilibrium flows:
  • Mason, Monchick, 1960–70, first transport algorithms for gas mixtures with internal degrees of freedom
  • Ferziger, Kaper, 1972; Ern, Giovangigli, 1994, development of transport algorithms

• Flows with strong vibrational non-equilibrium:
  • Multi-temperature models based on quasi-stationary vibrational distributions
    • Harmonic oscillators (Kuznetsov, 1965; Brun, 1980–90)
    • Anharmonic oscillators (Kustova, Nagnibeda, 1995–2005)
    • Polyatomic gases (Kustova, Nagnibeda, 1995–2005)
  • State-to-state models based on the solution of master equations for vibrational level populations (Kustova, Nagnibeda, 1998–2005)
Different approaches in the kinetic transport theory

- The most detailed state-to-state description is based on the following relation between characteristic times of microscopic collision processes

\[ \tau_{tr} \sim \tau_{rot} \ll \tau_{vibr} \sim \tau_{react} \sim \theta \]

- The most simple thermal equilibrium one-temperature description:

\[ \tau_{tr} \sim \tau_{rot} \sim \tau_{vibr} \ll \tau_{react} \sim \theta \]

In these limit cases, all vibrational relaxation mechanisms are considered in the same time scale (either microscopic or macroscopic); vibrational relaxation process cannot be divided to the rapid and slow stages. These approaches can be applied for both diatomic and polyatomic gases.
• Under some flow conditions vibrational relaxation can be separated to the rapid and slow stages accordingly to the rates of various relaxation mechanisms.

• For diatomic gas mixtures the relaxation channels are:
  - $VV$ exchange of vibrational quanta between molecules of the same chemical species
  - $VT$ transitions between vibrational and translational modes
  - $VV'$ exchange of vibrational quanta between unlike molecules

• Multi-temperature description of diatomic gas mixtures is based on the relation:

$$\tau_{tr} \sim \tau_{rot} \sim \tau_{VV} \ll \tau_{VV'} \sim \tau_{VT} \sim \tau_{react} \sim \theta$$

• For anharmonic oscillators under strong vibrational excitation, various mechanisms of vibrational relaxation can be preferential for different groups of vibrational levels
Polyatomic gas mixtures containing CO$_2$

- **CO$_2$ structure:**
  - symmetric mode ($\nu_1$)
  - doubly degenerated bending mode ($\nu_2$)
  - asymmetric mode ($\nu_3$)

- **Vibrational relaxation channels in a CO$_2$/N$_2$ mixture:**
  - Intra-mode $VV_m$ exchanges ($m = 1,2,3$ for CO$_2$; $m = 4$ for N$_2$)
  - Inter-mode $VV_{m-k}$ exchanges ($m, k = 1,2,3$)
    - $VV_{1-2}$ is the most probable since $\nu_1 \approx 2\nu_2$
    - $VV_{2-3}$
    - $VV_{1-2-3}$
  - Inter-molecular $VV_{3-4}$ exchange between N$_2$ and CO$_2$
    - asymmetric mode ($\nu_3 \approx \nu_4$)
  - $VT_m$ exchanges in each vibrational mode ($m = 1, 2, 3, 4$)
Multi-temperature models in CO$_2$/N$_2$ mixtures

- **5-temperature model** ($T, T_1, T_2, T_3, T_4$)

  \[ \tau_{VV_m} \ll \tau_{VV_{m-k}} \sim \tau_{VT_m} \sim \theta, \ m, k = 1, 2, 3, 4 \]

- **4-temperature model** ($T, T_{12}, T_3, T_4$)

  \[ \tau_{VV_m} \sim \tau_{VV_{1-2}} \ll \tau_{VV_{2-3}} \sim \tau_{VV_{1-2-3}} \sim \tau_{VV_{3-4}} < \tau_{VT_m} \sim \theta, \ m = 1, 2, 3, 4 \]

- **3- and 2-temperature models**
  - **3-temperature models**
    - $T, T_{12}, T_{34}$

      \[ \tau_{VV_m} \sim \tau_{VV_{1-2}} \sim \tau_{VV_{3-4}} \ll \tau_{VV_{2-3}} \sim \tau_{VV_{1-2-3}} < \tau_{VT_m} \sim \theta, \ m = 1, 2, 3, 4 \]

    - $T, T_3, T_4$

      \[ \tau_{VV_m} \sim \tau_{VV_{1-2}} \sim \tau_{VT_2} \ll \tau_{VV_{2-3}} \sim \tau_{VV_{1-2-3}} \sim \tau_{VV_{3-4}} < \tau_{VT_3} \sim \tau_{VT_4} \sim \theta \]

    - $T, T_{34}$

      \[ \tau_{VV_m} \sim \tau_{VV_{1-2}} \sim \tau_{VV_{3-4}} \sim \tau_{VT_2} \ll \tau_{VV_{2-3}} \sim \tau_{VV_{1-2-3}} < \tau_{VT_3} \sim \tau_{VT_4} \sim \theta \]
General procedure of the mathematical model development

- Establishment of the relaxation times hierarchy
- Small parameter $\epsilon = \tau_{rap}/\tau_{slow}$ and expansion of the distribution function over $\epsilon$
- Collision invariants of rapid processes
- Set of macroscopic parameters providing a closed flow description
- Governing equations for macroscopic parameters
  - conservation equations
  - relaxation equations
- Zero-order solution
- First-order solution
  - transport terms
  - transport and reaction rate coefficients
General procedure of the transport coefficients calculation

- Expansions of the unknown functions into the finite series of Sonine and Waldmann polynomials
- Transport coefficients in terms of polynomial expansion coefficients
- Reducing of integral equations to the set of linear algebraic equations for expansion coefficients. Matrices are composed of bracket integrals depending on the cross sections of rapid processes
- Simplification of brackets integrals
- Transport coefficients as solutions of the algebraic equation systems
Commonly used assumptions in CFD

- Invoking of phenomenological relations:
  - $\text{Pr} = \text{const}$
  - Viscosity coefficient is found using experimental results or some approximations
    - Pure gas: linear or power dependence on the temperature
    - Mixtures: mixing rules based on the species viscosity coefficients
  - $\text{Le} = \text{const}$
  - $\text{Sc} = \text{const}$
  - Thermal diffusion is neglected
  - Reaction rate coefficients are calculated neglecting first order effects (non-homogeneity and compressibility)

- Objective: development of rigorous self-consistent transport theory without using phenomenology
Problems encountered

- Optimal choice of polynomial systems and trial functions
- Convergency of polynomial expansions
- Data on the cross sections of microscopic collision processes
  - Cross sections of rapid processes: required for the calculation of transport and reaction rate coefficients
  - Cross sections of slow processes: required for the calculation of reaction rate coefficients and relaxation pressure
- Efficient algorithms for the solution of transport systems (systems of linear algebraic equations)
  - slow algorithms lead to highly time consuming CFD codes
State-to-state approach

- Macroscopic parameters:
  - \( n_{ci}(r, t), \ c = 1, \ldots, L, \ i = 0, \ldots, L_c \) – vibrational level populations
  - \( v(r, t) \) – macroscopic flow velocity
  - \( T(r, t) \) – gas temperature

- Transport terms
  - Pressure tensor
    \[
    \mathbf{P} = (p - p_{rel}) \mathbf{I} - 2\eta \mathbf{S} - \zeta \nabla \cdot \mathbf{v} \mathbf{I}
    \]
  - Diffusion velocity
    \[
    \mathbf{V}_{ci} = -\sum_{dk} D_{cidk} d_{dk} - D_{Tci} \nabla \ln T
    \]
  - Heat flux
    \[
    \mathbf{q} = -\chi' \nabla T - p \sum_{ci} D_{Tci} \mathbf{d}_{ci} + \sum_{ci} \left( \frac{5}{2} kT + \langle \epsilon_{ci} \rangle_{rot} + \epsilon_i^c + \epsilon^c \right) n_{ci} \mathbf{V}_{ci}
    \]
Transport coefficients

- \( \eta = \frac{kT}{10} [B, B] \) – shear viscosity coefficient
- \( \zeta = kT [F, F] \) – bulk viscosity coefficient
- \( p_{\text{rel}} = kT [F, G] \) – relaxation pressure
- \( D_{\text{cidd}} = \frac{1}{3n} \left[ D^{ci}, D^{dk} \right] \) – diffusion coefficients
- \( D_{\text{Tci}} = \frac{1}{3n} \left[ D^{ci}, A \right] \) – thermal diffusion coefficients
- \( \lambda' = \lambda_{\text{tr}} + \lambda_{\text{rot}} = \frac{k}{3} [A, A] \) – heat conductivity coefficient

Functions \( A, B, D^{ci}, F, G \) are found as solutions of linear integral equations for the first order correction to the distribution function
• Integral equation for the function $A_{cij}$

$$
\sum_{dk} \frac{n_{ci} n_{dk}}{n^2} l_{cijdk}(A) = \frac{1}{n} f^{(0)}_{cij} \left( \frac{m_c c_c^2}{2kT} - \frac{5}{2} + \frac{\varepsilon_{ij}^c - \langle \varepsilon_{ci}^c \rangle_{\text{rot}}}{kT} \right) c_c
$$

$l_{cijdk}(\phi)$ – linearized integral operator of rapid processes

• Polynomial expansion for the function $A_{cij}$

$$
A_{cij} = -\frac{m_c c_c}{2kT} \sum_{r} a_{ci} S_{3/2}^{(r)} \left( \frac{m_c c_c^2}{2kT} \right) P_j^{(p)} \left( \frac{\varepsilon_{ij}^c}{kT} \right)
$$

• Transport coefficients in terms of the polynomial expansion coefficients

$$
\lambda' = \sum_{ci} \frac{5}{4} k \frac{n_{ci}}{n} a_{ci,10} + \sum_{ci} \frac{m_c}{2} \frac{n_{ci}}{n} c_{ci} a_{ci,01}, \quad DT_{ci} = -\frac{1}{2n} a_{ci,00}
$$
• Linear algebraic equations for the expansion coefficients

\[
\sum_{dk} \sum_{r'p'} \Lambda_{rr'pp'}^{cidk} a_{dk,r'p'} = \frac{15kT}{2} \frac{n_{ci}}{n} \delta_{r1}\delta_{p0} + 3m_c T \frac{n_{ci}}{n} c_{rot}^{ci} \delta_{r0}\delta_{p1}
\]

\[c = 1, \ldots, L, \quad i = 0, 1, \ldots, L_c, \quad r, p = 0, 1, \ldots.\]

• Constraint

\[
\sum_{ci} \frac{\rho_{ci}}{\rho} a_{ci,00} = 0
\]

• Bracket integrals of the cross sections of rapid processes

\[
\Lambda_{rr'pp'}^{cidk} = \sqrt{m_c m_d} \left( \delta_{cd} \delta_{ik} \sum_{bl} \frac{n_{ci} n_{bl}}{n^2} \left[ Q^{rp}, Q^{r'p'} \right]_{cibl} + \frac{n_{ci} n_{dk}}{n^2} \left[ Q^{rp}, Q^{r'p'} \right]_{cidk} \right)
\]

\[
Q_{cij}^{rp} = \sqrt{\frac{m_c}{2kT}} c_c S_{3/2}^{(r)} \left( \frac{m_c c_c^2}{2kT} \right) P_{j}^{(p)} \left( \frac{\varepsilon_{ji}^{ci}}{kT} \right)
\]
• **Simplification of brackets integrals**
  - Using the Mason and Monchick assumptions, integral brackets can be reduced to the $\Omega$-integrals and rotational relaxation times
  - The choice of interaction potential and its parameters
    - Lennard-Jones potential at low temperatures
    - Repulsive potentials for high temperatures
  - The contribution of inelastic collision integrals:
    - Weak for the thermal conductivity, diffusion, shear viscosity coefficients (except some polar gases)
    - Essential for the bulk viscosity and relaxation pressure

• **Transport coefficients as solutions of the algebraic equation systems**
  - Cramer rule
  - Gauss method
  - New iterative algorithms (Ern, Giovangigli, 1994)
• Similar algorithms are applied for the calculation of
  • diffusion coefficients
  • shear and bulk viscosity coefficients
  • relaxation pressure
  • reaction rate coefficients

• Finally, all state-to-state transport coefficients are expressed in terms of \( n_{ci}, T \)

• Bracket integrals depend on the cross sections of elastic and RT collisions

• Reaction rate coefficients and relaxation pressure depend also on the cross sections of slow processes

• Reaction rate coefficients depend on the media non-homogeneity as well as compressibility through the velocity divergence.
Features of state-to-state transport properties

- Diffusion

\[ \mathbf{V}_{ci} = \mathbf{V}_{ci}^{MD} + \mathbf{V}_{ci}^{TD} + \mathbf{V}_{ci}^{DVE} \]

- Mass diffusion
- Thermal diffusion
- Diffusion of vibrational energy determined by the vibrational distributions:

\[ \mathbf{V}_{ci}^{DVE} = -\tilde{D} \nabla \ln \frac{n_{ci}}{n_c} \]

- Heat transfer

\[ \mathbf{q} = \mathbf{q}^{HC} + \mathbf{q}^{MD} + \mathbf{q}^{TD} + \mathbf{q}^{DVE} \]

- Heat conductivity (translational and rotational)
- Mass diffusion
- Thermal diffusion
- Diffusion of vibrational energy determined by the vibrational energy gradient:

\[ \mathbf{q}^{DVE} = -\tilde{D} \sum_c \rho_c \nabla E_{vibr, c} \]
Problems in state-to-state transport theory

- Time consuming algorithms:
  - \( N_{tot} = \sum_{c=1}^{L_{mol}} L_c + L_{at} \) – total number of chemical and vibrational species
  - \( L_{mol}, L_{at} \) – numbers of molecular and atomic species
  - \( L_c \) – total number of vibrational energy levels in species \( c \)
  - \( N_v = \sum_{c=1}^{L_{mol}} L_c \) – total number of vibrational states in a mixture
  - \( L = L_{mol} + L_{at} \) – total number of chemical species

- General case
  - \( \lambda_{TR} \) – 1 coefficient; system of \( 3N_v + 2L_{at} \) algebraic equations
  - \( D_{Tci} \) – \( N_{tot} \) coefficients; systems of \( 3N_v + 2L_{at} \) equations
  - \( D_{cidk} \) – \( N_{tot} (N_{tot} + 1)/2 \) independent coefficients found from systems of \( N_{tot} \) equations

- Example: \( N_2/N \) mixture, \( L_{N_2} = 46 \)
  - \( \lambda_{TR} \) – 1 coefficient (140 equations)
  - \( D_{Tci} \) – 47 coefficients (140 equations)
  - \( D_{cidk} \) – 1128 coefficients (47 equations)
Simplified state-to-state transport model

- Additional assumptions
  - Rigid rotator model
  - Cross sections of elastic collisions are independent from the vibrational states of colliding particles
- All coefficients are expressed in terms of: $n_{ci}$, $T$, elastic collision integrals and characteristic times of RT transitions
- Number of coefficients is reduced:
  - $\lambda_{TR}$ – 1 coefficient; a system of $3L_{mol} + 2L_{at}$ algebraic equations ($N_2/N$ mixture: 1 coefficient, 5 equations)
  - $D_{Tci}$ – $L$ coefficients; systems of $3L_{mol} + 2L_{at}$ equations ($N_2/N$: 2 coefficients, 5 equations)
  - $D_{cidk}$ – $N_v + L_{mol} + L(L + 1)/2$ independent coefficients; systems of $L + 1$ equations ($N_2/N$: 49 coefficients, 3 equations)
\( D_{\text{cici}, \text{m}^2/\text{s}} \)

Figure: Diffusion coefficients behind a shock wave as functions of \( i \). 
\( \text{N}_2/\text{N}, M_0 = 15, T_0 = 293 \text{ K}, p_0 = 100 \text{ Pa} \)
Figure: Heat flux behind a shock wave as a function of $x$. $N_2/N$, $M_0 = 15$, $T_0 = 293$ K, $p_0 = 100$ Pa
Simplified state-to-state model

- Main features:
  - Coefficients $\lambda, D_{Tci}, \eta, \zeta$ do not depend on the vibrational distributions;
  - coefficients $D_{cici}$ depend essentially on the vibrational distributions

- Advantages:
  - takes into account completely coupled state-to-state vibrational-chemical kinetics
  - good accuracy
  - simple analytical expressions for diffusion coefficients in binary $A_2/A$ gas mixtures
  - quite feasible for diatomic gas mixtures

- Disadvantage:
  - still numerically expensive for polyatomic gas mixtures
One-temperature approach

- **Macroscopic parameters:**
  - $n_c(\mathbf{r}, t), c = 1, \ldots, L$ – chemical species number densities
  - $\mathbf{v}(\mathbf{r}, t)$ – macroscopic flow velocity
  - $T(\mathbf{r}, t)$ – gas temperature

- **Transport terms:**
  - **Pressure tensor:** $\mathbf{P} = (p - p_{rel})\mathbf{I} - 2\eta \mathbf{S} - \zeta \nabla \cdot \mathbf{v}\mathbf{I}$
  - **Diffusion velocity:** $\mathbf{V}_c = -\sum_d D_{cd} \mathbf{d}_d - D_{Tc} \nabla \ln T$
  - **Total heat flux:** $\mathbf{q} = -\lambda' \nabla T - p \sum_c D_{Tc} \mathbf{d}_c + \sum_c \rho_c h_c \mathbf{V}_c$
Features of the one-temperature transport model

- **Diffusion**

\[
\mathbf{V}_c = \mathbf{V}_c^{MD} + \mathbf{V}_c^{TD} = \mathbf{V}_c^{QS}, \quad \mathbf{V}^{DVE} = 0
\]

- **Mass diffusion**
- **Thermal diffusion**

- **Heat transfer**

\[
\mathbf{q} = \mathbf{q}^{HC} + \mathbf{q}^{MD} + \mathbf{q}^{TD}
\]

- **Heat conductivity (translational and internal):**

\[
\mathbf{q}^{HC} = -\lambda' \nabla T = -(\lambda_{tr} + \lambda_{int}) \nabla T = -(\lambda_{tr} + \lambda_{rot} + \lambda_{vibr}) \nabla T
\]

- **Mass diffusion**
- **Thermal diffusion**

- **Neglecting inelastic cross-sections one can write**

\[
\mathbf{q}^{DVE} = -\lambda_{vibr} \nabla T
\]
• Advantages:
  • Simplicity
  • Low number of transport coefficients:
    • 1 thermal conductivity coefficient
    • 1 viscosity and 1 bulk viscosity coefficient
    • $L$ thermal diffusion coefficients
    • $L(L + 1)/2$ independent diffusion coefficient
  • Low order of linear transport systems
  • Arrhenius law for zero order reaction rate coefficients

• Disadvantages:
  • Very rough model of physical-chemical processes
  • Only equilibrium Boltzmann distributions over rotational and vibrational energy can be considered
  • It is impossible to account for
    • different rates of internal energy exchanges
    • coupling of vibrational relaxation and chemical reactions
Multi-temperature approach: diatomic gases

- Vibrational spectrum models
  - Harmonic oscillators $\rightarrow$ resonant VV exchange; Boltzmann vibrational distributions
  - Anharmonic oscillators $\rightarrow$ non-resonant VV exchange; non-Boltzmann (Treanor or combined) vibrational distributions

- Macroscopic parameters:
  - $n_c(r, t), c = 1, ..., L$ – chemical species number densities
  - $v(r, t)$ – macroscopic flow velocity
  - $T(r, t)$ – gas temperature

- Vibrational relaxation parameters:
  - Harmonic oscillators: $T_{v}^{c}(r, t), c = 1, ..., L_{mol}$ – vibrational temperature of $c$ molecular species
  - Anharmonic oscillators: $T_{1}^{c}(r, t), c = 1, ..., L_{mol}$ – temperature of the first vibrational level of $c$ molecular species
Transport terms:

- **Pressure tensor:** \( P = (p - p_{rel})I - 2\eta S - \zeta \nabla \cdot vI \)

- **Diffusion velocity:** \( V_c = -\sum_d D_{cd}d_d - D_{Tc} \nabla \ln T \)

- **Total heat flux:**
  - **Harmonic oscillators:**
    \[
    q = -(\lambda_{tr} + \lambda_{rot}) \nabla T - \sum_c \lambda_v^c \nabla T_v^c - p \sum_c D_{Tc}d_c + \sum_c \rho_c h_c V_c
    \]
  - **Anharmonic oscillators:**
    \[
    q = -(\lambda_{tr} + \lambda_{rot} + \lambda_a + \sum_c \lambda_v^c) \nabla T - \sum_c (\lambda_{tv}^c + \lambda_{vv}^c) \nabla T_1^c - \\
    -p \sum_c D_{Tc}d_c + \sum_c \rho_c h_c V_c
    \]

- **Vibrational energy flux:**
  - **Harmonic oscillators:** \( q_v^c = -\lambda_v^c \nabla T_v^c \)
  - **Anharmonic oscillators:** \( q_v^c = -\lambda_{vt}^c \nabla T - \lambda_{vv}^c \nabla T_1^c \)
Transport coefficients

• Heat conductivity coefficients: \( \lambda' = \lambda_{tr} + \lambda_{rot} + \lambda_a \), \( \lambda_a \) is particular for anharmonic oscillators

• \( \lambda^c_{vt}, \lambda^c_{tv} \) describe the energy transfer due to the non-resonant character of VV exchange

• \( \lambda^c_{vv} \) characterizes the flux of vibrational quanta in \( c \) species

• Bulk viscosity coefficient \( \zeta = \zeta_{rot} + \zeta_{vv} \)

• Relaxation pressure \( p_{rel} = p_{rel}^{rot} + p_{rel}^{vv} \)

• For harmonic oscillators \( \lambda^c_{vt} = \lambda^c_{tv} = \lambda_a; \ zeta_{vv} = 0; \ p_{rel}^{vv} = 0 \).
Features of the multi-temperature transport model

- **Diffusion**
  \[ \mathbf{V}_c = \mathbf{V}_c^{MD} + \mathbf{V}_c^{TD} = \mathbf{V}_c^{QS}, \quad \mathbf{V}^{DVE} = 0 \]
  - Mass diffusion
  - Thermal diffusion

- **Heat transfer**
  \[ \mathbf{q} = \mathbf{q}^{HC} + \mathbf{q}^{MD} + \mathbf{q}^{TD} + \mathbf{q}^{VHC} \]
  - Heat conductivity (translational, rotational)
  - Mass diffusion
  - Thermal diffusion
  - Vibrational energy transfer by heat conduction

- **Neglecting inelastic cross-sections one can write**
  - Anharmonic oscillators:
    \[ \mathbf{q}^{DVE} = \mathbf{q}^{VHC} = - (\lambda_a + \sum_c \lambda_{vt}^c) \nabla T - \sum_c (\lambda_{tv}^c + \lambda_{vv}^c) \nabla T_1^c \]
  - Harmonic oscillators:
    \[ \mathbf{q}^{DVE} = \mathbf{q}^{VHC} = - \sum_c \lambda_{vv}^c \nabla T_v^c \]
Transport coefficients

- $\lambda_{tr}$, $\lambda_{rot}$, $D_{Tc}$, $D_{cd}$, $\eta$, $\zeta_{rot}$ practically do not depend on $T_1^c$;
- $\lambda_a$, $\lambda_{vt}$, $\lambda_{tv}$, $\lambda_{vv}$, $\zeta_{vv}$ depend essentially on $T_1^c$.

Figure: Heat conductivity coefficients of N$_2$ at $T_1 = 5000$ K.

Legend:
1: $\lambda_{tr}$
2: $\lambda_{rot}$
3: $\lambda_{tv} + \lambda_{vv}$
4: $-\lambda_a - \lambda_{vt}$
Multi-temperature approach: polyatomic gas
3-temperature model for CO$_2$/CO/O. Harmonic oscillator.

- **Hierarchy of characteristic times:**
  \[ \tau_{tr} < \tau_{rot} < \tau_{VV_m} \sim \tau_{VV'_1-2} \ll \tau_{VT_2} \sim \tau_{VV'_2-3} \sim \tau_{VV'_1-2-3} < \tau_{VT_3} < \tau_{diss} \sim \theta \]

- **Relaxation steps:**
  - **Rapid stage:**
    - Equilibration of translational and rotational modes
    - Establishment of non-equilibrium vibrational distributions with different temperatures in each CO$_2$ mode due to intra-mode $VV_m$ exchanges
    - Equalizing of temperatures $T_1$ and $T_2$ due to rapid $VV'_1-2$ exchange ⇒ Reducing of symmetric and bending CO$_2$ modes to a single combined mode with temperature $T_{12}$
  - **Slow stage:**
    - Thermal equilibration due to $VT_m$ and inter-mode $VV'_2-3$, $VV'_1-2-3$ exchanges
    - Chemical equilibration as a result of dissociation coupled to $VV'$ and VT transitions
• **Macroscopic parameters:**
  • \( n_c(r, t), \ c = 1, 2, 3 \) – chemical species number densities
  • \( v(r, t) \) – macroscopic flow velocity
  • \( T(r, t) \) – gas temperature
  • \( T_{12}(r, t) \) – vibrational temperature of the combined CO\(_2\) mode
  • \( T_3(r, t) \) – temperature of the asymmetric CO\(_2\) mode

• **Vibrational distributions:**
  • Non-equilibrium Boltzmann distribution with temperature \( T_{12} \) in the combined CO\(_2\) mode
  • Non-equilibrium Boltzmann distribution with temperature \( T_3 \) in the asymmetric CO\(_2\) mode
  • Thermal equilibrium Boltzmann distribution in CO

• **Governing equations:**
  • Conservation equations for \( \rho, v, T \)
  • Equations of 3-temperature chemical kinetics for \( n_c \)
  • Relaxation equations for \( T_{12}, T_3 \)
Transport terms:

- Pressure tensor: \( P = (p - p_{\text{rel}})I - 2\eta \nabla \cdot \mathbf{v}l \)
- Diffusion velocity: \( \mathbf{V}_c = -\sum_d D_{cd} \mathbf{d}_d - D_{Tc} \nabla \ln T \)
- Total heat flux:
  \[
  \mathbf{q} = -\lambda \nabla T - \lambda_{vibr,12} \nabla T_{12} - \lambda_{vibr,3} \nabla T_3 - p \sum_c D_{Tc} \mathbf{d}_c + \sum_c \rho_c h_c \mathbf{V}_c
  \]
- Vibrational energy flux in the combined mode:
  \( \mathbf{q}_{12} = -\lambda_{vibr,12} \nabla T_{12} \)
- Vibrational energy flux in the asymmetric mode:
  \( \mathbf{q}_3 = -\lambda_{vibr,3} \nabla T_3 \)
Transport coefficients

- Heat conductivity coefficients: $\lambda = \lambda_{tr} + \lambda_{rot} + \lambda_{vibr}$, is the thermal conductivity coefficient of all degrees of freedom which occur in local thermal equilibrium. They include the translational and rotational modes as well as CO vibrational degrees of freedom. Thus the coefficient $\lambda_{vibr} = \lambda_{vibr, CO}$

- $\lambda_{vibr, 12}$ is the vibrational heat conductivity of the combined CO$_2$ mode

- $\lambda_{vibr, 3}$ is the vibrational heat conductivity of the asymmetric CO$_2$ mode

- Bulk viscosity coefficient $\zeta = \zeta_{rot, CO_2} + \zeta_{int, CO}$

- Relaxation pressure $p_{rel} = p_{rel}^{rot, CO_2} + p_{rel}^{int, CO}$
Model validation

![Graph showing experimental results and correlation formula for thermal equilibrium heat conductivity coefficients of CO₂ as functions of T.](image)

**Experimental results**
- [Gupta, Saxena]
- [Vargaftick]

**Correlation formula**
- [Vesovic et al]

*Figure:* Thermal equilibrium heat conductivity coefficients of CO₂ as functions of T.
**Model validation**

![Graph showing shear and bulk viscosity coefficients of CO₂ as functions of T.]  

**viscosity \cdot 10^6, Pa \cdot s**

**Correlation formula**  
- [Vesovic et al]

**Experimental results**  
- [Touloukian]
- [Weast]

**Figure:** Shear and bulk viscosity coefficients of CO₂ as functions of T.
Figure: Vibrational thermal conductivity coefficients of CO$_2$ as functions of $T$. Solid lines: $\lambda_{vibr,12}(T, T_{12})$; dashed lines: $\lambda_{vibr,3}(T, T_{3})$. 
Multi-temperature models:

- Intermediate between state-to-state and one-temperature models
  - Simpler than state-to-state approach
  - More rigorous compared to the one-temperature model
  - Suitable for engineering applications

- Allow for accounting for real gas effects
  - Different rates of vibrational energy exchanges
  - Coupling of vibrational relaxation and chemical reactions
  - Non-Boltzmann vibrational distributions
  - Complex structure of polyatomic molecules
**Heat transfer in non-equilibrium flows**

The developed methods have been applied for the evaluation of the heat transfer in real gas flows with VV, VT transitions, dissociation, recombination, and exchange reactions

- Behind strong shock waves
- In expanding flows
- In the vicinity of the stagnation point of a reentering body

**Steps**

- Numerical solution of simplified governing equations (in the Euler approximation or using simplified transport coefficients); evaluation of vibrational distributions and macroscopic parameters
- Calculation of transport coefficients and heat fluxes

**Main objective:** estimation of the contribution of various dissipative processes to the heat transfer
Shock wave
$N_2/N; \ T_0 = 293 \text{ K}, \ p_0 = 100 \text{ Pa}, \ M_0 = 15$

Figure: Contribution of various processes to the heat flux
Shock wave

- There is a strong competition between heat conduction and diffusion processes
  - Heat conduction tends to increase the heat flux
  - Diffusion compensates the effect of the heat conduction
- Role of thermal diffusion is weak
- Diffusion of vibrational energy is of great importance in the beginning of the relaxation zone, where vibrational distributions are far from the equilibrium ones
- State-to-state approach is necessary to get a satisfactory accuracy
Expanding flow
$N_2/N; 21^\circ, T_\ast = 7000 \text{ K}, p_\ast = 100 \text{ atm}$

Figure: Contribution of various processes to the heat flux
Expanding flow

- Contributions of heat conduction and diffusion processes are of the same sign.
- Heat conduction is more important in the vicinity of the throat.
- Contribution of thermal diffusion is negative and rather weak.
- Diffusion of vibrational energy influences weakly the total heat flux due to the rapid freezing of vibrational degrees of freedom; the role of this process is noticeable only near the throat (about 10%).
- Multi-temperature approaches are suitable for a correct prediction of the heat transfer.
Stagnation line problem (results by Dr. I. Armenise, Bari University)
5-component air mixture; $T_e = 7000 \text{ K}$, $P_e = 1000 \text{ N/m}^2$, $T_w = 1000 \text{ K}$; catalytic $\text{SiO}_2$ surface; state-to-state model

Figure: Contribution of various processes to the heat flux
Stagnation line problem in air

- For a non-catalytic surface, heat conduction dominates; the heat flux is determined by the Fourier part.
- For a catalytic surface, heat conduction and diffusion are of the same order in the vicinity of the stagnation point; at the external edge diffusion processes prevail.
- Contribution of thermal diffusion is weak at the external edge and cannot be neglected near the surface.
- The role of diffusion of vibrational energy is weak in the conditions considered.
Stagnation line (jointly with Von Karman Institute)

CO\(_2\)/CO/O\(_2\)/O/C mixture; \(p_e = 7000\) Pa; \(h_e = 14.53\) MJ/kg, 
\(T_e = 5909\) K; completely catalytic surface; 
thermal equilibrium conditions (one-temperature model)

**Figure:** Contribution of various processes to the heat flux
Stagnation line problem in CO$_2$

- There is a competition between mass diffusion and thermal diffusion processes. Thermal diffusion tends to reduce the absolute value of the heat flux, its contribution appears to be noticeable near the surface (more than 10%).
- The contribution of diffusion processes exceeds the one of heat conduction; it is a consequence of the surface catalycity.
- The influence of internal degrees of freedom is significant (about 20%) close to the surface, where the concentration of CO$_2$ molecules is high. Close to the outer edge, the role of internal modes is practically negligible. The effect of anharmonicity on the heat flux does not exceed 1% for the test case considered.
Conclusions

• In the general case, the heat flux is constituted of the contribution of several dissipative processes:
  • Heat conduction (HC)
  • Mass diffusion (MD)
  • Thermal diffusion (TD)
  • Diffusion of vibrational energy (DVE)

• In real gas flows there is a competition between dissipative processes; the type of competition depends on the flow

• Value of DVE flux shows
  • The importance of vibrational excitation and state-to-state distributions for the evaluation of the heat transfer
  • The influence of state-to-state vibrational distributions on the heat transfer is significant if the distributions are essentially non-Boltzmann at the low levels (shock heated gases)
  • When vibrational distributions at the low levels are close to the quasi-stationary ones, DVE can be simulated using multi-temperature models (expanding flows)
Conclusions

• Several approaches in the transport kinetic theory accounting for strong departures from equilibrium are elaborated:
  • State-to-state model for reacting mixtures
  • One-temperature model
  • Multi-temperature models for diatomic and polyatomic gas mixtures

• State-to-state model is the most detailed but complex:
  • Accounts for the complete coupling of state-to-state vibration-chemical kinetics, gas dynamics and transport
  • Too heavy for polyatomic gases

• One-temperature model is the most simple but rough:
  • Simple and time saving transport algorithms
  • Does not account for vibrational non-equilibrium and different rates of internal energy exchanges

• Multi temperature models are intermediate between state-to-state and one-temperature approaches
  • Have reasonable accuracy; suitable for engineering applications
  • Account for vibrational excitation, different rates of internal energy exchanges, complex structure of polyatomic molecules
  • Reduced number of transport coefficients and order of transport systems compared to the state-to-state model
  • Can be based on non-Boltzmann vibrational distributions
Perspectives

- Implementation of rigorous transport theory approaches to the CFD codes for the simulation of non-equilibrium viscous flows

- Elaboration of simplified models keeping the advantages of the state-to-state approach and satisfying feasibility requirements