

Kinetic relaxation models for reacting gas mixtures

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Outline

1 BGK Models for reacting gas mixtures

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- 3 ES-BGK model for a binary mixture

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- The **nonlinear Boltzmann equation** is an optimal tool of investigation for many gas dynamic regimes
- **Relaxation models of BGK type** are flexible and reliable kinetic approximations: based on much simpler collision operators, they retain the essential features of the Boltzmann equation (conservation laws, collision equilibria, *H*-theorem)
- In spite of severe basic difficulties, standard BGK approaches can be extended to **polyatomic molecules, gas mixtures, reactive flows** (Andries–Aoki–Perthame 2002, G.–Spiga 2004, Bisi–G.–Spiga 2009, Bisi–Caceres 2014), including the simple bimolecular reaction



Reactive Boltzmann equations

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- Seven conservation laws

$$\int (Q_i + Q_j) d\mathbf{v} = 0, \quad (i, j) = (1, 3), (1, 4), (2, 4),$$

$$\sum_{i=1}^4 \int m_i \mathbf{v} Q_i d\mathbf{v} = 0, \quad \sum_{i=1}^4 \int \left(\frac{1}{2} m_i v^2 + E_i \right) Q_i d\mathbf{v} = 0.$$

- Seven parameter family of collision equilibria

$$M_i(\mathbf{v}) = n_i \left(\frac{m_i}{2\pi KT} \right)^{3/2} \exp \left(- \frac{m_i}{2KT} (\mathbf{v} - \mathbf{u})^2 \right) \quad i = 1, \dots, 4$$

with number densities related by the mass action law

$$\frac{n_1 n_2}{n_3 n_4} = \left(\frac{m_1 m_2}{m_3 m_4} \right)^{3/2} \exp \left(\frac{\Delta E}{KT} \right), \quad \Delta E = E_3 + E_4 - E_1 - E_2$$

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- H -theorem in terms of the reactive entropy functional

$$H = \sum_{i=1}^4 \int f_i \log \left(f_i / m_i^3 \right) d\mathbf{v}.$$

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$$\mathcal{M}_i(\mathbf{v}) = \tilde{n}_i \left(\frac{m_i}{2\pi K \tilde{T}_i} \right)^{3/2} \exp \left(- \frac{m_i}{2K \tilde{T}_i} (\mathbf{v} - \tilde{\mathbf{u}}_i)^2 \right)$$

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- Auxiliary parameters $\tilde{n}_i, \tilde{\mathbf{u}}_i, \tilde{T}_i$ are determined by imposing that reactive Boltzmann and BGK equations prescribe the **same exchange rates for species densities, mass velocities and temperatures** (chemical exchange rates can be made explicit only under simplifying assumptions: Maxwell molecules, slow reaction) (G-Spiga 2004)

A different reactive BGK relaxation model (Bisi-G.-Spiga 2010)

- BGK collision terms

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- Auxiliary parameters $\bar{n}_i, \bar{\mathbf{u}}, \bar{T}$ are determined by imposing that reactive Boltzmann and BGK equations prescribe the **same collision invariants** (7 conditions) and the **mass action law** at equilibrium.

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- **DRAWBACK**: both models fail in quantitatively reproducing the proper transport coefficients in the asymptotic continuum limit

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$$x(0) = \tilde{x}, \quad f(x, v, 0) = f_0(x, v) \quad t \geq 0, \quad x, v \in \mathbb{R}.$$

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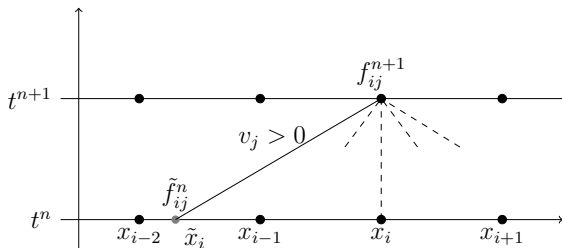
- Semi-lagrangian treatment of the convective part **avoids the classical CFL stability restriction.**

Implicit first order Semi-lagrangian scheme

Let $f_{ij}^n \approx f(x_i, v_j, t^n)$ be the approximate solution.
Possible stiffness (small ϵ) \Rightarrow implicit formulation.

$$f_{ij}^{n+1} = \tilde{f}_{ij}^n + \frac{\Delta t}{\epsilon} (M_{ij}^{n+1} - f_{ij}^{n+1}). \quad (1)$$

Here $\tilde{f}_{ij}^n = f(t^n, \tilde{x}_i = x_i - v_j \Delta t, v_j)$ can be calculated by (linear) interpolation from $\{f_j^n\}$.



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$$\langle f_{ij}^{n+1} \phi \rangle = \langle \tilde{f}_{ij}^n \phi \rangle + \frac{\Delta t}{\epsilon} \langle (M_{ij}^{n+1} - f_{ij}^{n+1}) \phi \rangle.$$

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From the conservation, we have

$$\langle (M_{ij}^{n+1} - f_{ij}^{n+1}) \phi \rangle = 0 \quad \Rightarrow \quad \langle f_{ij}^{n+1} \phi \rangle = \langle \tilde{f}_{ij}^n \phi \rangle$$

Hence we immediately find the macroscopic variables ρ_i^{n+1} , u_i^{n+1} and T_i^{n+1} corresponding to f_{ij}^{n+1} using \tilde{f}_{ij}^n and with these values the approximated Maxwellian is updated.

Higher order: RK and BDF schemes (G.-Russo-Stracquadanio 2014)

- **L- stable Diagonally implicit Runge-Kutta schemes (DIRK)** of order 2 and 3 have been considered to obtain high order in time, providing the correct fluid dynamic limit (Russo - Santagati 2011)
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$$f_{ij}^{n+1} = \frac{4}{3} f_{ij}^{(1)n} - \frac{1}{3} f_{ij}^{(2)n-1} + \frac{\Delta t}{\epsilon} (M_{ij}^{n+1} - f_{ij}^{n+1}) \quad (\text{BDF2})$$

$$f_{ij}^{n+1} = \frac{18}{11} f_{ij}^{(1)n} - \frac{9}{11} f_{ij}^{(2)n-1} + \frac{2}{11} f_{ij}^{(3)n-2} + \frac{\Delta t}{\epsilon} (M_{ij}^{n+1} - f_{ij}^{n+1}) \quad (\text{BDF3})$$

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$f_{ij}^{(s)n} = f^n(x_i - sv_j \Delta t, v_j)$, $s = 1, 2, 3$, obtained by interpolation. High order in space is obtained by **WENO reconstruction** (Carlini-Ferretti-Russo 2005).

Example: RK2 and BDF2

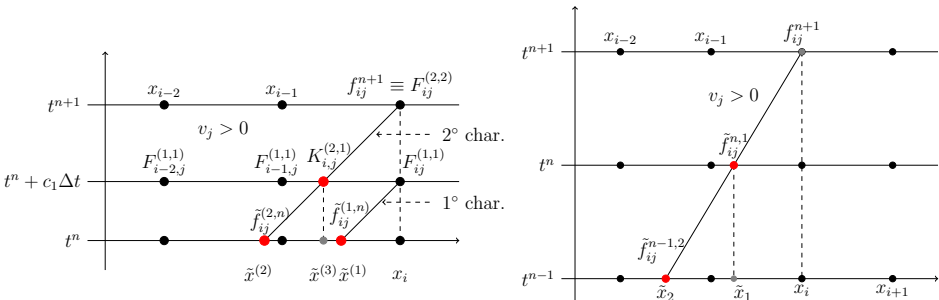


Figure: Left RK2, right BDF2. Interpolation is needed in red circles.

Remarks

- These high order semi-Lagrangian methods for the classical 1-D BGK equation, based on both DIRK and BDF schemes for time integration, have been successfully extended to
 - 3-D in velocity problems (Chu reduction)
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- The computational cost can be further reduced by developing variants that avoid interpolation and allow larger time steps
- These schemes are asymptotic preserving, namely able to capture the fluid dynamic limit

Numerical Test - Reactive BGK equations I

We considered a mixture of four gases with the following values of the molecular masses:

$$m_1 = 58.5, \quad m_2 = 18, \quad m_3 = 40, \quad m_4 = 36.5.$$

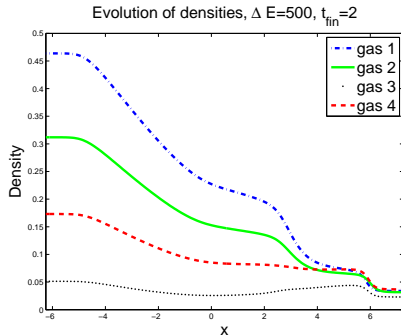
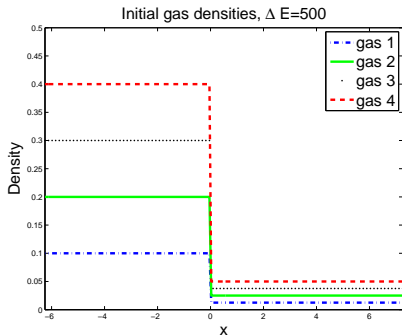
As initial data we have chosen Maxwellian reproducing the following moments (Riemann problem):

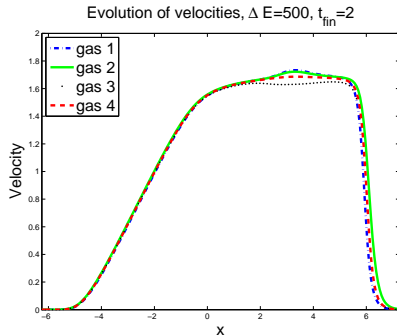
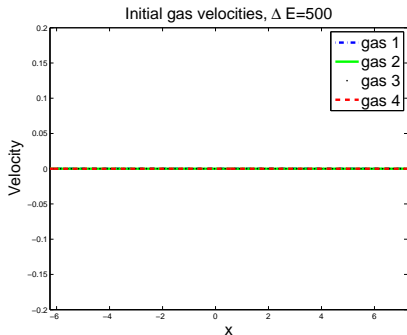
$$(\rho_0, u_0, p_0) = \begin{cases} (1, 0, 5/3), & x < 0.5, \\ (1/8, 0, 1/6), & x > 0.5, \end{cases}$$

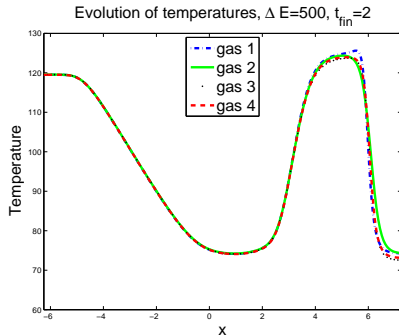
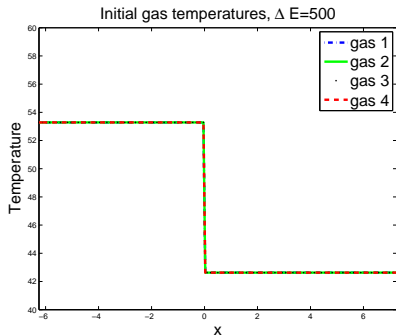
$$(\rho_{01}, \rho_{02}, \rho_{03}, \rho_{04}) = \begin{cases} (1/10, 2/10, 3/10, 4/10), & x < 0.5, \\ (1/80, 2/80, 3/80, 4/80), & x > 0.5, \end{cases},$$

$$u_{0i} = 0, \quad i = 1, \dots, 4.$$

Results obtained with the BDF2 scheme.

Evolution of densities, $\epsilon \sim 10^{-2}$ 

Evolution of velocities, $\epsilon \sim 10^{-2}$ 

Evolution of temperatures, $\epsilon \sim 10^{-2}$ 

ES-BGK models

- The **ellipsoidal BGK (ES-BGK) models** (Holway 1966, Andries et al. 2000, Brull–Schneider 2008) are devised to correctly reproduce transport coefficients: fundamental moments are bound to relax to equilibrium at a faster rate than the distribution function, allowing to fit transport coefficients from Chapman Enskog expansion in terms of the additional relaxation parameters

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- Recent substantial breakthrough in the **extension of ES–BGK models to inert gas mixtures** by Brull, Pavan, Schneider 2012: correct $N \times N$ Fick diffusion matrix, preserving positivity and consistency constraints, obtained by requiring equalization of species velocities ($N - 1$ additional relaxation parameters)

ES-BGK model for a binary inert mixture (G.-Monica-Spiga 2011)

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- ES-BGK collision operator: $\hat{Q}_i = \nu(G_i - f_i)$

$$G_i[f_1, f_2](\mathbf{v}) = n_i \left(\frac{m_i}{2\pi T^*} \right)^{\frac{3}{2}} \exp \left[-\frac{m_i}{2T^*} (\mathbf{v} - \mathbf{u}_i^*)^2 \right], \quad i = 1, 2$$

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Theorem

The pair (G_1, G_2) is the minimizer of the entropy

$$\mathcal{H}[f_1, f_2] = \sum_{i=1}^2 \int_{\mathbb{R}^3} (f_i \log f_i - f_i) d_3\mathbf{v}$$

in the class of distribution functions for which the ES-BGK operator \hat{Q}_i fulfils the conservation laws, drift velocities equalize with inverse relaxation times η , and species temperatures are equal.

Properties of the ES-BGK model

- Auxiliary fields \mathbf{u}_i^* , T^* determined in terms of the actual velocities \mathbf{u}_i and gas temperature T : $\mathbf{u}^{(G)} = \mathbf{u}$, $T^{(G)} = T$

$$\nu [(\mathbf{u}_1^* - \mathbf{u}_1) + (\mathbf{u}_2^* - \mathbf{u}_2)] = -\eta(\mathbf{u}_1 - \mathbf{u}_2)$$

from which

$$\mathbf{u}_i^* = \left(1 - \frac{\eta}{\nu}\right)\mathbf{u}_i + \frac{\eta}{\nu}\mathbf{u}$$

$$nKT^* = \sum_{i=1}^2 n_i K T_i + \frac{\eta}{3\nu} \left(2 - \frac{\eta}{\nu}\right) \sum_{i=1}^2 \rho_i (\mathbf{u}_i - \mathbf{u})^2$$

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- The ES-BGK model satisfies an H-theorem in terms of the Boltzmann H functional $\mathcal{H}[f_1, f_2]$
- Collision equilibria are Maxwellian distribution functions at common mean velocity and temperature

Asymptotic Chapman Enskog analysis

In the hydrodynamic limit w.r.t. the Knudsen number ε , two transport coefficients can be quantitatively fitted at leading order $O(\varepsilon)$, allowing to correctly reproduce the

Fick diffusion law

$$\mathbf{u}_j - \mathbf{u} = - \sum_{j=1}^2 D_{ij} \nabla n_j$$

$$D_{11} = \frac{\varepsilon}{\eta} \frac{KT}{\rho} \frac{\rho_2}{\rho_1}, \quad D_{12} = D_{21}, \quad \sum_{j=1}^2 D_{ij} \rho_j = 0$$

and the Newton law

$$\mathbf{P} = nKT\mathbf{I} - \mu \left(\nabla \mathbf{u} + \nabla \mathbf{u}^T - \frac{2}{3} \nabla \cdot \mathbf{u} \mathbf{I} \right), \quad \mu = \frac{\varepsilon}{\nu} nKT$$

but only qualitatively the Fourier conduction law (and also Soret and Dufour effects)

Reactive ES-BGK model (G.-Spiga 2014)

- A_2 excited state of species A_1 , with energy of chemical bond E ; common mass m
- Irreversible binary slow reaction (de-excitation process)



- Scaled reactive ES-BGK equations (dimensionless)

$$\frac{\partial f_i}{\partial t} + \mathbf{v} \cdot \nabla f_i = \frac{\nu}{\varepsilon} (G_i[f_1, f_2] - f_i) + J_i[f_1, f_2], \quad i = 1, 2$$

J_i chemical collision operator (Boltzmann-type, five-fold integral)

Weak form for any pair of smooth test functions $\varphi_i(\mathbf{v})$

$$\begin{aligned} & \sum_{i=1}^2 \int \varphi_i(\mathbf{v}) J_i[f_1, f_2](\mathbf{v}) d_3\mathbf{v} = \\ & = \iiint g \sigma_{21}^{11}(g, \chi) [\varphi_1(\mathbf{v}_{21}^{11}) + \varphi_1(\mathbf{w}_{21}^{11}) - \varphi_2(\mathbf{v}) - \varphi_1(\mathbf{w})] f_2(\mathbf{v}) f_1(\mathbf{w}) d\mathbf{v} d\mathbf{w} d\hat{n}' \\ & + \iiint g \sigma_{22}^{12}(g, \chi) [\varphi_1(\mathbf{v}_{22}^{12}) + \varphi_2(\mathbf{w}_{22}^{12}) - \varphi_2(\mathbf{v}) - \varphi_2(\mathbf{w})] f_2(\mathbf{v}) f_1(\mathbf{w}) d\mathbf{v} d\mathbf{w} d\hat{n}' \end{aligned}$$

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post-collisional velocities

$$\mathbf{v}_{ij}^{hk} = \frac{1}{2} \left(\mathbf{v} + \mathbf{w} + g_{ij}^{hk} \hat{n}' \right) \quad \mathbf{w}_{ij}^{hk} = \frac{1}{2} \left(\mathbf{v} + \mathbf{w} - g_{ij}^{hk} \hat{n}' \right)$$

$$g_{21}^{11} = g_{22}^{12} = g_+ = \left(g^2 + \frac{4E}{m} \right)^{\frac{1}{2}}$$

- Collision invariants for the whole ES-BGK collision operator $\hat{Q}_i + J_i$

$$(1, 1) \quad (m\mathbf{v}, m\mathbf{v}) \quad \left(\frac{1}{2}mv^2, \frac{1}{2}mv^2 + E \right)$$

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- Collision equilibrium

$$f_1^{eq}(\mathbf{v}) = n \left(\frac{m}{2\pi T}\right)^{\frac{3}{2}} \exp\left[-\frac{m}{2T}(\mathbf{v} - \mathbf{u})^2\right], \quad f_2^{eq}(\mathbf{v}) = 0$$

- Five exact but not closed macroscopic conservation equations for number density n , momentum $\rho\mathbf{u}$ and total energy $\frac{1}{2}\rho u^2 + \frac{3}{2}nT + n_2E$

Macroscopic equations

The **hydrodynamic limit** for $\varepsilon \rightarrow 0$ by a Chapman-Enskog asymptotic expansion up to the **Navier-Stokes level** requires **invariants of the dominant operator** \hat{Q} alone (all species densities, momentum, and kinetic energy), whose equilibria are Maxwellians with free densities and temperature.

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Macroscopic “conservation” equations

$$\frac{\partial n}{\partial t} + \nabla \cdot (n\mathbf{u}) = 0$$

$$\frac{\partial}{\partial t}(\rho\mathbf{u}) + \nabla \cdot (\rho\mathbf{u} \otimes \mathbf{u}) + \nabla(nT) + \nabla \cdot \mathbf{\Pi} = \mathbf{0}$$

$$\frac{\partial}{\partial t} \left(\frac{1}{2}\rho u^2 + \frac{3}{2}nT + En_2 \right) + \nabla \cdot \left[\left(\frac{1}{2}\rho u^2 + \frac{5}{2}nT + En_2 \right) \mathbf{u} + \mathbf{\Pi} \cdot \mathbf{u} + \mathbf{q} + En_2(\mathbf{u}_2 - \mathbf{u}) \right] = 0$$

$$\frac{\partial n_2}{\partial t} + \nabla \cdot (n_2\mathbf{u}) = -\nabla \cdot [n_2(\mathbf{u}_2 - \mathbf{u})] - \sum_{j=1}^2 S_{2j}$$

Asymptotic expansion

- Presence of inhomogeneous terms S_{2j} (reactive rates), contributed by the slow process and vanishing at chemical equilibrium

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with n_1, n_2, \mathbf{u}, T unexpanded, and with

$$\mathbf{u}_i = \mathbf{u} + \varepsilon \mathbf{u}_i^{(1)}, \quad T_i = T + \varepsilon T_i^{(1)}, \quad S_{2j} = S_{2j}^{(0)} + \varepsilon S_{2j}^{(1)}$$

subject to constraints

$$\sum_{i=1}^2 \rho_i \mathbf{u}_i^{(1)} = \mathbf{0}, \quad \sum_{i=1}^2 n_i T_i^{(1)} = 0$$

Leading term

$$f_i^{(0)} = f_i^M(\mathbf{v}) = n_i \left(\frac{m_i}{2\pi T} \right)^{3/2} \exp \left(- \frac{m}{2T} (\mathbf{v} - \mathbf{u})^2 \right) \quad i = 1, 2$$

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$$S_{2j}^{(0)} = n_2 n_j \left(\frac{m}{2\pi T} \right)^3 \iint g \sigma_{2j}^{ch}(g) \exp \left[- \frac{m}{2T} (v^2 + w^2) \right] d\mathbf{v} d\mathbf{w}$$

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First order correction

$$f_i^\varepsilon = G_i[f_1^\varepsilon, f_2^\varepsilon] - \frac{\varepsilon}{\nu} \left(\frac{\partial f_i^M}{\partial t} + \mathbf{v} \cdot \nabla f_i^M \right) + \frac{\varepsilon}{\nu} J_i[f_1^M, f_2^M] + O(\varepsilon^2)$$

with $J_i[f_1^M, f_2^M] = J_i^{CH(0)}$ explicit (but complicated) functions of the hydrodynamic variables, **isotropic in $\mathbf{c} = \mathbf{v} - \mathbf{u}$**

First order correction - II

- Time derivatives of Maxwellians may be eliminated through "conservation" equations

$$\frac{\partial f_i^M}{\partial t} + \mathbf{v} \cdot \nabla f_i^M = \left(\frac{Df_i^M}{Dt} \right)_{ME} + \left(\frac{Df_i^M}{Dt} \right)_{CH} \quad (2)$$

Mechanical contribution is orthogonal to any isotropic function of \mathbf{c}
 Chemical contribution is isotropic w.r.t. \mathbf{c}

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- Ellipsoidal terms

$$G_i[f_1^\varepsilon, f_2^\varepsilon] = f_i^M(\mathbf{v}) + \varepsilon f_i^M(\mathbf{v}) \frac{m}{T} \left(1 - \frac{\eta}{\nu} \right) \mathbf{u}_i^{(1)} \cdot \mathbf{c} + O(\varepsilon^2)$$

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- First order distribution functions

$$f_i^{(1)}(\mathbf{v}) = f_i^M(\mathbf{v}) \psi_i(\mathbf{v}) = f_i^M(\mathbf{v}) \left[\psi_i^{ME}(\mathbf{v}) + \psi_i^{CH}(\mathbf{v}) \right]$$

with again mechanical contribution orthogonal to isotropic functions of \mathbf{c} and chemical contribution isotropic in \mathbf{c}

First order correction - III

- Re-computation of $\mathbf{u}_i^{(1)}$ by integration leads to Fick law

$$\mathbf{u}_1^{(1)} = -\frac{1}{\eta} \frac{T}{\rho} \frac{n_2}{n_1} \nabla n_1 + \frac{1}{\eta} \frac{T}{\rho} \nabla n_2$$

$$\mathbf{u}_2^{(1)} = \frac{1}{\eta} \frac{T}{\rho} \nabla n_1 - \frac{1}{\eta} \frac{T}{\rho} \frac{n_1}{n_2} \nabla n_2$$

No thermal diffusion (Soret effect) because of the equal masses

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No thermal diffusion (Soret effect) because of the equal masses

- Diffusion velocities do not depend on the chemical reaction, due to isotropy arguments
- Moreover, chemical contributions do not affect viscous stress and heat flux ($O(\varepsilon)$ terms), that remain the same as for the inert case
- Conversely, elastic collisions do not affect the chemical terms at Navier-Stokes level

Navier-Stokes equations

$$\frac{\partial n}{\partial t} + \nabla \cdot (n\mathbf{u}) = 0$$

$$\frac{\partial(\rho\mathbf{u})}{\partial t} + \nabla \cdot (\rho\mathbf{u} \otimes \mathbf{u}) + \nabla(nT) = -\varepsilon \nabla \cdot \mathbf{\Pi}^{(1)}$$

$$\begin{aligned} & \frac{\partial}{\partial t} \left(\frac{1}{2} \rho u^2 + \frac{3}{2} nT + En_2 \right) + \nabla \cdot \left[\left(\frac{1}{2} \rho u^2 + \frac{5}{2} nT + En_2 \right) \mathbf{u} \right] \\ & = -\varepsilon \nabla \cdot \left(\mathbf{\Pi}^{(1)} \cdot \mathbf{u} + \mathbf{q}^{(1)} + En_2 \mathbf{u}_2^{(1)} \right) \end{aligned}$$

$$\frac{\partial n_2}{\partial t} + \nabla \cdot (n_2 \mathbf{u}) + \sum_{j=1}^2 S_{2j}^{(0)} = -\varepsilon \nabla \cdot (n_2 \mathbf{u}_2^{(1)}) - \varepsilon \sum_{j=1}^2 S_{2j}^{(1)}$$

Navier-Stokes equations

- Newton law

$$\mathbf{\Pi}^{(1)} = -\frac{1}{\nu} n T \left(\nabla \mathbf{u} + (\nabla \mathbf{u})^T - \frac{2}{3} \nabla \cdot \mathbf{u} \mathbf{I} \right)$$

viscosity $\frac{\varepsilon}{\nu} n T$

- Fourier law

$$\mathbf{q}^{(1)} = -\frac{1}{\nu} \frac{5}{2} \frac{n T}{m} \nabla T$$

thermal conductivity $\frac{\varepsilon}{\nu} \frac{5}{2} \frac{n T}{m}$

no Dufour effect since masses are equal

- Elastic collisions do not affect the chemical source terms $S_{2j}^{(1)}$ of the reactive Navier-Stokes equations

Concluding Remarks

- Same mechanical constitutive equations of the corresponding inert gas mixture, since the evolution is driven by elastic collisions
- Chemical source terms are $O(1)$ and are independent from the mechanical parameters
- The relaxation parameter η may be used to fit exactly the Fick diffusion matrix
- The parameter ν may be used to fit either viscosity or thermal conductivity, but not both coefficients simultaneously

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- The relaxation parameter η may be used to fit exactly the Fick diffusion matrix
- The parameter ν may be used to fit either viscosity or thermal conductivity, but not both coefficients simultaneously
- Future works:
 - introduction of a further relaxation parameter to control the Prandtl number
 - extension of the high order semi-Lagrangian methods to ES-BGK models