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Srboljub Simić, Milana Pavić-Čolić
and Damir Madjarević

Non-equilibrium mixtures of gases: modelling and computation

Abstract. These notes present the material about the modelling of non-equilibrium processes in mixtures of gases. It is mainly concerned with the mixtures described within the context of extended thermodynamics, but also covers certain features of the kinetic theory of mixtures. General introduction puts extended thermodynamics into a proper position with respect to the other approaches (TIP and kinetic theory of gases). Extended thermodynamics of multi-temperature mixtures of Euler fluids is properly established and analyzed. Shock waves as a particular non-equilibrium problem are thoroughly discussed. The kinetic modeling of mixtures is also discussed and related to the results of extended thermodynamics. The notes contain new results related to the comparison of extended thermodynamic model of mixtures with the Maxwell-Stefan diffusion model, and the shock structure analysis in the viscous multi-temperature model.

Keywords. Mixtures of gases, extended thermodynamics, kinetic theory of mixtures, diffusion, shock waves.

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Contents

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1 - Introduction

Mixtures of gases are ubiquitous. We are surrounded by them in everyday life, use them in science and technology and need them to control their behaviour in different environments and physico-chemical situations. Although we are aware of their presence, it is not uncommon to treat them in a simplified manner, as simple gases with the properties which reflect corresponding properties of the constituents in the average sense. However, contemporary applications are rather demanding and require deeper knowledge of the processes in which the mixtures are involved, proper modelling and reliable simulations. This wide spectrum of problems cannot be approached by a unique theory. Consequently, there are different approaches to mixtures, more or less interconnected, which treat them at different scales and different levels of accuracy.

These notes are intended to give an account on the recent research directed towards one particular model of gaseous mixtures – the multi-temperature model. This model is developed within the theoretical framework given by *extended thermodynamics* [**60**]. It is a macroscopic theory which presents a bridge between the classical continuum theories, like thermodynamics of irreversible processes (TIP) [**25**], and the kinetic theory of gases as a mesoscopic theory [**22**]. The model goes deeper than the classical continuum approach by extending the list of state variables. On the other hand, it provides an information about the non-equilibrium processes coarser than kinetic theory, but still valuable in the sense of accuracy. Being somewhere in between could be comfortable, but not always pleasant: at least at the beginning there will always be more people who support traditional approaches than the ones who take the challenge and proceed along the new path. This account is an outcome of our intention to expose the extended thermodynamics of mixtures, in all its beauty, to a wider audience.

The paper is organized as follows. Section 2 contains a brief review of continuum and kinetic modelling of gases. Although the material about classical continuum models and the Boltzmann equation is well-known, it will help to put our main tool, the extended thermodynamics, into a proper perspective. Namely, it “borrows” certain methods and structures from former approaches (entropy principle, moment equations), but also brings new tools (method of multipliers). In Section 3 the mixture theory is developed using the formalism of extended thermodynamics. A review of the classical mixture theory is given for completeness. Basic postulates, the so-called metaphysical principles, are elaborated and the method of multipliers is used in exploitation of the entropy inequality. Consequently, the closed set of governing equations is derived for the mixture of Euler fluids with multiple temperatures. Section 4 is devoted to a deeper analysis of multi-temperature mixtures. The notions of equilibrium and average temperature are defined, and the entropy and the dynamic pressure are carefully analyzed. Classical limit of the MT mixture is studied using the Maxwellian iteration – generalized Fick’s law of classical TIP is recovered and non-local equations for the temperatures of the constituents are derived. Also, the Maxwell-Stefan model of diffusion is reconsidered with the aim of comparison with extended models. This analysis reveals that certain classical models may be considered as truncated equations of extended models, and phenomenological coefficients of the latter ones can be calculated in such a way. In Section 5 the shock structure problem in a binary mixture is studied. The simplicity of the model permits the systematic analysis of the shock structure, in contrast to the numerical simulations based upon kinetic theory which represent a collection of limited number of particular cases. The influence of Mach number, equilibrium concentration and mass ratio of the constituents is analyzed. It is revealed that temperature overshoot of the heavier constituent depends non-monotonically on the mass ratio. This outstanding feature appears to be the consequence of the small amount of exchange of internal energy between the constituents. It is also shown that other dissipative mechanisms, like momentum and heat transfer due to viscosity and heat conductivity, cannot attenuate the temperature overshoot. Since the multi-temperature model is fully developed within the framework of extended thermodynamics at the Euler level, Section 6 is devoted to the delineation of the path which connects the kinetic theory of mixtures with it. It requires usual analysis of the kinetic theory itself, definition of corresponding macroscopic variables and a proper scaling of Boltzmann equations which will lead, in the first approximation, to the local Maxwellians with different velocities and temperatures of the constituents. The paper is concluded with final remarks indicating topics which remained outside the scope of these notes.

Remark about notation. In the following text we shall use both direct and index notation. Although it certainly makes the exposition incoherent, in certain situations it is much more convenient to use the direct notation, while other situations call for the use of index one.

2 - A review of continuum and kinetic modelling of gases

The modelling is the first issue which we shall focus on in the study of gases and their mixtures. The choice of the model depends on the level of accuracy desired in the study. Different modelling approaches rely on the different assumptions, usually depending on the scale on which the processes are described. Although they refer to different scales, different models can be interconnected in the asymptotic sense. The aim of this Section is to give a short review of the continuum and kinetic modelling of gases and provide a framework for subsequent study of the mixtures.

2.1 - *Classical continuum theories of fluids*

In continuum theories one describes a gas as a continuous medium. Its state is determined by the associated fields of the mass density $\rho \in \mathbb{R}^+$, the velocity $\mathbf{v} \in \mathbb{R}^3$ and the temperature $T \in \mathbb{R}^+$, termed *state variables*. The time rate of change of the state variables is determined by the *balance laws* of mass, momentum and energy [**41**]:

$$
\begin{aligned}
&\frac{\partial \rho}{\partial t} + \operatorname{div}(\rho \mathbf{v}) = 0,\\
&\frac{\partial(\rho \mathbf{v})}{\partial t} + \operatorname{div}(\rho \mathbf{v} \otimes \mathbf{v} - \mathbf{t}) = \mathbf{0},\\
&\frac{\partial\left(\frac{1}{2}\rho v^2 + \rho\varepsilon\right)}{\partial t} + \operatorname{div}\left\{\left(\frac{1}{2}\rho v^2 + \rho\varepsilon\right)\mathbf{v} - \mathbf{t}\mathbf{v} + \mathbf{q}\right\} = 0.
\end{aligned}
\tag{1}
$$

The balance laws have to be adjoined with the *constitutive relations* which provide a mathematical description of the material response by relating the internal energy density $\varepsilon \in \mathbb{R}$, the stress tensor $\mathbf{t} \in \mathbb{M}^{3\times 3}$ and the heat flux $\mathbf{q} \in \mathbb{R}^3$ to the basic fields ρ, $\mathbf{v}$ and T. These relations have to obey restrictions imposed by the material objectivity (independence of the observer) and the entropy principle. The simplest set of constitutive relations describe an ideal inviscid gas (Euler fluid):

$$
\varepsilon = \frac{k_B}{(\gamma - 1)m} T, \quad \mathbf{t} = -p\,\mathbf{I}, \quad p = \rho \frac{k_B}{m} T, \quad \mathbf{q} = \mathbf{0},
\tag{2}
$$

where m is the atomic mass, k_B the Boltzmann constant, γ the ratio of specific heats and p the pressure. In such a way one obtains the closed system of Euler gas dynamics equations.

Along with the balance laws and the constitutive relations, the entropy inequality presents the third important ingredient of continuum theories:

$$
\frac{\partial(\rho s)}{\partial t} + \operatorname{div}(\rho s \mathbf{v} + \boldsymbol{\Phi}) = \Sigma \geq 0,
\tag{3}
$$

where $s \in \mathbb{R}$ is the entropy density, $\boldsymbol{\Phi} \in \mathbb{R}^3$ is the non-convective entropy flux and $\Sigma \in \mathbb{R}$ is the entropy production. At first, it was used to determine the physically admissible processes for a given set of balance laws and constitutive relations. On the other hand, modern continuum theories [**23**] use it as a master equation which imposes thermodynamic restrictions on the constitutive relations, such that all thermodynamic processes are compatible with it. The second approach is exploited in thermodynamics of irreversible processes (TIP) to derive the constitutive relations of Navier-Stokes-Fourier type [**25**].

To get an appreciation of the way in which the entropy inequality is used in TIP, recall its basic assumptions: (a) every infinitesimal volume is considered to be in the state of *local thermodynamic equilibrium* and (b) the non-convective entropy flux is proportional to the heat flux. These assumptions come out from the classical equilibrium thermodynamics, the first one yielding the Gibbs' relation:

$$\mathrm{d}s = \frac{1}{T}\left(\mathrm{d}\varepsilon - \frac{p}{\rho^2}\mathrm{d}\rho\right), \quad \boldsymbol{\Phi} = \frac{\mathbf{q}}{T}. \tag{4}$$

Rewriting the balance laws (1) and Gibbs' relation $(4)_1$ using the material derivative $\mathrm{d}/\mathrm{d}t = \partial/\partial t + \mathbf{v}\cdot\nabla_{\mathbf{x}}$, one arrives at:

$$\begin{aligned}
&\frac{\mathrm{d}\rho}{\mathrm{d}t} + \rho\,\mathrm{div}\,\mathbf{v} = 0, \\
&\rho\frac{\mathrm{d}\mathbf{v}}{\mathrm{d}t} - \mathrm{div}\,\mathbf{t} = \mathbf{0}, \qquad\qquad \frac{\mathrm{d}s}{\mathrm{d}t} = \frac{1}{T}\left(\dot{\varepsilon} - \frac{p}{\rho^2}\dot{\rho}\right), \\
&\rho\frac{\mathrm{d}\varepsilon}{\mathrm{d}t} - \mathbf{t} : \mathrm{grad}\,\mathbf{v} + \mathrm{div}\,\mathbf{q} = 0,
\end{aligned}$$

where $\mathbf{A} : \mathbf{B} = \mathrm{tr}(\mathbf{AB})$. By combining them, one can recover the entropy inequality (3) in the form:

$$\rho\frac{\mathrm{d}s}{\mathrm{d}t} + \mathrm{div}\left(\frac{\mathbf{q}}{T}\right) = \Sigma \geq 0,$$

where the entropy production reads:

$$\Sigma = -\frac{1}{T^2}\mathbf{q}\cdot\mathrm{grad}\,T + \frac{1}{T}\mathbf{t}^D : \mathbf{D}^D + \frac{1}{T}\left(\frac{1}{3}\mathrm{tr}\,\mathbf{t} + p\right)\mathrm{div}\,\mathbf{v} \geq 0, \tag{5}$$

$\mathbf{t}^D$ and $\mathbf{D}^D$ being deviatoric parts of the stress tensor and the symmetrized velocity gradient:

$$\mathbf{t}^D = \mathbf{t} - \frac{1}{3}(\mathrm{tr}\,\mathbf{t})\mathbf{I}, \quad \mathbf{D} = \frac{1}{2}\left(\mathrm{grad}\,\mathbf{v} + (\mathrm{grad}\,\mathbf{v})^T\right), \quad \mathbf{D}^D = \mathbf{D} - \frac{1}{3}(\mathrm{tr}\,\mathbf{D})\mathbf{I}.$$

In TIP (5) is interpreted as the sum of the products of thermodynamic forces and thermodynamic fluxes. To secure the inequality for any thermodynamic process, TIP assumes linear relations between the forces and the fluxes of the same tensorial order, thus arriving at the quadratic form. In particular, the Navier-Stokes-Fourier constitutive relations are obtained for the heat flux, the stress tensor and the dynamic pressure π:

$$\mathbf{q} = -\kappa\,\mathrm{grad}\,T, \quad \mathbf{t}^D = 2\mu\,\mathbf{D}^D, \quad \pi = -\left(\frac{1}{3}\mathrm{tr}\,\mathbf{t} + p\right) = -\lambda\,\mathrm{div}\,\mathbf{v}, \tag{6}$$

where $\kappa \geq 0$, $\mu \geq 0$ and $\lambda \geq 0$ are the phenomenological coefficients which have the physical meaning of heat conductivity, shear viscosity and bulk viscosity, respectively.

This brief review reveals that modelling in the context of classical continuum theories comprises three basic ingredients: the balance laws, the constitutive relations and the entropy principle. The first presents the set of physical laws valid for any continuous media. The second one describes the response of specific materials while the third one imposes thermodynamic restrictions on the constitutive relations. As an outcome, the closed system of governing equations is obtained which describes the physically admissible thermodynamic processes.

One has to bear in mind that heat conductivity and viscosities are determined only up to the sign. No further information on them can be obtained within this framework, but rather brought from experimental evidence or some deeper theoretical insight going beneath the macroscopic level.

Another drawback comes from the particular structure of constitutive relations (6). To illustrate, we shall analyze two particular problems (see [**60**], Chapter 2, for details). First, consider the heat conduction through a rigid conductor at rest. Assume $\rho = \text{const.}$ and $\mathbf{v} = \mathbf{0}$, which turn the balance laws $(1)_{1,2}$ into identities, while the energy balance law $(1)_3$ together with the Fourier's law $(6)_1$ reduces to:

$$\frac{\partial T}{\partial t} = \frac{\kappa}{\rho \varepsilon_T} \Delta T, \tag{7}$$

$\varepsilon_T = \partial \varepsilon / \partial T$. Second, consider incompressible isothermal shear flow of a fluid described by $\rho = \text{const.}$, $T = \text{const.}$, $\mathbf{v} = (0, v(x_1, t), 0)$. This reduces the balance laws $(1)_{1,3}$ to identities, while the momentum balance law $(1)_2$ together with $(6)_2$ yields:

$$\frac{\partial v}{\partial t} = \frac{\mu}{\rho} \frac{\partial^2 v}{\partial x_1^2}. \tag{8}$$

Both equations, (7) and (8), share the same mathematical structure – they are parabolic and they predict the infinite speed of propagation of disturbances. Although this fact is overlooked in most engineering applications, it is nevertheless non-physical and requires a proper explanation. One possible way to do that is provided by the kinetic theory of gases.

2.2 - *Kinetic theory of monatomic gases*

Kinetic theory is concerned with modelling the gases through a large number of mutually interacting particles. Apart from classical treatises [**22, 45**], there are a lot of expositions of the subject ranging from (mostly) physical to mathematical aspects [**50, 37, 20, 82, 21, 77, 81**]. We shall give a superficial review of the topics which are of interest to our subject.

The phase space of particles includes the macroscopic variables, time $t \in [0, \infty)$ and position $\mathbf{x} \in \mathbb{R}^3$, as well as the microscopic ones. Therefore, it may be said that kinetic theory describes the gases at the mesoscopic level, in contrast to classical continuum theories which describe them at the macroscopic level. In the simplest case of single monatomic gas, whose particles are modelled as elastic spheres, the microscopic variables will be the velocities of particles $\xi \in \mathbb{R}^3$.

Particle interactions – *collisions* – are assumed to be binary (interaction of more than two particles at the same time is rare event) and elastic. The interaction time is assumed to be much shorter than the mean time of free flight between the collisions. Therefore, change of the state of particles is governed by the momentum and energy conservation laws for binary elastic collisions:

$$\begin{aligned} \xi' + \xi'_* &= \xi + \xi_*, \\ |\xi'|^2 + |\xi'_*|^2 &= |\xi|^2 + |\xi_*|^2, \end{aligned} \tag{9}$$

where (ξ, ξ_*) denote the velocities of outgoing particles, while (ξ', ξ'_*) are the velocities of incoming particles.

2.2.1 - The Boltzmann equation

The main tool in the analysis is the velocity distribution function $f := f(t, \mathbf{x}, \xi) \in \mathbb{R}^+$ which statistically describes the state of the gas. Actually, $f(t, \mathbf{x}, \xi)\, \mathrm{d}\mathbf{x}\, \mathrm{d}\xi$ determines the number of atoms in the infinitesimal volume $\mathrm{d}\mathbf{x}\, \mathrm{d}\xi$ in the phase space at time t. The time rate of change of the distribution function is determined by the Boltzmann equation:

$$\frac{\partial f}{\partial t} + \sum_{i=1}^{3} \xi_i \frac{\partial f}{\partial x_i} = Q(f,f), \tag{10}$$

where the collision integral $Q(f,f)$ determines the change of f due to mutual interaction of particles. It reads:

$$Q(f,f) = \int\limits_{\mathbb{R}^3} \int\limits_{S^2} (f'f'_* - ff_*)\mathcal{B}(\xi - \xi_*, \boldsymbol{\sigma})\, \mathrm{d}\boldsymbol{\sigma}\, \mathrm{d}\xi_*, \tag{11}$$

where $\boldsymbol{\sigma} \in S^2$, and the collision cross section $\mathcal{B}(\xi - \xi_*, \boldsymbol{\sigma})$ describes the model of interaction between the atoms (hard spheres, repulsive potential, ...).

A remarkable property of the collision integral (11) is that there exist test functions $\psi(\xi)$, *collision invariants*, independent of the collision cross section and the distribution function, such that:

$$\int\limits_{\mathbb{R}^3} \psi(\xi) Q(f,f)\, \mathrm{d}\xi = 0. \tag{12}$$

They satisfy the relation $\psi(\xi') + \psi(\xi'_*) = \psi(\xi) + \psi(\xi_*)$ and the complete set of collision invariants is:

$$\psi_0 = 1; \quad \psi_i = \xi_i \ (i = 1, 2, 3); \quad \psi_4 = |\xi|^2.$$

They also relate the distribution function f to the macroscopic quantities – mass, momentum and energy density (m is the atomic mass) – through the *moments of the distribution function*:

$$\begin{pmatrix} \rho \\ \rho v_i \\ \rho|\mathbf{v}|^2 + 2\rho\varepsilon \end{pmatrix} = \int\limits_{\mathbb{R}^3} m \begin{pmatrix} 1 \\ \xi_i \\ |\xi|^2 \end{pmatrix} f(t, \mathbf{x}, \xi)\, \mathrm{d}\xi. \tag{13}$$

Since the momentum density implicitly defines the mean mass velocity $\mathbf{v} = (v_i)_{i=1}^3$, one may define the *peculiar velocity* as $\mathbf{C} = (C_i)_{i=1}^3$, $C_i = \xi_i - v_i$, which yields proper definitions of the internal energy density and non-convective fluxes of momentum and energy, i.e. the pressure tensor p_{ij} and the heat flux q_i, through the so-called *central moments* of the distribution function:

$$\begin{aligned} \rho\varepsilon &= \int\limits_{\mathbb{R}^3} \frac{1}{2} m|\mathbf{C}|^2 f(t, \mathbf{x}, \mathbf{v} + \mathbf{C})\, \mathrm{d}\mathbf{C}, \\ p_{ij} &= \int\limits_{\mathbb{R}^3} m C_i C_j f(t, \mathbf{x}, \mathbf{v} + \mathbf{C})\, \mathrm{d}\mathbf{C} = -t_{ij}, \\ q_i &= \int\limits_{\mathbb{R}^3} \frac{1}{2} m|\mathbf{C}|^2 C_i f(t, \mathbf{x}, \mathbf{v} + \mathbf{C})\, \mathrm{d}\mathbf{C}. \end{aligned} \tag{14}$$

Note that one half of the trace of the pressure tensor equals internal energy density, the relation exclusively applicable to the monatomic gases. Since pressure $p = \mathrm{tr}\{p_{ij}\}/3$, using the thermal equation of state $(2)_3$ one may relate the *kinetic temperature* to the mean kinetic energy of the atoms:

$$T = \frac{2m}{3k_B}\varepsilon = \frac{m}{3k_B\rho} \int\limits_{\mathbb{R}^3} m|\mathbf{C}|^2 f(t, \mathbf{x}, \mathbf{v} + \mathbf{C})\, \mathrm{d}\mathbf{C}. \tag{15}$$

Taking into account (12), as well as the definitions of macroscopic variables (13) and fluxes (14), transfer equations for the moments of distribution function $\int \psi_\alpha f\, \mathrm{d}\xi$ can be deduced from the Boltzmann equation (10):

$$\frac{\partial}{\partial t} \int\limits_{\mathbb{R}^3} \psi_\alpha f\, \mathrm{d}\xi + \sum_{i=1}^{3} \frac{\partial}{\partial x_i} \int\limits_{\mathbb{R}^3} \xi_i \psi_\alpha f\, \mathrm{d}\xi = 0, \quad (\alpha = 0, \dots, 4),$$

that exactly reproduce the macroscopic conservation laws of mass, momentum and energy:

$$
\begin{aligned}
&\frac{\partial\rho}{\partial t}+\sum_{i=1}^{3}\frac{\partial}{\partial x_i}(\rho v_i)=0,\\
&\frac{\partial}{\partial t}(\rho v_j)+\sum_{i=1}^{3}\frac{\partial}{\partial x_i}(\rho v_j v_i+p_{ji})=0,\quad (j=1,2,3),\\
&\frac{\partial}{\partial t}\left(\frac{1}{2}\rho|\mathbf{v}|^2+\rho\varepsilon\right)+\sum_{i=1}^{3}\frac{\partial}{\partial x_i}\left\{\left(\frac{1}{2}\rho|\mathbf{v}|^2+\rho\varepsilon\right)v_i+\sum_{j=1}^{3}p_{ji}v_j+q_i\right\}=0.
\end{aligned}
\tag{16}
$$

It must be noted that the system (16) is not closed: the pressure tensor p_{ij} and the heat flux q_i are neither in the list of state variables, nor have prescribed relation to them. This problem will be further enlightened in the subsequent text.

By deferring the solution of the closure problem we opened the door to other remarkable properties of the Boltzmann equation – equilibrium distribution and celebrated $H-$theorem. By equilibrium distribution f_E it is assumed the velocity distribution function which annihilates the collision integral, $Q(f_E,f_E)=0$. It can be shown that $\log f_E$ is a collision invariant and, after using the definitions of macroscopic variables (13) and kinetic temperature (15), the following form of *equilibrium* (*Maxwellian*) *distribution* is obtained:

$$
f_E=\frac{\rho}{m}\left(\frac{m}{2\pi k_B T}\right)^{3/2}\exp\left\{-\frac{|\xi-\mathbf{v}|^2}{2(k_B/m)T}\right\}.
\tag{17}
$$

Note that only for uniform and constant in time macroscopic variables ρ, $\mathbf{v}$ and T equilibrium distribution f_E identically satisfies the Boltzmann equation (10). However, f_E with macroscopic variables $\rho(t,\mathbf{x})$, $\mathbf{v}(t,\mathbf{x})$ and $T(t,\mathbf{x})$ determine the so-called *local equilibrium distribution* (local Maxwellian) which also annihilates the collision integral.

Apart from the macroscopic balance laws, the Boltzmann equation induces also the kinetic counterpart of the entropy inequality. Formal definitions of the entropy density $\mathcal{H}$, the entropy flux $\mathcal{J}_i$ and the entropy production functional $D(f)$ are:

$$
\mathcal{H}=\int_{\mathbb{R}^3} f\,\log f\,\mathrm{d}\xi,\ \mathcal{J}_i=\int_{\mathbb{R}^3}\xi_i f\log f\,\mathrm{d}\xi,\ D(f)=\int_{\mathbb{R}^3}\log f\,Q(f,f)\,\mathrm{d}\xi.
\tag{18}
$$

The $H-$theorem describes the dissipative character of the Boltzmann equation.

Theorem 2.1. *Assume that the cross section $\mathcal{B}$ is positive a.e. and $f \geq 0$ is such that $Q(f,f)$ and $D(f)$ are well defined. Then:*

1. *The entropy production is non-positive, $D(f) \leq 0$.*
2. *The following statements are equivalent*
    - (a) *For any $\xi \in \mathbb{R}^3$, $Q(f,f) = 0$;*
    - (b) *The entropy production vanishes, $D(f) = 0$;*
    - (c) *There exists $\rho > 0$, $T > 0$ and $\mathbf{v} \in \mathbb{R}^3$ such that*

$$f = \frac{\rho}{m}\left(\frac{m}{2\pi k_B T}\right)^{3/2} \exp\left\{-\frac{|\xi - \mathbf{v}|^2}{2(k_B/m)T}\right\}.$$

Along with dissipation, given in the first part, the $H-$theorem relates the equilibrium (global and local) to the vanishing of entropy production. This is equivalent to the vanishing of entropy production in classical continuum physics. Namely, in equilibrium described by (17), either local or global, the pressure tensor becomes diagonal and the heat flux vanishes:

$$p_{ijE} = p\,\delta_{ij}, \quad q_{iE} = 0.$$

In the case of local Maxwellian, this provides a proper kinetic interpretation of the local equilibrium state, used as an assumption in TIP.

In general, the kinetic entropy density, entropy flux and entropy production (18) are related through the following balance law:

$$\frac{\partial \mathcal{H}}{\partial t} + \sum_{i=1}^{3} \frac{\partial \mathcal{J}_i}{\partial x_i} = D(f) \leq 0, \tag{19}$$

for any solution f of the Boltzmann equation (10). Up to the sign, this is equivalent to the entropy inequality (3) in the continuum approach. As a final remark, note that status of the entropy inequality is different in continuum and kinetic approach: in continuum theory it is a basic principle, while in kinetic theory it is a theorem – a consequence of fundamental relations.

2.2.2 - Hydrodynamic approximation

The fact that macroscopic balance laws can be recovered from the Boltzmann equation motivates the question of hydrodynamic approximation derived from it and proper solution of the closure problem [**22, 50, 7, 52**]. To that end it is convenient to rewrite the Boltzmann equation in the dimensionless form. Let t_0 be the macroscopic observation time scale, l the macroscopic length scale, T_0 the reference temperature, $v = \sqrt{2(k_B/m)T_0}$ the reference velocity, and $t_a = l/v$ the acoustic time scale. By introducing dimensionless variables, distribution function and cross section:

$$\hat{t} = \frac{t}{t_0}, \quad \hat{x}_i = \frac{x_i}{l}, \quad \hat{\xi}_i = \frac{\xi_i}{v}, \quad \hat{f} = (mv^3/\rho_0)f, \quad \hat{\mathcal{B}} = \frac{\mathcal{B}}{\sqrt{2}\pi d^2 v},$$

where ρ_0 is the reference mass density and d the molecular diameter, the dimensionless (scaled) Boltzmann equation can be derived:

$$\mathrm{Sh}\frac{\partial \hat{f}}{\partial \hat{t}} + \sum_{i=1}^{3} \hat{\xi}_i \frac{\partial \hat{f}}{\partial \hat{x}_i} = \frac{1}{\mathrm{Kn}} \hat{Q}(\hat{f},\hat{f}), \tag{20}$$

where:

$$\mathrm{Sh} = \frac{t_a}{t_0}, \quad \mathrm{Kn} = \frac{\lambda}{l}, \quad \lambda = \frac{m}{\sqrt{2}\pi \rho_0 d^2},$$

are the Strouhal number, the Knudsden number and the mean free path, respectively. Assuming $\mathrm{Sh} = O(1)$, we may focus on the Knudsen number which can serve for the classification of different flow regimes according to degree of rarefaction [78]:

(a) $\mathrm{Kn} \lesssim 0.01$ – the hydrodynamic regime;
(b) $0.01 \lesssim \mathrm{Kn} \lesssim 0.1$ – the slip flow regime;
(c) $0.1 \lesssim \mathrm{Kn} \lesssim 10$ – the transition regime → ET and BE;
(d) $\mathrm{Kn} \gtrsim 10$ – the free flight → DSMC.

In the hydrodynamic regime and, to a certain extent, in the slip flow regime one can rely on the continuum approach and the Navier-Stokes-Fourier model. The transition regime calls for deeper insight which can be achieved by means of extended thermodynamics (ET) or the Boltzmann equation (BE). For a free flight regime, the direct simulation Monte Carlo method (DSMC) is adequate.

Further analysis of the scaled Boltzmann equation (20) will be performed for $\mathrm{Sh} = O(1)$ and $\mathrm{Kn} \sim \varepsilon \ll 1$ treated as small parameter (hats are dropped for simplicity):

$$\frac{\partial f^\varepsilon}{\partial t} + \sum_{i=1}^{3} \xi_i \frac{\partial f^\varepsilon}{\partial x_i} = \frac{1}{\varepsilon} Q(f^\varepsilon,f^\varepsilon), \tag{21}$$

where f^ε is parameter dependent solution of (21). Equation (21) is the singularly perturbed Boltzmann equation and can be rewritten using the material derivative and the peculiar velocity:

$$Df^\varepsilon + \sum_{i=1}^{3} C_i \frac{\partial f^\varepsilon}{\partial x_i} = \frac{1}{\varepsilon} Q(f^\varepsilon,f^\varepsilon), \quad D = \frac{\partial}{\partial t} + \sum_{i=1}^{3} v_i \frac{\partial}{\partial x_i}.$$

Its solution is sought in the asymptotic form, and the material derivative operator is formally expanded, as well:

$$f^{\varepsilon} = f^{(0)} + \sum_{k=1}^{\infty} \varepsilon^k f^{(k)}, \quad D = D_0 + \sum_{k=1}^{\infty} \varepsilon^k D_k. \tag{22}$$

Inserting (22) into (21) one obtains the system of recursive equations. First two of them read:

$$\begin{aligned} Q(f^{(0)}, f^{(0)}) &= 0, \\ 2Q(f^{(0)}, f^{(1)}) &= D_0 f^{(0)} + \sum_{i=1}^{3} C_i \frac{\partial f^{(0)}}{\partial x_i}, \end{aligned} \tag{23}$$

clearly showing that f^{ε} in first approximation can be approximated by the local Maxwellian, $f^{(0)} = f_E$. Note that t and $\mathbf{x}$ dependence of the local Maxwellian (17) is not explicit, but through the hydrodynamic variables ρ, $\mathbf{v}$ and T. Second approximation is found as a solution of the integral equation $(23)_2$. Since solution f^{ε} has to be compatible with macroscopic variables (13), the following compatibility conditions also have to be satisfied:

$$\int_{\mathbb{R}^3} m\psi_{\alpha} f^{(k)} \, \mathrm{d}\boldsymbol{\xi} = 0, \quad \forall k \geq 1, \ \alpha = 0, \ldots, 4.$$

The idea of the Chapman-Enskog expansion is not only to asymptotically expand the solution, but also to expand the corresponding macroscopic equations and use them to eliminate the material derivatives from $(23)_2$:

$$\begin{aligned} & D_0 \rho + \sum_{j=1}^{3} \frac{\partial v_j}{\partial x_j} = 0, & & D_k \rho = 0, & \\ & \rho D_0 v_i + \frac{\partial p}{\partial x_i} = 0, & & \rho D_k v_i + \sum_{j=1}^{3} \frac{\partial p^{(k)}_{\langle ij \rangle}}{\partial x_j} = 0, & \forall k \geq 1 \\ & \frac{3}{2} \rho \frac{k_B}{m} D_0 T + p \sum_{j=1}^{3} \frac{\partial v_j}{\partial x_j} = 0, & & \frac{3}{2} \rho \frac{k_B}{m} D_k T + \sum_{i,j=1}^{3} p^{(k)}_{\langle ij \rangle} \frac{\partial v_i}{\partial x_j} + \sum_{j=1}^{3} \frac{\partial q^{(k)}_j}{\partial x_j} = 0. & \end{aligned}$$

The left column consists of the conservation laws in the first approximation, while the right column gives all the higher order approximations, $p_{\langle ij \rangle} = p_{ij} - (1/3)\mathrm{tr}(p_{ij})$ being the traceless (deviatoric) part of the pressure tensor. By writing the second approximation in the form $\varepsilon f^{(1)} = f^{(0)} \phi$, and linearizing the collision integral in $(23)_2$ in the neighborhood of $f^{(0)}$, one arrives at a linear integral equation which can be solved for ϕ:

$$\phi = -\frac{A}{T} \sum_{i=1}^{3} C_i \frac{\partial T}{\partial x_i} - \frac{m}{k_B T} B \sum_{i,j=1}^{3} C_i C_j \frac{\partial v_{\langle i}}{\partial x_{j \rangle}}. \tag{24}$$

The coefficients A and B can be appropriately expressed in terms of the collision integral. The details of this procedure can be found in [**22, 52, 7**] and will be omitted here. Nevertheless, the consequences of (24) on the macroscopic non-convective fluxes are important for our appreciation of classical TIP. The pressure tensor $p_{\langle ij\rangle}$ and the heat flux q_i vanish in first approximation, $p^{(0)}_{\langle ij\rangle} = 0$ and $q^{(0)}_i = 0$, so that:

$$p_{\langle ij\rangle} = \int\limits_{\mathbb{R}^3} mC_iC_jf^\varepsilon\,\mathrm{d}\boldsymbol{\xi} = \sum_{k=1}^{\infty} \varepsilon^k p^{(k)}_{\langle ij\rangle}, \quad q_i = \int\limits_{\mathbb{R}^3} \frac{m}{2}C_i|\mathbf{C}|^2f^\varepsilon\,\mathrm{d}\boldsymbol{\xi} = \sum_{k=1}^{\infty} \varepsilon^k q^{(k)}_i.$$

Therefore, taking (24) the following second approximation for the pressure tensor and the heat flux is obtained:

$$p^{(1)}_{\langle ij\rangle} = -2\mu\frac{\partial v_{\langle i}}{\partial x_{j\rangle}}, \quad q^{(1)}_i = -\lambda\frac{\partial T}{\partial x_i}, \tag{25}$$

where μ and λ can be calculated once the collision cross section is specified. This result shows that Navier-Stokes-Fourier constitutive relations can be recovered as a part of the asymptotic solution of the Boltzmann equation. Moreover, it shows that they give a proper description only for processes whose deviation from the state described by the local Maxwellian $f^{(0)} = f_E$ is not large.

This section will be concluded with some remarks motivated by the asymptotic method of Chapman-Enskog. First, the notion of the local thermodynamic equilibrium, which TIP borrowed from classical thermostatics, has a precise meaning in the kinetic theory – it is a state described by the local Maxwellian (17). Moreover, the macroscopic variables $\rho(t,\mathbf{x})$, $\mathbf{v}(t,\mathbf{x})$ and $T(t,\mathbf{x})$ cannot be arbitrary, but satisfy the Euler gas dynamics equations [**7**]:

$$\begin{aligned}
&\frac{\partial\rho}{\partial t} + \sum_{i=1}^{3}\frac{\partial}{\partial x_i}(\rho v_i) = 0,\\
&\frac{\partial}{\partial t}(\rho v_j) + \sum_{i=1}^{3}\frac{\partial}{\partial x_i}(\rho v_j v_i + p\delta_{ji}) = 0,\\
&\frac{\partial}{\partial t}\left(\frac{1}{2}\rho|\mathbf{v}|^2 + \rho\varepsilon\right) + \sum_{i=1}^{3}\frac{\partial}{\partial x_i}\left\{\left(\frac{1}{2}\rho|\mathbf{v}|^2 + \rho\varepsilon + p\right)v_i\right\} = 0,
\end{aligned}\tag{26}$$

where pressure p and internal energy ε are described by thermal and caloric equations of state:

$$p = \rho\frac{k_B}{m}T, \quad \varepsilon = \frac{3}{2}\frac{p}{\rho}.$$

Second, small deviations from the local thermodynamic equilibrium are expressed by $f \approx f^{(0)}(1+\phi)$, where ϕ is determined by (24). It leads to a second approximation of the pressure tensor and the heat flux in the form:

$$p_{ij} = p\,\delta_{ij} + p^{(1)}_{\langle ij\rangle}, \quad q_i = q^{(1)}_i, \tag{27}$$

where $p^{(1)}_{\langle ij\rangle}$ and $q^{(1)}_i$ are described by (25). In this case, the macroscopic variables satisfy the so-called compressible Navier-Stokes equations:

$$\begin{aligned}
&\frac{\partial \rho}{\partial t} + \sum_{i=1}^{3} \frac{\partial}{\partial x_i}(\rho v_i) = 0, \\
&\frac{\partial}{\partial t}(\rho v_j) + \sum_{i=1}^{3} \frac{\partial}{\partial x_i}(\rho v_j v_i + p_{ji}) = 0, \\
&\frac{\partial}{\partial t}\left(\frac{1}{2}\rho|\mathbf{v}|^2 + \rho\varepsilon\right) \\
&\qquad + \sum_{i=1}^{3} \frac{\partial}{\partial x_i}\left\{\left(\frac{1}{2}\rho|\mathbf{v}|^2 + \rho\varepsilon + p\right)v_i + \sum_{j=1}^{3} p_{ji} v_j + q_i\right\} = 0,
\end{aligned} \tag{28}$$

for p_{ij} and q_i determined by (27). Thus, Chapman-Enskog method is the asymptotic method of solution of the Boltzmann equation, but it also puts the notions and constitutive relations of TIP in the new perspective.

2.2.3 - The method of moments

Grad proposed the method of moments in his seminal paper [**34**], accompanied with a precise description of the mathematical apparatus needed for it [**35**]. It provides another look on the relation between the Boltzmann equation and the macroscopic description of the non-equilibrium processes in gases. First, the moment of order n of the distribution function is defined as:

$$F_{i_1\cdots i_n} = \int_{\mathbb{R}^3} m \xi_{i_1} \cdots \xi_{i_n} f \, \mathrm{d}\boldsymbol{\xi}. \tag{29}$$

To (29) proper transfer equations are naturally associated by averaging the Boltzmann equation (10) over the velocity space:

$$\frac{\partial}{\partial t} F_{i_1\cdots i_n} + \sum_{k=1}^{3} \frac{\partial}{\partial x_k} F_{i_1\cdots i_n k} = P_{i_1\cdots i_n}, \tag{30}$$

where the fluxes $F_{i_1\cdots i_n k}$ and the source terms $P_{i_1\cdots i_n}$ are defined as follows:

$$F_{i_1\cdots i_n k} = \int_{\mathbb{R}^3} m \xi_k \xi_{i_1} \cdots \xi_{i_n} f \, \mathrm{d}\boldsymbol{\xi}, \quad P_{i_1\cdots i_n} = \int_{\mathbb{R}^3} m \xi_{i_1} \cdots \xi_{i_n} Q(f,f) \, \mathrm{d}\boldsymbol{\xi}.$$

Note that $P = 0$, $P_i = 0$, $\sum_{i=1}^{3} P_{ii} = 0$ due to collision invariants.

The moment equations have some features that will be important for our further study. They become apparent if we write them in a proper way:

$$
\begin{aligned}
&\frac{\partial}{\partial t}F+\sum_{k=1}^{3}\frac{\partial}{\partial x_k}F_k=0,\\
&\frac{\partial}{\partial t}F_{i_1}+\sum_{k=1}^{3}\frac{\partial}{\partial x_k}F_{i_1k}=0,\\
&\frac{\partial}{\partial t}F_{i_1i_2}+\sum_{k=1}^{3}\frac{\partial}{\partial x_k}F_{i_1i_2k}=P_{i_1i_2},\\
&\qquad\vdots\\
&\frac{\partial}{\partial t}F_{i_1\cdots i_n}+\sum_{k=1}^{3}\frac{\partial}{\partial x_k}F_{i_1\cdots i_nk}=P_{i_1\cdots i_n},\\
&\qquad\vdots
\end{aligned}
\tag{31}
$$

In particular, they possess hierarchical structure which is due to the fact that fluxes of order m become densities of order $m+1$. Higher order moments provide deeper insight into the state of gas, although there is no proper "macroscopic" explanation of their character. They present an interpolation between hydrodynamic and kinetic description [**38**].

Hierarchy of the moment equations is infinite, in general. However, if the system is truncated at order n, the fluxes of order $n+1$ and the source terms remain undetermined. This brings the closure problem into the focus. Usually, densities are used as the state variables and undetermined fluxes and source terms are supposed to be expressed in terms of them. Grad proposed a solution of the closure problem by means of expansion of the non-equilibrium distribution function in terms of tensorial Hermite polynomials [**34, 35**]. The choice of Hermite polynomials is rather natural due to the structure of equilibrium distribution, and quite convenient due to the orthogonality of the polynomials. However, in formal sense this solution is equivalent to a polynomial expansion of the non-equilibrium distribution function in the neighborhood of the local Maxwellian f_E:

$$
f=f_E\left(a+\sum_{i=1}^{3}a_iC_i+\sum_{i,j=1}^{3}a_{ij}C_iC_j+\sum_{i,j,k=1}^{3}a_{ijk}C_iC_jC_k+\cdots\right).
\tag{32}
$$

The coefficients $a, a_i, \ldots$ in the expansion are functions of t and $\mathbf{x}$. The structure of approximate distribution function (32) is dictated by the choice of the moments in the truncated set of moment equations. Namely, once the set of moments (densities) is chosen, the corresponding coefficients of the same tensorial order in the expansion are retained. Their structure is determined by the compatibility of approximate distribution function with the moments through relation (29). Thus, the coefficients depend on t and $\mathbf{x}$ indirectly, via moments.

Probably the most famous set of moment equations is the 13 moments system for monatomic gases. Choice of the moments is motivated by their physical interpretation: apart from the hydrodynamic state variables ρ, v_i and T, the non-equilibrium fluxes $p_{\langle ij\rangle}$ and q_i are chosen, as well. Their identification with the moments is straightforward:

$$\begin{aligned}
&\rho = F, \quad \rho v_i = F_i, \quad \rho|\mathbf{v}|^2 + 3\rho\frac{k_B}{m}T = \sum_{i=1}^{3} F_{ii},\\
&\rho v_i v_j + p_{ij} = F_{ij}, \quad \left(\rho|\mathbf{v}|^2 + 3\rho\frac{k_B}{m}T\right)v_i + 2\sum_{k=1}^{3} p_{ik}v_k + 2q_i = \sum_{k=1}^{3} F_{ikk}.
\end{aligned}$$

Approximate Grad's 13 moments non-equilibrium distribution function then reads:

$$f_{13} = f_E\left\{1 + \frac{2}{\rho}\left(\frac{m}{2k_BT}\right)^2\left[\sum_{i,j=1}^{3} p_{\langle ij\rangle}C_iC_j + \frac{4}{5}\sum_{i=1}^{3} q_iC_i\left(\frac{m}{2k_BT}|\mathbf{C}|^2 - \frac{5}{2}\right)\right]\right\}. \tag{33}$$

As a consequence, one obtains the balance laws for moments of the distribution function f_{13}. The first group of equations, corresponding to the hydrodynamic moments F, F_i and the trace of F_{ij}, are the conservation laws of mass, momentum and energy (28). In addition, the balance laws for F_{ij} and the trace of F_{ijk} represent the evolution equations of momentum and energy fluxes:

$$\begin{aligned}
&\frac{\partial}{\partial t}(\rho v_i v_j + p_{ij})\\
&\quad + \sum_{k=1}^{3}\frac{\partial}{\partial x_k}\{\rho v_i v_j v_k + v_i p_{jk} + v_j p_{ki} + v_k p_{ij} + p_{ijk}\} = P_{ij},\\
&\frac{\partial}{\partial t}\left\{\left(\frac{1}{2}\rho|\mathbf{v}|^2 + \rho\varepsilon\right)v_i + \sum_{k=1}^{3} p_{ik}v_k + q_i\right\}\\
&\quad + \sum_{j=1}^{3}\frac{\partial}{\partial x_j}\left\{\left(\frac{1}{2}\rho|\mathbf{v}|^2 + \rho\varepsilon\right)v_iv_j + \sum_{k=1}^{3}(v_iv_kp_{jk} + v_jv_kp_{ik} + v_kp_{ijk})\right.\\
&\qquad\qquad \left. + \frac{1}{2}\rho|\mathbf{v}|^2p_{ij} + q_iv_j + q_jv_i + q_{ij}\right\} = Q_i.
\end{aligned} \tag{34}$$

Thanks to (33), the non-convective fluxes can be expressed in terms of the central moments:

$$p_{ijk}^{(13)} = \int\limits_{\mathbb{R}^3} mC_iC_jC_kf_{13}\,\mathrm{d}\mathbf{C} = \frac{2}{5}\left(q_i\delta_{jk} + q_j\delta_{ki} + q_k\delta_{ij}\right),$$

$$q_{ij}^{(13)} = \frac{1}{2}\int\limits_{\mathbb{R}^3} mC_iC_j|\mathbf{C}|^2f_{13}\,\mathrm{d}\mathbf{C} = \frac{7}{2}\frac{p}{\rho}\,p_{ij} - \frac{p^2}{\rho}\,\delta_{ij},$$

as well as the source terms, that are given here in linearized form [**52**]:

$$P_{ij}^{(13)} = \int\limits_{\mathbb{R}^3} m\xi_i\xi_jQ(f_{13},f_{13})\,\mathrm{d}\xi \approx -\frac{1}{\tau}p_{\langle ij\rangle},$$

$$Q_i^{(13)} = \frac{1}{2}\int\limits_{\mathbb{R}^3} m|\xi|^2\xi_iQ(f_{13},f_{13})\,\mathrm{d}\xi \approx \frac{2}{3\tau}q_i,$$

where:

$$\tau = \frac{5m}{16\rho}\left(\frac{m}{\pi k_BT}\right)^{1/2}\frac{1}{\Omega^{(2,2)}},$$

where $\Omega^{(2,2)}$ is an integral expression related to the cross section.

At this stage we shall draw the attention to some important features of the system just derived. First, Grad's 13 moments distribution (33) represents a finite-dimensional approximation of the exact non-equilibrium distribution function. It corresponds to the finite (truncated) set of moments chosen as state variables and their transfer equations. However, the choice of the moments is neither automatic, nor arbitrary. It depends on one's aims in the study of non-equilibrium processes. Second, the closure of the system is obtained in the spirit of kinetic theory, by expanding the non-equilibrium distribution in the neighborhood of the local Maxwellian, and making it compatible with the chosen moments. Finally, the deviatoric pressure tensor $p_{\langle ij\rangle}$ and the heat flux q_i are no longer determined by the constitutive relations of Navier-Stokes-Fourier type. Now they belong to the set of state variables and their behaviour is determined by the evolution equations – balance laws (34). It can be shown, by one kind of asymptotic analysis, that NSF relations (25) are truncated form of the balance laws (34) in which the time and certain convective rate of change is neglected.

Final remark is concerned with the entropy density and the entropy flux in the context of the moments method. In the local equilibrium state, described by the local Maxwellian f_E, the entropy density and the entropy flux have the following form:

$$\rho s_E = -k\frac{\rho}{m}\left\{\log\left(\frac{\rho}{m}\left(\frac{m}{2\pi kT}\right)^{3/2}\right) - \frac{3}{2}\right\}, \quad \phi_{iE} = 0.$$

Moreover, the Gibbs' relation is also recovered in local equilibrium:

$$\mathrm{d}s_E = \frac{1}{T}\left\{\mathrm{d}\varepsilon - \frac{p}{\rho^2}\mathrm{d}\rho\right\}.$$

If one determines the entropy density and the entropy flux using Grad's 13 moments distribution (33), the following results are obtained [**60, 52**]:

$$\begin{aligned}\rho s^{(13)} &= \rho s_E - \frac{1}{4}\frac{k}{m}\frac{\rho}{p^2}\sum_{i,j=1}^{3} p_{\langle ij\rangle}p_{\langle ij\rangle} - \frac{1}{5}\frac{k}{m}\frac{\rho^2}{p^3}\sum_{i=1}^{3} q_i q_i,\\ \phi_i^{(13)} &= \frac{q_i}{T} - \frac{2}{5}\frac{k}{m}\frac{\rho}{p^2}\sum_{j=1}^{3} p_{\langle ij\rangle}q_j.\end{aligned}$$

The entropy density is obviously extended, retaining its convexity with respect to the state variables, whereas the entropy flux is no longer proportional to the heat flux. These relations will appear to be of great importance in the further study of non-equilibrium processes within extended thermodynamics.

2.3 - *Extended thermodynamics of monatomic gases*

Extended thermodynamics (ET) emerged as an attempt to give a systematic and physically consistent resolution of the paradox of infinite pulse speeds ([**60**], Chapter 2). At first instance, it actually extended the methods of TIP. To take into account non-equilibrium effects it extended the Gibbs' relation by thermodynamic fluxes, i.e. stress tensor and heat flux, and eventually reached the extended version of the entropy inequality. Two main outcomes may be mentioned at this stage. First, the entropy flux was no longer proportional to the heat flux but contained additional terms. Second, reduction of the entropy production rate to a quadratic form yielded relations for the stress tensor and the heat flux whose nuclei contained classical NSF terms. Nevertheless, they also contained material derivatives of thermodynamic fluxes giving these relations the form of balance laws. Apart from removal of the paradox of infinite pulse speeds for heat conduction and shear waves, the most striking result was, however, apparent similarity with Grad's 13 moments equations.

Success of the early version of extended thermodynamics motivated further applications. It reached maturity through a stream of results which enlarged its scope and put it into a proper relation with TIP, as well as with kinetic theory. A complete information with exhaustive list of references can be found in the monograph of Müller and Ruggeri [**60**]. In the sequel, a brief overview of the basic structure of extended thermodynamics will be given, bringing only the principal ideas to the forefront and enabling to build the extended mixture theory on them.

A refrain which resonates in almost all applications of ET is the property of finite pulse speeds, which is brought by the particular structure of mathematical models – hyperbolic systems of balance laws [**12**]. Let $\mathbf{u}(\mathbf{x}, t) \in \mathbb{R}^n$ be the vector of state variables. The governing equations are balance laws, which have the following local form:

$$\frac{\partial \mathbf{F}^0}{\partial t} + \sum_{i=1}^{3} \frac{\partial \mathbf{F}^i}{\partial x_i} = \mathbf{P}. \tag{35}$$

In ET it is assumed that the densities $\mathbf{F}^0(\mathbf{u}) \in \mathbb{R}^n$, the fluxes $\mathbf{F}^i(\mathbf{u}) \in \mathbb{R}^n$, $i = 1, 2, 3$, and the productions $\mathbf{P}(\mathbf{u}) \in \mathbb{R}^n$ depend on the state variables only locally, i.e. they depend on their values at point $\mathbf{x}$ and time t. Therefore, the constitutive relations for densities, fluxes and productions are local in space–time, which give the system (35) the structure of a quasi-linear system of first-order PDE's:

$$\mathbf{A}^0(\mathbf{u}) \frac{\partial \mathbf{u}}{\partial t} + \sum_{i=1}^{3} \mathbf{A}^i(\mathbf{u}) \frac{\partial \mathbf{u}}{\partial x_i} = \mathbf{P}(\mathbf{u}),$$

where $\mathbf{A}^0 = \partial \mathbf{F}^0 / \partial \mathbf{u}$ and $\mathbf{A}^i = \partial \mathbf{F}^i / \partial \mathbf{u}$. The possible speeds can be calculated from the eigenvalue problem:

$$\left(-\lambda \mathbf{A}^0(\mathbf{u}) + \sum_{i=1}^{3} n_i \mathbf{A}^i(\mathbf{u}) \right) \mathbf{r} = \mathbf{0}, \tag{36}$$

with the eigenvalues λ and the eigenvectors $\mathbf{r}$, where n_i are the components of the unit vector $\mathbf{n}$. The system (35) is *hyperbolic in the t-direction* if $\det \mathbf{A}^0 \neq 0$ and the eigenvalue problem (36) admits only real eigenvalues λ and a set of linearly independent eigenvectors $\mathbf{r}$ for all unit vectors $\mathbf{n}$. Note that the assumption of local dependence of fluxes on the state variables rules out the NSF constitutive relations in which fluxes depend on the values of state variables in the neighborhood of a given point.

Apart from the hyperbolicity, ET imposes another two important requirements on the governing equations. First one is the invariance with respect to the Galilean transformations, e.g. the principle of relativity. It permits identification of the velocity dependence of densities, fluxes and source terms. It is particularly important for the identification of convective and non-convective parts $\mathbf{G}^i$ of the fluxes, $\mathbf{F}^i = \mathbf{F}^0 v^i + \mathbf{G}^i$. Ruggeri [**66**] showed that balance laws in two inertial reference frames related by the Galilean transformation are equivalent if and only if one is a linear combination of the other. If the state variables are represented as $\mathbf{u} = (\mathbf{v}, \mathbf{w})$, then there exists a matrix $\mathbf{X}(\mathbf{v})$ such that:

$$\begin{aligned} \mathbf{F}^0(\mathbf{w},\mathbf{v}) &= \mathbf{X}(\mathbf{v})\hat{\mathbf{F}}^0(\mathbf{w}), \quad & \hat{\mathbf{F}}^0(\mathbf{w}) &= \mathbf{F}^0(\mathbf{w},\mathbf{0}), \\ \mathbf{G}^i(\mathbf{w},\mathbf{v}) &= \mathbf{X}(\mathbf{v})\hat{\mathbf{G}}^i(\mathbf{w}), \quad & \hat{\mathbf{G}}^i(\mathbf{w}) &= \mathbf{G}^i(\mathbf{w},\mathbf{0}), \\ \mathbf{P}(\mathbf{w},\mathbf{v}) &= \mathbf{X}(\mathbf{v})\hat{\mathbf{P}}(\mathbf{w}), \quad & \hat{\mathbf{P}}(\mathbf{w}) &= \mathbf{P}(\mathbf{w},\mathbf{0}), \end{aligned} \tag{37}$$

where the terms with hats are the so-called intrinsic parts of densities, fluxes and source terms. Moreover, for any $\mathbf{v}^1$ and $\mathbf{v}^2$, it holds: $\mathbf{X}(\mathbf{v}^1+\mathbf{v}^2) = \mathbf{X}(\mathbf{v}^1)\mathbf{X}(\mathbf{v}^2)$, $\mathbf{X}(\mathbf{0}) = \mathbf{I}$.

Second restriction is imposed by the entropy inequality:

$$\frac{\partial h^0}{\partial t} + \sum_{i=1}^{3} \frac{\partial h^i}{\partial x_i} = \Sigma \leq 0, \tag{38}$$

where $-h^0$, $-h^i$ and $-\Sigma$ are the entropy density, the entropy flux and the entropy production, respectively. The entropy inequality is adjoined with an additional requirement of convexity of the entropy density for the reason of thermodynamic stability, but there were no *a priori* restrictions on the structure of the entropy flux h^i [**58**]. To exploit the entropy inequality in the spirit of continuum mechanics, i.e. as a restriction on the structure of constitutive relations, one has to devise a procedure more general than the use of Gibbs' inequality, if it is to be applied on the system (35). Liu [**53, 54**] developed the method of Lagrange multipliers by taking the entropy balance law (38) as a master equation, and the governing equations (35) as constraints. The Lagrange multipliers $\Lambda \in \mathbb{R}^n$ are used to remove the constraints and extend the entropy inequality:

$$\frac{\partial h^0}{\partial t} + \sum_{i=1}^{3} \frac{\partial h^i}{\partial x_i} - \Lambda \cdot \left(\frac{\partial \mathbf{F}^0}{\partial t} + \sum_{i=1}^{3} \frac{\partial \mathbf{F}^i}{\partial x_i} - \mathbf{P} \right) = \Sigma \leq 0. \tag{39}$$

Due to the local dependence of densities and fluxes on the state variables, (39) yields the entropy–entropy flux integrability relations:

$$\frac{\partial h^0}{\partial \mathbf{u}} = \Lambda \cdot \frac{\partial \mathbf{F}^0}{\partial \mathbf{u}}, \quad \frac{\partial h^i}{\partial \mathbf{u}} = \Lambda \cdot \frac{\partial \mathbf{F}^i}{\partial \mathbf{u}}, \tag{40}$$

as well as the *residual inequality*:

$$\Sigma = \Lambda \cdot \mathbf{P} \leq 0. \tag{41}$$

Actually, once the multipliers Λ are determined from the integrability conditions (40), equation (41) helps to determine the structure of source terms $\mathbf{P}$ compatible with the entropy inequality (38). However, the Lagrange multipliers are not exhausted by their supporting role in the entropy principle – they can act as the principal state variables (main field, entropic variables) due to entropy convexity [**64**]. The mapping $\mathbf{u} \mapsto \Lambda$ implies the transformation of the system (35) into a symmetric hyperbolic form, particularly useful in the study of existence and uniqueness of solutions [**65, 12**].

Euler (elastic) fluids represent a simple, but useful example of hyperbolic system, whose properties will be exploited in the sequel. The state variables $\mathbf{u} = (\rho, v_i, \varepsilon) = (\mathbf{v}, \mathbf{w})$, $\mathbf{w} = (\rho, \varepsilon)$, are governed by the Euler gas dynamics equations (1). Densities and fluxes have the form:

$$\mathbf{F}^0(\mathbf{u}) = \begin{pmatrix} \rho \\ \rho v_i \\ \frac{1}{2}\rho v^2 + \rho\varepsilon \end{pmatrix} \quad \hat{\mathbf{F}}^0(\mathbf{w}) = \begin{pmatrix} \rho \\ 0_i \\ \rho\varepsilon \end{pmatrix}$$

$$\mathbf{G}^j(\mathbf{u}) = \begin{pmatrix} 0_j \\ -t_{ij} \\ -t_{ij}v_i + q_j \end{pmatrix} \quad \hat{\mathbf{G}}^j(\mathbf{w}) = \begin{pmatrix} 0_j \\ -t_{ij} \\ q_j \end{pmatrix}$$

while non-convective fluxes are determined by the constitutive relations $t_{ij} = -p(\rho, \varepsilon)\,\delta_{ij}$, $q_i = 0$. Galilean invariance is achieved by means of the matrix $\mathbf{X}$:

$$\mathbf{X}(\mathbf{v}) = \begin{pmatrix} 1 & 0 & 0 \\ v_i & \delta_{ij} & 0 \\ \frac{1}{2}v^2 & v_j & 1 \end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 & 0 & 0 \\ v_1 & 1 & 0 & 0 & 0 \\ v_2 & 0 & 1 & 0 & 0 \\ v_3 & 0 & 0 & 1 & 0 \\ \frac{1}{2}v^2 & v_1 & v_2 & v_3 & 1 \end{pmatrix},$$

whereas Lagrange multipliers read:

$$\Lambda = \begin{pmatrix} \Lambda^\rho \\ \Lambda^{v_i} \\ \Lambda^\varepsilon \end{pmatrix} = \begin{pmatrix} \frac{1}{T}\left(g - \frac{1}{2}v^2\right) \\ \frac{v_i}{T} \\ -\frac{1}{T} \end{pmatrix},$$

where $g = \varepsilon - Ts + p/\rho$ is the free enthalpy.

We arrived now to the main issue of ET: how to include the viscous, heat conducting fluids into the scope, without loosing the hyperbolicity of the governing equations? First answer came with extended TIP. Later development gave rise to *rational extended thermodynamics* – a macroscopic theory closely related to the kinetic theory of gases, especially Grad's moments method. In this context ET relies on the following pillars:

(a) extended list of the state variables, $\mathbf{u} = (\rho, v_i, \varepsilon, t_{ij}, q_i)$;

(b) extended set of the governing equations – balance laws for the stress tensor t_{ij} and the heat flux q_i have to be included;

(c) formal hierarchical structure of balance laws is "borrowed" from the equations for moments in the kinetic theory of gases;

(d) closure problem is resolved by the application of entropy principle.

In fact, the core idea of ET in this context is to use the truncated hierarchy of moment equations *ab initio* [**12**]:

$$\begin{aligned}
\frac{\partial}{\partial t}F + \sum_{k=1}^{3}\frac{\partial}{\partial x_k}F_k &= 0,\\
\frac{\partial}{\partial t}F_{i_1} + \sum_{k=1}^{3}\frac{\partial}{\partial x_k}F_{i_1k} &= 0,\\
\frac{\partial}{\partial t}F_{i_1i_2} + \sum_{k=1}^{3}\frac{\partial}{\partial x_k}F_{i_1i_2k} &= P_{i_1i_2},\\
\frac{\partial}{\partial t}F_{i_1i_2i_3} + \sum_{k=1}^{3}\frac{\partial}{\partial x_k}F_{i_1i_2i_3k} &= P_{i_1i_2i_3},
\end{aligned}$$

and to resolve the closure problem using the entropy principle. The moments $F_{i_1\cdots i_n}$ can be related to the moments of the distribution function (29), as well as the central moments $\rho_{i_1\cdots i_n} = \int mC_{i_1}\cdots C_{i_n} f\,\mathrm{d}\xi$:

$$\begin{gathered}
F = \rho, \quad F_i = \rho_i + \rho v_i, \quad F_{ij} = \rho_{ij} + 2\rho_{(i}v_{j)} + \rho v_i v_j,\\
F_{ijk} = \rho_{ijk} + 3\rho_{(ij}v_{k)} + 3\rho_{(i}v_j v_{k)} + \rho v_i v_j v_k,\\
F_{ijkl} = \rho_{ijkl} + 4\rho_{(ijk}v_{l)} + 6\rho_{(ij}v_k v_{l)} + 4\rho_{(i}v_j v_k v_{l)} + \rho v_i v_j v_k v_l,
\end{gathered}$$

where the braces denote symmetrization and[1]:

$$\rho_i = 0; \quad \rho_{ij} = p_{ij} = -t_{ij}; \quad \rho_{ppk} = 2q_k.$$

Since only 13 moments have apparent physical interpretation in the case of monatomic gases, 13 balance laws will be selected from truncated system for the densities:

$$\mathbf{F}(\mathbf{u}) = \left(F, F_i, F_{pp}, F_{\langle ij\rangle}, F_{ppi}\right), \quad F_{\langle ij\rangle} = F_{ij} - \frac{1}{3}F_{pp}\delta_{ij},$$

which obviously correspond to mass, momentum and energy density, and momentum and energy fluxes acting as densities in the extended set of variables. The

---

[1] In the remaining part of this section the Einstein's summation convention will be used.

governing equations then read:

$$
\begin{aligned}
&\partial_t F + \partial_i F_i = 0, && \\
&\partial_t F_i + \partial_j F_{ij} = 0, && \\
&\partial_t F_{pp} + \partial_i F_{ppi} = 0, \qquad && \partial_t F_{\langle ij\rangle} + \partial_k F_{\langle ij\rangle k} = P_{\langle ij\rangle}, \\
& && \partial_t F_{ppi} + \partial_k F_{ppik} = P_{ppi}.
\end{aligned} \tag{42}
$$

The left column contains the conservation laws of mass, momentum and energy, while the right column comprises the balance laws for momentum flux deviator and energy flux. Application of the entropy principle introduces the Lagrange multipliers:

$$
\Lambda = \left(\Lambda^\rho, \Lambda_i, \Lambda^\varepsilon, \Lambda_{\langle ij\rangle}, \Lambda_{ppi}\right),
$$

that have the form:

$$
\begin{aligned}
\Lambda^\rho &= \frac{1}{T}\left(g - \frac{v^2}{2} + \frac{1}{2p}\sigma_{ij}v_iv_j - \frac{\rho}{5p^2}q_iv_iv^2\right) \\
\Lambda_i &= \frac{1}{T}\left(v_i - \frac{1}{p}\sigma_{ij}v_j + \frac{\rho}{5p^2}\left(v^2q_i + 2q_jv_jv_i\right)\right) \\
\Lambda^\varepsilon &= -\frac{1}{T}\left(1 - \frac{2\rho}{3p^2}q_kv_k\right) \\
\Lambda_{\langle ij\rangle} &= -\frac{1}{T}\left\{\frac{1}{2T}\sigma_{ij} + \frac{\rho}{5p^2}\left(v_iq_j + v_jq_i - \frac{2}{3}v_kq_k\delta_{ij}\right)\right\} \\
\Lambda_{ppi} &= \frac{\rho}{5Tp^2}q_i
\end{aligned}
$$

where the stress tensor is decomposed as follows $t_{ij} = -p\,\delta_{ij} + \sigma_{ij}$. Therefore, the final structure of densities is:

$$
\begin{aligned}
F = \rho, \quad F_i = \rho v_i, \quad F_{pp} &= \rho v^2 + 2\rho\varepsilon, \\
F_{\langle ij\rangle} &= \rho\left(v_iv_j - \frac{1}{3}v^2\delta_{ij}\right) - \sigma_{ij}, \\
F_{ppi} &= \left(\rho v^2 + 2\rho\varepsilon + 2p\right)v_i - 2\sigma_{ij}v_j + 2q_i,
\end{aligned}
$$

while the fluxes determined through the closure procedure read:

$$
\begin{aligned}
F_{ijk} &= \rho v_iv_jv_k + (pv_i + (2/5)q_i)\delta_{jk} + \left(pv_j + (2/5)q_j\right)\delta_{ki} \\
&\quad + (pv_k + (2/5)q_k)\delta_{ij} - v_i\sigma_{jk} - v_j\sigma_{ki} - v_k\sigma_{ij}, \\
F_{\langle ij\rangle k} &= F_{ijk} - \frac{1}{3}F_{ppk}\delta_{ij}, \\
F_{ppij} &= \left(\rho v^2 + 7p\right)v_iv_j + (p\,\delta_{ij} - \sigma_{ij})v^2 - \sigma_{ik}v_jv_k - \sigma_{jk}v_iv_k \\
&\quad + \frac{14}{5}(q_iv_j + q_jv_i) + \frac{4}{5}q_kv_k\delta_{ij} + \frac{p}{\rho}(5p\delta_{ij} - 7\sigma_{ij}).
\end{aligned}
$$

Finally, the source terms in balance laws have the following structure:

$$P_{\langle ij \rangle} = \frac{1}{\tau_\sigma}\sigma_{ij}, \quad P_{ppi} = \frac{2}{\tau_\sigma}\sigma_{ij}v_j - \frac{2}{\tau_q}q_i, \tag{43}$$

where $\tau_\sigma(\rho, \varepsilon)$ and $\tau_q(\rho, \varepsilon)$ are the so-called relaxation times.

This is the right place to introduce the notion of an *equilibrium subsystem*. If we reconsider the residual inequality (41) in 13 moments case, we can see that the entropy production rate vanishes when $\Lambda_{\langle ij \rangle}$ and Λ_{ppi} vanish. This condition is fulfilled for $\sigma_{ij} = 0$ and $q_i = 0$, i.e. $P_{\langle ij \rangle} = 0$ and $P_{ppi} = 0$. Thus, in equilibrium the entropy principle is applied to the balance laws which correspond to non-vanishing multipliers, i.e. to the conservation laws of mass, momentum and energy. This set of equations – Euler gas dynamics equations – represents the equilibrium subsystem of the 13 moments equations.

Several remarks will be given at the end of this analysis. First, hyperbolicity of the system (42) is not easy to be checked. As a first step one may calculate the characteristic speeds in equilibrium state $\mathbf{u}_0 = (\rho, 0, (3k_B/2m)T, 0, 0)$ in the one-dimensional case:

$$\lambda_1 = -1.6503c_S,\ \lambda_2 = -0.6297c_S,\ \lambda_3 = 0,\ \lambda_4 = 0.6297c_S,\ \lambda_5 = 1.6503c_S,$$

where $c_S = \{(3k_B/2m)T\}^{1/2}$ is the speed of sound. It was shown that there exists a region of hyperbolicity in the state space with equilibrium state in its interior. Therefore, the 13 moments model is not globally hyperbolic, but has this property in a certain neighborhood of equilibrium state. Second, source terms suffer from the same deficiency as other continuum theories with closure achieved through the entropy principle: relaxation times τ_σ and τ_q have phenomenological character and can be determined only up to the sign. For further information about their structure one has to divert either to some deeper theoretical arguments (e.g. kinetic theory), or to experimental data. Third, it can be shown by an asymptotic analysis that the balance laws for momentum and energy flux recover classical NSF constitutive relations in the limit of small relaxation times. The importance of this result is twofold: on one hand it supports the statement that NSF theory describes small deviations from the local equilibrium state; on the other hand it shows that NSF constitutive relations are truncated forms of balance laws in which inertial and convective parts are neglected. All these aspects will be re-examined from the standpoint of mixture theory.

3 - Extended thermodynamics of mixtures

By a *mixture* we consider a body composed of identifiable constituents. Once we distinguish them, we can recognize diverse phenomena which occur in mixtures, such as diffusion, dissociation, chemical reactions, energy exchange and dissipation etc. The aim of the mixture theories is to describe these processes, as well as to produce a theoretical framework which unites mechanical and thermodynamical description in the spirit of modern continuum approach [**23**]. One of the important steps towards this goal was made by Green and Naghdi [**39**]. However, a consistent mixture theory was not developed in this sense until the work of Müller [**59**]. Nice account on basic theory, historical development and applications can be found in [**5, 6**]. A comprehensive treatment of the flow modelling and non-equilibrium processes in mixtures, including important mathematical issues, is given by Giovangigli [**30**].

In the study of mixtures different levels of description may be adopted, which are reflected in different choices of the state variables. To get an impression about them, we shall label n different constituents by Greek indices which run from 1 to n, and recognize the following descriptions in the increasing order of complexity:

(1) $(\rho, \mathbf{v}, \varepsilon)$ – constituents are not distinguished; mixture properties are averaged out through the global state variables;

(2) $(\rho_\alpha, \mathbf{v}, \varepsilon)$ – this level of description is the hallmark of classical TIP; as for pure materials, it suffers from the paradox of infinite pulse speeds;

(3) $(\rho_\alpha, \mathbf{v}_\alpha, \varepsilon)$ – this choice of state variables was introduced in extended thermodynamics of mixtures; its proper use removed the paradox of infinite pulse speeds;

(4) $(\rho_\alpha, \mathbf{v}_\alpha, \varepsilon_\alpha)$ – multi-temperature extended model; it brought the mutual exchange of energy between the constituents into focus.

Only at level (1) there is no distinction between the constituents. In all other cases, there is always certain information about the composition, mechanics and thermodynamics of the mixture.

The main goal of this section is to expose the *multi-temperature* (MT) model of mixtures developed within the framework of ET [**69**]. Basic feature of the model is that it ascribes to each constituent its own temperature field T_α. This assumption goes along the basic postulates of rational thermodynamics of mixtures, discussed in the sequel, which introduce the internal energy densities of the constituents as the state variables.

Although the MT model will be built up as a macroscopic one, basic motifs come from deeper levels in the structure of matter. Namely, temperature can be viewed from the two different standpoints: as a macroscopic variable, thermodynamic temperature is an equilibrium quantity; at mesoscopic level, kinetic temperature is a measure of the mean kinetic energy of particles. The latter approach seems to be more appropriate in the description of non-equilibrium processes.

What kind of multiple temperatures do appear in the non-equilibrium processes? Even in single-component gases, multiple temperatures could appear due to violation of the equipartition of energy with respect to the translational degrees of freedom. In such a way the whole tensor of internal energy can be introduced or, more simply, the translational temperatures T_x, T_y and T_z. As a consequence, in propagation of normal shock waves, one can distinguish temperature $T_{\|}$ in the direction of propagation and temperature $T_{\perp}$ in the perpendicular plane. This motivated a BGK–like model in kinetic theory with the anisotropic equilibrium distribution [**46, 4**] and the MT model for continuum and near-continuum flow [**84**]. In the context of polyatomic gases, whose molecules are not spherically symmetric, the non-equilibrium processes are accompanied by an excitation of the non-translational (rotational and vibrational) degrees of freedom [**85, 61, 40**]. New degrees of freedom formally introduce new temperatures. These temperatures are eventually relaxed after certain number of molecular collisions; e.g. the rotational temperature T_{rot} requires about 10 collisions for relaxation, while the vibrational temperature T_{vib} has longer relaxation time. Finally, in mixtures, the constituents with disparate masses eventually reach different kinetic energies (temperatures) in the non-equilibrium processes [**1, 51**]. Typical examples are temperatures of ions (i) and electrons (e) in plasma, $T_e \gg T_i$, and temperatures of atoms in the mixture of inert gases like helium and argon ($m_{\mathrm{He}} \ll m_{\mathrm{Ar}}$). These last examples motivate the study of the multi-temperature mixtures at a macroscopic level.

This section will thus be devoted to the modelling issues in the mixture theory. First, a brief review of the classical theory will be given. Then, rational thermodynamics of mixtures will be described, which provides a general framework for extended thermodynamics of mixtures. Finally, the multi-temperature model will be developed using the principles of ET.

3.1 - *Classical mixture theory*

Classical mixture theory is well developed within TIP [**25**]. Its description is relied on the state variables $\mathbf{u} = (\rho_\alpha, \mathbf{v}, \varepsilon)$, $\alpha = 1, \ldots, n$, which distinguish the constituents only through their mass density contributions and retain the velocity $\mathbf{v}$ and the internal energy ε of the mixture. Governing equations incorporate the mass balance laws for the constituents, which describe their mass rate of change due to mass flux $\rho_\alpha \mathbf{v}_\alpha$ and chemical reactions τ_α:

$$
\begin{aligned}
&\frac{\partial \rho_\alpha}{\partial t} + \operatorname{div}(\rho_\alpha \mathbf{v}_\alpha) = \tau_\alpha, \\
&\frac{\partial (\rho \mathbf{v})}{\partial t} + \operatorname{div}(\rho \mathbf{v} \otimes \mathbf{v} - \mathbf{t}) = \mathbf{0}, \\
&\frac{\partial \left(\frac{1}{2}\rho v^2 + \rho\varepsilon\right)}{\partial t} + \operatorname{div}\left\{\left(\frac{1}{2}\rho v^2 + \rho\varepsilon\right)\mathbf{v} - \mathbf{t}\mathbf{v} + \mathbf{q}\right\} = 0.
\end{aligned}
\tag{44}
$$

The velocities of the constituents $\mathbf{v}_\alpha$ are not state variables, but constitutive quantities. Usually, they enter into the model through the *diffusion fluxes*:

$$\mathbf{J}_\alpha = \rho_\alpha \mathbf{u}_\alpha, \quad \mathbf{u}_\alpha = \mathbf{v}_\alpha - \mathbf{v},$$

where $\mathbf{u}_\alpha$ is the *diffusion velocity*. The Gibbs' relation is extended to take into account the contribution of the constituents:

$$\frac{\mathrm{d}s}{\mathrm{d}t} = \frac{1}{T}\left(\frac{\mathrm{d}\varepsilon}{\mathrm{d}t} - \frac{p}{\rho^2}\frac{\mathrm{d}\rho}{\mathrm{d}t} - \sum_{b=1}^{n-1}(\mu_b - \mu_n)\frac{\mathrm{d}c_b}{\mathrm{d}t}\right)$$

where μ_α are the chemical potentials of the constituents, and $c_\alpha = \rho_\alpha/\rho$ are their mass concentrations.

The constitutive theory based upon restrictions imposed by the entropy inequality yields the following constitutive relations for the heat and diffusion flux:

$$\begin{aligned} \mathbf{q} &= -\frac{1}{T^2} L \operatorname{grad} T - \sum_{c=1}^{n-1} L_c \operatorname{grad}\left(\frac{\mu_c - \mu_n}{T}\right), \\ \mathbf{J}_b &= -\frac{1}{T^2} L_b \operatorname{grad} T - \sum_{c=1}^{n-1} L_{bc} \operatorname{grad}\left(\frac{\mu_c - \mu_n}{T}\right), \end{aligned} \tag{45}$$

$b = 1, \dots, n-1$, while equations for the stress deviator and the dynamic pressure have the same form as in NSF theory for single-component fluids. Equation $(45)_1$ is generalized Fourier law, while equations $(45)_2$ represent generalized Fick's law. L–coefficients in (45) are the phenomenological coefficients. Constitutive relations generalize the classical laws of the heat conduction and diffusion through cross-effects – influence of the concentration gradient on the heat flux (Dufour effect) and the temperature gradient on the diffusion flux (Soret effect).

3.2 - *Rational thermodynamics of mixtures*

A new approach to the thermodynamics of mixtures given by Müller perfectly fitted within the framework of *rational thermodynamics*. The formal structure of the model is well described by the *metaphysical principles*, i.e. postulates put forward by Truesdell [**80**], which read:

(I) All properties of the mixture must be mathematical consequences of properties of the constituents.

(II) So as to describe the motion of a constituent, we may in imagination isolate it from the rest of the mixture, provided we allow properly for the actions of the other constituents upon it.

(III) The motion of the mixture is governed by the same equations as is a single body.

To elaborate them, we shall start with the first principle. If ρ_α, $\mathbf{v}_\alpha$ and ε_α determine the state of the constituents, then the state (properties) of the mixture ρ, $\mathbf{v}$ and ε ought to be related to them through the functional relations:

$$\rho = \hat{\rho}(\rho_\alpha, \mathbf{v}_\alpha, \varepsilon_\alpha), \quad \mathbf{v} = \hat{\mathbf{v}}(\rho_\alpha, \mathbf{v}_\alpha, \varepsilon_\alpha), \quad \varepsilon = \hat{\varepsilon}(\rho_\alpha, \mathbf{v}_\alpha, \varepsilon_\alpha). \tag{46}$$

The second principle states that the rate of change of the state variables $(\rho_\alpha, \mathbf{v}_\alpha, \varepsilon_\alpha)$ is determined by the same physical laws – balance laws of mass, momentum and energy – which nevertheless take into account the mutual interaction of the constituents through the appropriate source terms τ_α, $\mathbf{m}_\alpha$ and e_α:

$$\begin{aligned}
&\frac{\partial \rho_\alpha}{\partial t} + \mathrm{div}(\rho_\alpha \mathbf{v}_\alpha) = \tau_\alpha,\\
&\frac{\partial (\rho_\alpha \mathbf{v}_\alpha)}{\partial t} + \mathrm{div}(\rho_\alpha \mathbf{v}_\alpha \otimes \mathbf{v}_\alpha - \mathbf{t}_\alpha) = \mathbf{m}_\alpha,\\
&\frac{\partial\left(\frac{1}{2}\rho_\alpha v_\alpha^2 + \rho_\alpha \varepsilon_\alpha\right)}{\partial t} + \mathrm{div}\left\{\left(\frac{1}{2}\rho_\alpha v_\alpha^2 + \rho_\alpha \varepsilon_\alpha\right)\mathbf{v}_\alpha - \mathbf{t}_\alpha \mathbf{v}_\alpha + \mathbf{q}_\alpha\right\} = e_\alpha.
\end{aligned} \tag{47}$$

This principle reflects the ideas of classical dynamics of particle systems (and kinetic theory of gases). Finally, the third principle postulates that the state variables for the mixture evolve in accordance with the same equations as if it were a single body:

$$\begin{aligned}
&\frac{\partial \rho}{\partial t} + \mathrm{div}(\rho \mathbf{v}) = 0,\\
&\frac{\partial (\rho \mathbf{v})}{\partial t} + \mathrm{div}(\rho \mathbf{v} \otimes \mathbf{v} - \mathbf{t}) = \mathbf{0},\\
&\frac{\partial\left(\frac{1}{2}\rho v^2 + \rho \varepsilon\right)}{\partial t} + \mathrm{div}\left\{\left(\frac{1}{2}\rho v^2 + \rho \varepsilon\right)\mathbf{v} - \mathbf{t}\mathbf{v} + \mathbf{q}\right\} = 0.
\end{aligned} \tag{48}$$

In Truesdell's own words [**80**], "in its motion as a whole a body does not know whether it is a mixture or not".

To all the formal statements (46)-(48) one more has to be added. The mutual interactions τ_α, $\mathbf{m}_\alpha$ and e_α describe the processes of mass, momentum and energy exchanges among the constituents. However, these quantities has to be conserved when the mixture is regarded as a whole. Therefore, the *axioms of balance for mixtures* states:

$$\sum_{\alpha=1}^{n} \tau_\alpha = 0, \quad \sum_{\alpha=1}^{n} \mathbf{m}_\alpha = \mathbf{0}, \quad \sum_{\alpha=1}^{n} e_\alpha = 0, \tag{49}$$

without which it would have been impossible to get (48). To recover the conservation laws for the mixture, one has to sum up the balance laws for the constituents (47), exploit the axiom of balance (49), and properly define the state variables and fluxes of the mixture in terms of the properties of the constituents:

$$
\begin{aligned}
&\rho = \sum_{\alpha=1}^{n} \rho_\alpha, \quad \mathbf{v} = \frac{1}{\rho}\sum_{\alpha=1}^{n} \rho_\alpha \mathbf{v}_\alpha, \quad \mathbf{u}_\alpha = \mathbf{v}_\alpha - \mathbf{v}, \\
&\varepsilon_I = \frac{1}{\rho}\sum_{\alpha=1}^{n} \rho_\alpha \varepsilon_\alpha, \quad \varepsilon = \varepsilon_I + \frac{1}{2\rho}\sum_{\alpha=1}^{n} \rho_\alpha u_\alpha^2, \\
&\mathbf{t} = \sum_{\alpha=1}^{n} (\mathbf{t}_\alpha - \rho_\alpha \mathbf{u}_\alpha \otimes \mathbf{u}_\alpha), \\
&\mathbf{q} = \sum_{\alpha=1}^{n} \left\{ \mathbf{q}_\alpha + \rho_\alpha \left(\varepsilon_\alpha + \frac{1}{2} u_\alpha^2 \right) \mathbf{u}_\alpha - \mathbf{t}_\alpha \mathbf{u}_\alpha \right\},
\end{aligned}
\tag{50}
$$

where $\mathbf{u}_\alpha$ is the diffusion velocity of the constituent, and ε_I is the intrinsic part of internal energy density. Note that the internal energy density ε, the momentum flux (stress tensor) $\mathbf{t}$ and the internal energy flux (heat flux) $\mathbf{q}$ are not simple sums of the corresponding properties of the constituents, but take into account relative motion of the constituents through the diffusion velocity.

Final step in modelling the thermomechanics of mixtures is the choice of governing equations. The state of the mixture is described by $5n$ variables $(\rho_\alpha, \mathbf{v}_\alpha, \varepsilon_\alpha)$ and it seems at first sight that the balance laws (47) provide the desired model. However, this is not the only choice since one may use the properties of the mixture as state variables at the expense of dropping the state variables for one constituent (say n) from the list, $(\rho, \mathbf{v}, \varepsilon, \rho_b, \mathbf{v}_b, \varepsilon_b)$, $b = 1, \dots, n-1$. Consequently, one should replace the balance laws for the n^{th} constituent with conservation laws for the mixture (48), so that the governing equations read:

$$
\begin{aligned}
&\frac{\partial \rho}{\partial t} + \operatorname{div}(\rho \mathbf{v}) = 0, \\
&\frac{\partial (\rho \mathbf{v})}{\partial t} + \operatorname{div}(\rho \mathbf{v} \otimes \mathbf{v} - \mathbf{t}) = \mathbf{0}, \\
&\frac{\partial \left(\frac{1}{2}\rho v^2 + \rho\varepsilon\right)}{\partial t} + \operatorname{div}\left\{ \left(\frac{1}{2}\rho v^2 + \rho\varepsilon \right) \mathbf{v} - \mathbf{t}\mathbf{v} + \mathbf{q} \right\} = 0, \\
&\frac{\partial \rho_b}{\partial t} + \operatorname{div}(\rho_b \mathbf{v}_b) = \tau_b, \\
&\frac{\partial (\rho_b \mathbf{v}_b)}{\partial t} + \operatorname{div}(\rho_b \mathbf{v}_b \otimes \mathbf{v}_b - \mathbf{t}_b) = \mathbf{m}_b, \\
&\frac{\partial \left(\frac{1}{2}\rho_b v_b^2 + \rho_b\varepsilon_b\right)}{\partial t} + \operatorname{div}\left\{ \left(\frac{1}{2}\rho_b v_b^2 + \rho_b\varepsilon_b \right) \mathbf{v}_b - \mathbf{t}_b\mathbf{v}_b + \mathbf{q}_b \right\} = e_b.
\end{aligned}
\tag{51}
$$

In conclusion, we have to mention that a crucial step towards the modelling of mixtures in ET was made by Müller [**59**] who extended the list of state variables of classical TIP by including the velocities of the constituents, $(\rho, \mathbf{v}, \varepsilon, \rho_b, \mathbf{v}_b)$, but not taking their internal energies, and thus creating the *multi-velocity* model. This extension led to a hyperbolic model of mixtures, since non-local constitutive relations for diffusion fluxes were replaced by the balance laws for momenta of the constituents. Moreover, it was shown that these equations recover the generalized Fick's law $(45)_2$ in the limit of small relaxation time [**44**]. An interesting interpretation of these equations was given by Ruggeri [**67**] in the case of binary mixture of Euler fluids. Namely, the mixture heat flux $\mathbf{q}$ is proportional to the relative velocity of the constituents $\mathbf{w} = \mathbf{v}_1 - \mathbf{v}_2$. The governing equations can then be recast into the form which describes the binary mixture as a single heat conducting fluid with the structure, brought in through concentration variable. This set of equations also generalizes the Cattaneo equation in which the notion of thermal inertia is properly explained.

3.3 - *Multi-temperature mixture of Euler fluids*

Our main concern will be the MT model for mixtures of Euler fluids [**69**]. At the beginning of this Section we gave the physical motivation for introduction of the multiple temperatures, and provided the conceptual framework through the metaphysical principles and corresponding mathematical consequences. However, we still need a proper closure of the model (47), or (51). To that end we shall rely on the fundamental principles of ET – the Galilean invariance and the entropy principle.

The relativity principle (Galilean invariance of governing equations) implies restrictions on the velocity dependence of densities, fluxes and source terms. The balance laws (51) obviously possess the conservative form (35) to which we can apply the Galilean invariance conditions (37). For the vector of densities $\mathbf{F}^0$, and its intrinsic part $\hat{\mathbf{F}}^0$:

$$\mathbf{F}^0 = \begin{pmatrix} \rho \\ \rho v^k \\ \frac{1}{2}\rho v^2 + \rho\varepsilon \\ \rho_b \\ \rho_b\left(v^k + u_b^k\right) \\ \frac{1}{2}\rho_b\left(\mathbf{v} + \mathbf{u}_b\right)^2 + \rho_b\varepsilon_b \end{pmatrix}, \quad \hat{\mathbf{F}}^0 = \begin{pmatrix} \rho \\ 0^k \\ \rho\varepsilon \\ \rho_b \\ \rho_b u_b^k \\ \frac{1}{2}\rho_b u_b^2 + \rho_b\varepsilon_b \end{pmatrix},$$

one can easily recover the transformation matrix $\mathbf{X}(\mathbf{v})$ which fulfills $(37)_1$:

$$\mathbf{X}(\mathbf{v}) = \begin{pmatrix} 1 & 0_k & 0 & 0 & 0_k & 0 \\ v^j & \delta^{jk} & 0^j & 0^j & 0^{jk} & 0^j \\ \frac{1}{2}v^2 & v_k & 1 & 0 & 0_k & 0 \\ 0 & 0_k & 0 & 1 & 0_k & 0 \\ 0^j & 0^{jk} & 0^j & v^j & \delta^{jk} & 0^j \\ 0 & 0_k & 0 & \frac{1}{2}v^2 & v_k & 1 \end{pmatrix}. \tag{52}$$

It also satisfies the condition $(37)_2$ for the vector of non-convective fluxes $\mathbf{G}^i$ and its intrinsic part $\hat{\mathbf{G}}^i$:

$$\mathbf{G}^i = \begin{pmatrix} 0^i \\ -t^{ij} \\ -t^{ik}v_k + q^i \\ \vdots \end{pmatrix}, \quad \hat{\mathbf{G}}^i = \begin{pmatrix} 0^i \\ -t^{ij} \\ q^i \\ \vdots \end{pmatrix}.$$

The main benefit of the Galilean invariance comes from revealing the velocity dependence of source terms $\mathbf{P}$. For:

$$\mathbf{P} = \begin{pmatrix} 0 \\ 0^k \\ 0 \\ \tau_b \\ m_b^k \\ e_b \end{pmatrix}, \quad \hat{\mathbf{P}}(\mathbf{w}) = \begin{pmatrix} 0 \\ 0^k \\ 0 \\ \hat{\tau}_b \\ \hat{m}_b^k \\ \hat{e}_b \end{pmatrix},$$

$(37)_3$ yields the following relation:

$$\begin{aligned} \tau_b &= \hat{\tau}_b, \\ \mathbf{m}_b &= \hat{\tau}_b \mathbf{v} + \hat{\mathbf{m}}_b, \\ e_b &= \hat{\tau}_b \frac{v^2}{2} + \hat{\mathbf{m}}_b \cdot \mathbf{v} + \hat{e}_b \,. \end{aligned} \tag{53}$$

In further analysis of the closure problem we shall restrict to Euler fluids:

$$\mathbf{t}_\alpha = -p_\alpha \mathbf{I}, \quad \mathbf{q}_\alpha = \mathbf{0}, \tag{54}$$

and reduced form of the momentum and energy flux for the mixture which now depend on the diffusion velocities solely:

$$\mathbf{t} = -p\,\mathbf{I} - \sum_{\alpha=1}^{n} \rho_\alpha \mathbf{u}_\alpha \otimes \mathbf{u}_\alpha, \quad p = \sum_{\alpha=1}^{n} p_\alpha,$$
$$\mathbf{q} = \sum_{\alpha=1}^{n} \left\{ \rho_\alpha \left(\varepsilon_\alpha + \frac{1}{2} u_\alpha^2 \right) + p_\alpha \right\} \mathbf{u}_\alpha,$$

where p is the total pressure. Even more, we shall assume that the partial pressures p_α and the partial internal energy densities ε_α are determined by the thermal and caloric equations of state of ideal gases:

$$p_\alpha = \rho_\alpha \frac{k_B}{m_\alpha} T_\alpha, \quad \varepsilon_\alpha = \frac{k_B}{m_\alpha(\gamma_\alpha - 1)} T_\alpha. \tag{55}$$

The main consequence of these assumptions is *global hyperbolicity* of the MT model for mixtures. It can be proved by calculating the characteristic speeds for the system (47) in the case of Euler fluids. It consists of n blocks of Euler gas dynamics equations for the constituents. Since characteristic speeds do not depend on source terms, they can be calculated almost trivially:

$$\lambda_\alpha^{(1)} = v_{\alpha n} - a_\alpha, \quad \lambda_\alpha^{(2,3,4)} = v_{\alpha n}, \quad \lambda_\alpha^{(5)} = v_{\alpha n} + a_\alpha, \tag{56}$$
$$v_{\alpha n} = \mathbf{v}_\alpha \cdot \mathbf{n}, \quad a_\alpha = \left\{ \gamma_\alpha \frac{k_\mathrm{B}}{m_\alpha} T_\alpha \right\}^{1/2},$$

where $v_{\alpha n}$ is the normal component to the wave front of the particle velocity of constituent α, $\mathbf{n}$ is the unit normal to the wave front and a_α is the local speed of sound of the constituent α. Characteristic speeds of the system (51) are the same as the ones of (47) since they are obtained by the transformation of variables [**27**].

The second step in the closure procedure is the application of the entropy inequality:

$$\partial_t h^0 + \partial_i \left(h^0 v^i + \Psi^i \right) = \Sigma \leq 0,$$

where h^0 is negative entropy density of the mixture, defined as:

$$h^0 = -\rho s = -\sum_{\alpha=1}^{n} \rho_\alpha s_\alpha,$$

and Ψ^i are the components of the non-convective entropy flux. The entropy inequality imposes restrictions on the source terms and help us to determine at least some of their possible functional forms. Using the method of Lagrange multipliers it can be applied either to (47), or to (51). The detailed procedure can be found in [**69**], whereas we shall concentrate here on the most important results. By applying the integrability relations (40) to the system of balance laws (47) the following set of Lagrange multipliers is obtained:

$$\tilde{\boldsymbol{\Lambda}} = \left(\tilde{\Lambda}^{\rho_\alpha}, \tilde{\boldsymbol{\Lambda}}^{\mathbf{v}_\alpha}, \tilde{\Lambda}^{\varepsilon_\alpha}\right) = \left(\frac{1}{T_\alpha}\left(\mu_\alpha - \frac{1}{2}v_\alpha^2\right), \frac{\mathbf{v}_\alpha}{T_\alpha}, -\frac{1}{T_\alpha}\right),$$

where μ_α are chemical potentials of the constituents. The Lagrange multipliers for the composite system (51) are determined by the following relations:

$$\begin{aligned}
&\boldsymbol{\Lambda} = \left(\Lambda^{\rho}, \boldsymbol{\Lambda}^{\mathbf{v}}, \Lambda^{\varepsilon}, \Lambda^{\rho_b}, \boldsymbol{\Lambda}^{\mathbf{v}_b}, \Lambda^{\varepsilon_b}\right),\\
&\Lambda^{\rho} = \tilde{\Lambda}^{\rho_n}, \quad \boldsymbol{\Lambda}^{\mathbf{v}} = \tilde{\boldsymbol{\Lambda}}^{\mathbf{v}_n}, \quad \Lambda^{\varepsilon} = \tilde{\Lambda}^{\varepsilon_n},\\
&\Lambda^{\rho_b} = \tilde{\Lambda}^{\rho_b} - \tilde{\Lambda}^{\rho_n}, \quad \boldsymbol{\Lambda}^{\mathbf{v}_b} = \tilde{\boldsymbol{\Lambda}}^{\mathbf{v}_b} - \tilde{\boldsymbol{\Lambda}}^{\mathbf{v}_n}, \quad \Lambda^{\varepsilon_b} = \tilde{\Lambda}^{\varepsilon_b} - \tilde{\Lambda}^{\varepsilon_n}.
\end{aligned}$$

An important feature of the main field (the multipliers) is the relation to its intrinsic (velocity independent) part through the matrix of transformation $\mathbf{X}$, $\hat{\boldsymbol{\lambda}} = \boldsymbol{\lambda}\mathbf{X}$. Therefore, the residual inequality can be reduced to:

$$\Sigma = \boldsymbol{\Lambda} \cdot \mathbf{P} = \hat{\boldsymbol{\Lambda}} \cdot \hat{\mathbf{P}} \leq 0.$$

In such a way we obtain:

$$\begin{aligned}
\Sigma &= \sum_{b=1}^{n-1}\left(\hat{\Lambda}^{\rho_b}\hat{\tau}_b + \hat{\boldsymbol{\Lambda}}^{\mathbf{v}_b} \cdot \hat{\mathbf{m}}_b + \hat{\Lambda}^{\varepsilon_b}\hat{e}_b\right)\\
&= \sum_{b=1}^{n-1}\left\{\left(\frac{\mu_b - \frac{1}{2}u_b^2}{T_b} - \frac{\mu_n - \frac{1}{2}u_n^2}{T_n}\right)\hat{\tau}_b\right.\\
&\quad \left. + \left(\frac{\mathbf{u}_b}{T_b} - \frac{\mathbf{u}_n}{T_n}\right) \cdot \hat{\mathbf{m}}_b + \left(-\frac{1}{T_b} + \frac{1}{T_n}\right)\hat{e}_b\right\} \leq 0.
\end{aligned} \tag{57}$$

The residual inequality imposes a restriction on the structure of source terms – they must have the form which does not violate it for any thermodynamic process. The simplest way to obey this condition is to choose the source terms such that the entropy production rate Σ becomes a negative semi-definite quadratic form, i.e. to express them as linear combinations of the Lagrange multipliers. This can be done in two ways. Simpler form of the source terms read:

$$\begin{aligned}
\hat{\tau}_b &= -\sum_{c=1}^{n-1}\varphi_{bc}\left(\frac{\mu_c - \frac{1}{2}u_c^2}{T_c} - \frac{\mu_n - \frac{1}{2}u_n^2}{T_n}\right),\\
\hat{\mathbf{m}}_b &= -\sum_{c=1}^{n-1}\psi_{bc}\left(\frac{\mathbf{u}_c}{T_c} - \frac{\mathbf{u}_n}{T_n}\right),\\
\hat{e}_b &= -\sum_{c=1}^{n-1}\theta_{bc}\left(-\frac{1}{T_c} + \frac{1}{T_n}\right),
\end{aligned} \tag{58}$$

and they do not contain cross-coupling. The phenomenological coefficients φ_{bc}, ψ_{bc} and θ_{bc} constitute positive definite matrix functions. The source terms which take into account cross-couplings have the form:

$$\hat{\tau}_b = -\sum_{c=1}^{n-1}\Big(\varphi^{\tau}_{bc}\hat{\Lambda}^{\rho_c} + \theta^{\tau}_{bc}\hat{\Lambda}^{\varepsilon_c}\Big),$$

$$\hat{\mathbf{m}}_b = -\sum_{c=1}^{n-1}\psi_{bc}\hat{\boldsymbol{\Lambda}}^{\mathbf{v}_b}, \quad \hat{e}_b = -\sum_{c=1}^{n-1}\Big(\varphi^{\varepsilon}_{bc}\hat{\Lambda}^{\rho_c} + \theta^{\varepsilon}_{bc}\hat{\Lambda}^{\varepsilon_c}\Big).$$

In most of the applications in the sequel we shall analyze the non-reacting mixtures for which $\hat{\tau}_\alpha = 0$. As in other models derived within the framework of ET, phenomenological coefficients cannot be determined. This limitation will be overcome by making proper relations with experimental data or kinetic theory.

4 - Analysis of multi-temperature mixtures

The MT model of mixtures was built upon the principles of extended thermodynamics, relativity and entropy principle, with the use of basic postulates of rational thermodynamics, i.e. the metaphysical principles. Although the model is closed, there are still open questions to be answered. We shall, therefore, turn our attention to the problem of defining the average temperature of the mixture and the appropriate structure of total pressure. Furthermore, the classical limit of the MT model will be revealed, as well as its relation with the Maxwell-Stefan diffusion model, particularly important in phenomena in which non-Fickian diffusion occurs. Finally, an indication will be given about the validity of the model. Most of the results in this section can be found in [**72, 70, 71**], while the Maxwell-Stefan diffusion is discussed in this context for the first time.

4.1 - *Equilibrium, average temperature, entropy and dynamic pressure*

In the sequel, we shall restrict our attention to the non-reacting mixtures, $\tau_\alpha = 0$. The residual inequality (57) in this case reads:

$$\Sigma = \sum_{b=1}^{n-1}\Big(\hat{\boldsymbol{\Lambda}}^{\mathbf{v}_b}\cdot\hat{\mathbf{m}}_b + \hat{\Lambda}^{\varepsilon_b}\hat{e}_b\Big) \le 0, \tag{59}$$

and one possible form of source terms, which satisfy it for any thermodynamic process, is the following:

$$\hat{\mathbf{m}}_b = -\sum_{c=1}^{n-1} \psi_{bc}\left(\frac{\mathbf{u}_c}{T_c} - \frac{\mathbf{u}_n}{T_n}\right), \quad \hat{e}_b = -\sum_{c=1}^{n-1} \theta_{bc}\left(-\frac{1}{T_c} + \frac{1}{T_n}\right), \tag{60}$$

where ψ_{bc} and θ_{bc} are positive definite matrix functions. The entropy inequality is a statement about dissipation, and the entropy production rate Σ presents its measure. The source terms (60) then provide an information about the cause of dissipation in MT mixtures. These are mutual exchange of momentum ($\hat{\mathbf{m}}_b$) and mutual exchange of internal energy ($\hat{e}_b$) between the constituents. Note that only mutual interactions appear as sources of dissipation since we neglected internal dissipation within the constituents (due to viscosity and heat conductivity) assumed to be Euler fluids.

Equilibrium state is the state in which the entropy production vanishes, $\Sigma = 0$. Since we took the source terms as linear combinations of the Lagrange multipliers, vanishing of the entropy production can be achieved through vanishing of the source terms. Direct consequences are the following:

$$\begin{aligned} \hat{\mathbf{m}}_b = \mathbf{0} \quad &\Rightarrow \quad \mathbf{u}_\alpha = \mathbf{v}_\alpha - \mathbf{v} = \mathbf{0}, \\ \hat{e}_b = 0 \quad &\Rightarrow \quad T_\alpha = T, \end{aligned} \tag{61}$$

i.e. the velocities and the temperatures of the constituents are the same. This motivates introduction of new variables which describe the non-equilibrium state in a more natural way – the concentration variable c_α, the diffusion velocity $\mathbf{u}_\alpha$ and the diffusion temperature Θ_α:

$$c_\alpha = \frac{\rho_\alpha}{\rho}, \quad \mathbf{u}_\alpha = \mathbf{v}_\alpha - \mathbf{v}, \quad \Theta_\alpha = T_\alpha - T. \tag{62}$$

From the definitions of ρ and $\mathbf{v}$, (50) the following restrictions on new variables emerge:

$$\sum_{\alpha=1}^{n} c_\alpha = 1, \quad \sum_{\alpha=1}^{n} \rho_\alpha \mathbf{u}_\alpha = \mathbf{0}. \tag{63}$$

Since $\mathbf{u}_\alpha$ and Θ_α describe departure of the velocities and temperatures from certain mean values (not necessarily equilibrium ones), we can propose the following change of variables:

$$(\rho_\alpha, \mathbf{v}_\alpha, T_\alpha) \to (\rho, \mathbf{v}, T, c_b, \mathbf{u}_b, \Theta_b).$$

However, we still do not have a proper definition of the average mixture temperature T.

Average temperature can be defined in different ways. For a two-component system at kinetic level it can be defined in terms of the algebraic average of the mean square velocities for the two distributions [**28**]. At macroscopic level it can be defined through the total pressure, i.e. Dalton's law. It is nevertheless deeply physically motivated to use the energy definition of the average temperature based upon intrinsic (thermal) part ε_I of internal energy (50), $\rho\varepsilon_I = \sum_{\alpha=1}^{n}\rho_\alpha\varepsilon_\alpha$. Intrinsic part of the internal energy is a global (mixture) state variable which is supposed to depend on the (mean) mixture temperature T, $\varepsilon_I = \varepsilon_I(\rho_\alpha, T)$. On the other hand, internal energies of the constituents ε_α are functions of their temperatures T_α, $\varepsilon_\alpha = \varepsilon_\alpha(\rho_\alpha, T_\alpha)$. Since the average temperature T reflects the mean kinetic energy of the particles in the whole mixture, it must be recovered from the internal energies of the constituents as if they all have the same temperature:

$$\rho\varepsilon_I(\rho_\alpha, T) = \sum_{\alpha=1}^{n}\rho_\alpha\varepsilon_\alpha(\rho_\alpha, T) = \sum_{\alpha=1}^{n}\rho_\alpha\varepsilon_\alpha(\rho_\alpha, T_\alpha). \tag{64}$$

This definition is obviously implicit. The explicit form of the average temperature can be obtained only in linear approximation:

$$T = \frac{\sum_{\alpha=1}^{n}\rho_\alpha c_{V\alpha}T_\alpha}{\sum_{\alpha=1}^{n}\rho_\alpha c_{V\alpha}}, \quad c_{V\alpha} = \frac{\partial\varepsilon_\alpha(\rho_\alpha, T)}{\partial T_\alpha}. \tag{65}$$

The linear approximation implies also the restriction on the diffusion temperatures Θ_α:

$$\sum_{\alpha=1}^{n}\rho_\alpha c_{V\alpha}\Theta_\alpha = 0.$$

This definition of the average temperature does not take into account the dynamic (diffusive) contribution to the internal energy. This choice can be defended on purely theoretical ground [**15**], or through the measure of its contribution in the non-equilibrium processes [**56**], which will be done in the next section.

The use of (64) gives rise to direct proof that the entropy attains its maximum in equilibrium. Starting from the definition of the entropy of the mixture, $\rho s = \sum\rho_a s_\alpha$, we may expand it in the neighborhood of equilibrium state $T_\alpha = T$:

$$\begin{aligned}\rho s = \sum_{\alpha=1}^{n}\rho_\alpha s_\alpha(\rho_\alpha, T) + \sum_{\alpha=1}^{n}\rho_\alpha\frac{\partial s_\alpha}{\partial T_\alpha}(\rho_\alpha, T)\Theta_\alpha \\ +\frac{1}{2}\sum_{\alpha=1}^{n}\rho_\alpha\frac{\partial^2 s_\alpha}{\partial T_\alpha^2}(\rho_\alpha, T)\Theta_\alpha^2 + O(\Theta_\alpha^3).\end{aligned}$$

The same can be done with the definition of the average temperature (64):

$$\sum_{\alpha=1}^{n}\rho_\alpha\frac{\partial\varepsilon_\alpha}{\partial T_\alpha}(\rho_\alpha, T)\Theta_\alpha = -\frac{1}{2}\sum_{\alpha=1}^{n}\rho_\alpha\frac{\partial^2\varepsilon_\alpha}{\partial T_\alpha^2}(\rho_\alpha, T)\Theta_\alpha^2 + O(\Theta_\alpha^3).$$

Since we are restricted to Euler fluids, we may exploit the Gibbs' relation for the constituents:

$$T_\alpha \mathrm{d}s_\alpha = \mathrm{d}\varepsilon_\alpha - \frac{p_\alpha}{\rho_\alpha^2}\mathrm{d}\rho_\alpha,$$

to obtain the following relations in equilibrium:

$$\begin{aligned}\frac{\partial s_\alpha}{\partial T_\alpha}(\rho_\alpha, T) &= \frac{1}{T}\frac{\partial \varepsilon_\alpha}{\partial T_\alpha}(\rho_\alpha, T) = \frac{c_{V\alpha}}{T},\\ \frac{\partial^2 s_\alpha}{\partial T_\alpha^2}(\rho_\alpha, T) &= -\frac{1}{T^2}\frac{\partial \varepsilon_\alpha}{\partial T_\alpha}(\rho_\alpha, T) + \frac{1}{T}\frac{\partial^2 \varepsilon_\alpha}{\partial T_\alpha^2}(\rho_\alpha, T),\end{aligned}$$

and eventually obtain the following expression for the entropy in the neighborhood of equilibrium:

$$\rho s = \sum_{\alpha=1}^{n} \rho_\alpha s_\alpha(\rho_\alpha, T) - \frac{1}{2T^2}\sum_{\alpha=1}^{n} \rho_\alpha c_{V\alpha} \Theta_\alpha^2 + O(\Theta_\alpha^3). \tag{66}$$

Since $c_{V\alpha} > 0$, there exists a neighborhood of the equilibrium state $\Theta_\alpha = 0$ in which the non-equilibrium part of the total entropy is negative definite quadratic form of Θ_α, and thus the entropy of the mixture reaches its local maximum in equilibrium. This estimate is a consequence of particular definition of the average temperature (64) and cannot be obtained in such a direct way using other definitions.

An interesting observation can be given about the total pressure of the mixture, $p = \sum p_\alpha(\rho_\alpha, T_\alpha)$. It can be expanded in the neighborhood of equilibrium state $T_\alpha = T$ ($\Theta_\alpha = 0$) to obtain:

$$p = p_0 + \pi_\theta(\rho_\alpha, T, \Theta_b), \quad p_0 = \sum_{\alpha=1}^{n} p_\alpha(\rho_\alpha, T),$$

where p_0 represents the equilibrium pressure and $\pi_\theta(\rho_\alpha, T, \Theta_b)$ is the non-equilibrium part, the so-called *dynamic pressure*. The notion of dynamic pressure is usually related to the excess of the trace of stress tensor from the hydrostatic pressure. Classical NSF theory connects it to the bulk viscosity of the fluid [**25**], and thus to the momentum transport. In contrast to that description, the dynamic pressure is here related to thermal non-equilibrium, i.e. it appears as a consequence of the non-zero diffusion temperature Θ_α. It is easy to show that the dynamic pressure can be expressed in the first approximation as:

$$\pi_\theta = \sum_{b=1}^{n-1} r_b \Theta_b, \quad r_b = \frac{1}{\rho_n c_{Vn}}\left\{\rho_n c_{Vn}\frac{\partial p_b}{\partial T_b}(\rho_b, T) - \rho_b c_{Vb}\frac{\partial p_n}{\partial T_n}(\rho_n, T)\right\},$$

while for the mixture of ideal gases it reads:

$$\pi_\theta = \sum_{b=1}^{n-1} \rho_b c_{Vb}(\gamma_b - \gamma_n)\Theta_b.$$

Note that it vanishes (at least theoretically) when the mixture is consisted of molecularly similar constituents, with the same ratio of specific heats, $\gamma_b = \gamma_n$.

4.2 - *Classical limit of the MT mixture*

Extended models tend to describe the non-equilibrium processes in a more elaborate way than the classical ones. This usually leads to a greater complexity in the mathematical structure. To compare the extended model with the classical one, the process of reduction is needed. One possible procedure was indicated by the Chapman-Enskog expansion used in kinetic theory of gases. It is relied on the existence of a small parameter and an asymptotic expansion of both the solution and the macroscopic equations. A similar procedure, *Maxwellian iteration*, can be established for macroscopic equations of extended models. It was, actually, the way in which the classical NSF constitutive relations were recovered from the balance laws (42). The procedure was established by Ikenberry and Truesdell [47] and successfully applied in many circumstances in continuum mechanics as a sort of macroscopic Chapman-Enskog procedure, i.e. an asymptotic expansion in powers of relaxation times.

To grasp the idea, before embarking to the analysis of mixtures, consider the system of 2 × 2 balance laws in one space dimension:

$$\begin{aligned} &\partial_t u + \partial_x f(u,v) = 0, \\ &\partial_t v + \partial_x g(u,v) = -\frac{1}{\tau}(v - h(u)), \end{aligned} \tag{67}$$

where τ denotes the small parameter – relaxation time, u can be regarded as an equilibrium variable, whereas v is a non-equilibrium one, $(67)_2$ being its governing equation. Relation $v_E = h(u)$ determines the equilibrium manifold on which the source term in $(67)_2$ vanishes, and the system is reduced to a conservation law:

$$\partial_t u + \partial_x F(u) = 0, \quad F(u) = f(u, h(u)). \tag{68}$$

Equilibrium value of v is treated as zero$-th$ iteration, $v^{(0)} = v_E = h(u)$. First iteration $v^{(1)}$ is calculated by plugging $v^{(0)}$ into the left-hand side of $(67)_2$, and $v^{(1)}$ into its right-hand side. The time derivative of u is replaced using $(67)_1$ with $v = v^{(0)}$. As an outcome, one obtains:

$$\begin{aligned} v^{(1)} = h(u) - \tau\{ &g_u(u,h(u)) + h'(u) g_v(u,h(u)) \\ &- h'(u)[f_u(u,h(u)) + h'(u) f_v(u,h(u))]\}\partial_x u. \end{aligned} \tag{69}$$

First iteration (69) shows that the deviation from the equilibrium, $v^{(1)} - h(u)$, is proportional to the gradient of equilibrium variable.

The procedure described above can be applied to the MT model of mixtures (51). The role of non-equilibrium variables is reserved for the diffusion fluxes $\mathbf{J}_\alpha = \rho_\alpha \mathbf{u}_\alpha$, and the diffusion temperatures Θ_α. Taking into account the source terms (58), their equilibrium values (zero$-th$ iteration) are:

$$\begin{aligned} \mathbf{v}_\alpha^{(0)} &= \mathbf{v} \ \ \Rightarrow \mathbf{u}_\alpha^{(0)} = \mathbf{0}, \mathbf{J}_\alpha^{(0)} = \mathbf{0}, \\ T_\alpha^{(0)} &= T \ \Rightarrow \ \Theta_\alpha^{(0)} = 0. \end{aligned}$$

Omitting the details of calculation, which can be found in [**72**], first iteration of the source term $(60)_1$ in the momentum balance laws $(51)_5$ is

$$\hat{\mathbf{m}}_b^{(1)} = -\frac{1}{T}\sum_{d=1}^{n-1} \psi_{bd}^{(0)} \left(\sum_{a=1}^{n-1} F_{ad} \mathbf{J}_a^{(1)} \right), \quad F_{ad} = \frac{\delta_{ad}}{\rho_a} - \frac{1}{\rho_n}.$$

After some transformations, the following expression for the diffusion fluxes is obtained:

$$\mathbf{J}_a^{(1)} = \sum_{b=1}^{n-1} L_{ab} \operatorname{grad}\left(\frac{\mu_b - \mu_n}{T} \right) + L_a \operatorname{grad}\left(\frac{1}{T} \right), \tag{70}$$

where the phenomenological coefficients have the form:

$$\begin{aligned} L_{ab} &= -T^2 \Big[\mathbf{F}^{-1} \psi^{-1} \mathbf{F}^{-1} \Big]_{ab}^{(0)}, \\ L_a &= \sum_{b=1}^{n-1} (-T^3) \Big[\mathbf{F}^{-1} \psi^{-1} \mathbf{F}^{-1} \Big]_{ab}^{(0)} \left\{ T \frac{\partial}{\partial T} \left(\frac{\mu_b - \mu_n}{T} \right) - \frac{\partial}{\partial T} \left(\frac{p_b}{\rho_b} - \frac{p_n}{\rho_n} \right) \right\}^{(0)}. \end{aligned}$$

It is inevitable that (70) has the same form as the diffusion flux of classical TIP [**25**], as well as first Maxwellian iteration obtained for the single-temperature mixtures [**60**].

Turning our attention to the diffusion temperatures, we derive first iteration of the source terms $(60)_2$ in the energy balance laws $(51)_6$:

$$\hat{e}_b^{(1)} = -\frac{1}{T^2} \sum_{c=1}^{n-1} \theta_{bc}^{(0)} \sum_{d=1}^{n-1} \left(\Phi_{cd} \Theta_d^{(1)} \right), \quad \Phi_{cd} = \delta_{cd} + \frac{\rho_d c_{Vd}}{\rho_n c_{Vn}}.$$

After some transformations, one arrives at the explicit form of first iteration of the diffusion temperatures [**72**]:

$$\Theta_a^{(1)} = -k_a \operatorname{div} \mathbf{v}, \tag{71}$$

where the phenomenological coefficients have the following structure:

$$k_a = T\sum_{b=1}^{n-1}\left[\boldsymbol{\Phi}^{-1}\theta^{-1}\right]_{ab}^{(0)}\Omega_b,$$

$$\Omega_b = \frac{\rho_b T}{\left(\frac{\partial s}{\partial T}\right)^{(0)}}\left\{\rho\left(\frac{\partial s_b}{\partial T_b}\right)^{(0)}\left(\frac{\partial s}{\partial \rho}\right)^{(0)} - \rho_b\left(\frac{\partial s}{\partial T}\right)^{(0)}\left(\frac{\partial s_b}{\partial \rho_b}\right)^{(0)}\right\}.$$

Equation (71) determines the diffusion temperatures in the non-local form, like the constitutive relations of classical TIP. Note, however, that there is no counterpart for (71) in TIP. Nevertheless, Gouin and Ruggeri [**33**] derived the same equation as constitutive relation using the procedure akin to the exploitation of the entropy inequality in classical TIP. Second remark is concerned with the mixture of ideal gases. In that case, the phenomenological coefficients read:

$$\Omega_b = \rho_b T c_{Vb}\frac{\sum_{\alpha=1}^{n}\rho_\alpha c_{V\alpha}(\gamma_b-\gamma_\alpha)}{\sum_{\alpha=1}^{n}\rho_\alpha c_{V\alpha}}.$$

$\Omega_b \neq 0$ when the constituents have different molecular structure (different γ's), which is possible since the mixture of Euler fluids is not restricted to the mixture of monatomic gases. However, when all the constituents have the same ratio of specific heats, $\Omega_b = 0$, first Maxwellian iteration does not distinguish the temperatures of the constituents from the average temperature of the mixture. This deficiency can be overcome if we proceed to second iteration, which is a matter of current research. Using a variant of the Chapman-Enskog expansion, Goldman and Sirovich [**32**] showed in the case of binary mixture of monatomic gases that the diffusion temperature is second order effect, which is in accordance with the conclusion made above.

4.3 - *Maxwell-Stefan diffusion model revisited*

Fick's law of diffusion is probably one of the most popular models, but it is not universal. There are processes in which "anomalous" (better to say non-Fickian) diffusion occurs and another description is required. Extended thermodynamics offers another view on the diffusion phenomena. It does not relate the diffusion flux directly to the concentration gradient as its cause. It rather goes deeper, taking into account mutual interactions of the constituents as a cause of the change of momenta (and internal energies) of the constituents. Eventually, one ends up with the balance laws instead of the non-local constitutive relations.

A different approach to diffusion was proposed by Maxwell and Stefan [**22**]. It is based upon momentum principle and gives rise to a model which has considerable advantages with respect to the Fick's one, especially in the multi-component mixtures (when the number of the constituents is $n \geq 3$). We shall give a brief account of the Maxwell-Stefan diffusion model in the sequel, mainly following the exposition of [**79**], and then make a comparison with extended thermodynamics of mixtures.

4.3.1 - Maxwell-Stefan diffusion model

The study of the Maxwell-Stefan diffusion model will be restricted to ideal gas mixtures. The mass conservation equation:

$$\frac{\partial \rho_\alpha}{\partial t} + \operatorname{div}(\rho_\alpha \mathbf{v}_\alpha) = 0,$$

is a fundamental physical law in diffusion modelling. It describes the rate of change of the mass or molar densities, or equivalently the mass or molar concentrations. However, there appear the diffusion fluxes, $\mathbf{J}_\alpha = \rho_\alpha \mathbf{v}_\alpha$, whose structure is not known beforehand and ought to be related to the basic field quantities. The Maxwell-Stefan model gives a way to describe these relations by means of the momentum transfer between the constituents.

The model itself is built around certain *assumptions*:

(A1) temperatures of the constituents are equal and constant;
(A2) total pressure of the mixture is constant;
(A3) there exists a concentration gradient of the constituents.

These assumptions imply certain consequences:

(C1) concentration gradient implies the gradient of partial pressure;
(C2) the pressure gradient is balanced by the momentum exchange between the constituents;
(C3) the momentum exchange is proportional to the difference of velocities of the constituents.

The consequence (C1) comes from the assumptions (A1) and (A3), and the thermal equation of state for ideal gases:

$$p_\alpha = \rho_\alpha \frac{k_B}{m_\alpha} T = n_\alpha k_B T, \tag{72}$$

where $n_\alpha = \rho_\alpha / m_\alpha$ are the number densities of the constituents. The consequence (C2) expresses the momentum principle, $-\nabla p_\alpha = \mathbf{m}_\alpha$. It treats the pressure gradient as a force which causes the change of momentum, rather then a part of the non-convective momentum flux. Finally, although it looks like assumption, (C3) is a consequence of the momentum exchange through collisions between the constituents at the molecular level (see [**22**] and [**79**]).

Although the Maxwell-Stefan model showed to be superior over the Fick's one in multi-component mixtures, the nucleus of the idea will be presented in a simpler setting of binary mixture. Afterwards, it will be generalized to the multi-component case. Consider a binary gaseous mixture whose constituents are labeled by 1 and 2 and whose molecules have masses m_1 and m_2. The balances of momenta can be written in the following forms:

$$\begin{aligned} \nabla p_1 &= -f^*_{12} n_1 n_2 (\mathbf{u}_1 - \mathbf{u}_2) = -f_{12} x_1 x_2 (\mathbf{u}_1 - \mathbf{u}_2), \\ \nabla p_2 &= -f^*_{21} n_1 n_2 (\mathbf{u}_2 - \mathbf{u}_1) = -f_{21} x_1 x_2 (\mathbf{u}_2 - \mathbf{u}_1), \end{aligned} \tag{73}$$

where x_1, x_2 are the molar concentrations and $f^*_{12}, f^*_{21}, f_{12}, f_{21}$ are the drag coefficients. Note that the difference of diffusion velocities is equal to the difference of velocities of the constituents, $\mathbf{u}_1 - \mathbf{u}_2 = \mathbf{v}_1 - \mathbf{v}_2$. Assumption (A2) of constant total pressure p, $p = p_1 + p_2$, and temperature T helps to recast (73) in the following form:

$$\mathbf{d}_1 = \frac{1}{p}\nabla p_1 = -\frac{x_1 x_2}{D_{12}}(\mathbf{u}_1 - \mathbf{u}_2), \quad \mathbf{d}_2 = \frac{1}{p}\nabla p_2 = -\frac{x_1 x_2}{D_{21}}(\mathbf{u}_2 - \mathbf{u}_1), \tag{74}$$

where we introduced the Maxwell-Stefan diffusivities:

$$D_{12} = \frac{p}{f_{12}} = \frac{k_B T}{n f^*_{12}}, \quad D_{21} = \frac{p}{f_{21}} = \frac{k_B T}{n f^*_{21}}.$$

From (72) and the assumption (A1) it follows $\mathbf{d}_\alpha = (1/p)\nabla p_\alpha = \nabla x_\alpha$, and one easily obtains the *Maxwell-Stefan relations*:

$$\nabla x_1 = -\frac{x_1 x_2}{D_{12}}(\mathbf{u}_1 - \mathbf{u}_2), \quad \nabla x_2 = -\frac{x_1 x_2}{D_{21}}(\mathbf{u}_2 - \mathbf{u}_1). \tag{75}$$

This form of the Maxwell-Stefan relations facilitates derivation of an important property of diffusion coefficients. Namely, since $x_1 + x_2 = 1$, we have $\nabla x_1 + \nabla x_2 = 0$ which leads to $D_{12} = D_{21}$ – the symmetry of the binary diffusion coefficients.

Generalization of relations (74) to the multi-component mixtures is straightforward. By the momentum principle, the motion of α^{th} constituent is driven by the negative gradient of partial pressure, and the rate of change of momentum is caused by the drag exerted by its relative motion with respect to the other constituents. This observation leads to the natural generalization:

$$\mathbf{d}_\alpha = \frac{1}{p}\nabla p_\alpha = -\sum_{\beta=1}^{n} \frac{x_\alpha x_\beta}{D_{\alpha\beta}}(\mathbf{u}_\alpha - \mathbf{u}_\beta). \tag{76}$$

This may be regarded as the simplest possible model within the Maxwell-Stefan framework depicted above. Other equivalent forms may be found in [**79**]. However, few remarks have to be given. First, the structure of (76) trivially excludes collisions between the molecules of the same species from the rate of change of momentum. Moreover, collisions between the molecules which do not involve α^{th} constituent are also excluded, and one may speculate about their possible influence on the rate of change of momentum of α^{th} constituent. If we assume that (76) contains the term $\mathbf{u}_\beta - \mathbf{u}_\gamma, \beta, \gamma \neq \alpha$, it is easy to show that it can be "absorbed" into existing terms by a simple manipulation:

$$\mathbf{u}_\beta - \mathbf{u}_\gamma = (\mathbf{u}_\alpha - \mathbf{u}_\gamma) - (\mathbf{u}_\alpha - \mathbf{u}_\beta).$$

In other words, terms of the type $\mathbf{u}_\beta - \mathbf{u}_\gamma$ are redundant in the Maxwell-Stefan diffusion relation for the constituent α. Second, the symmetry of diffusion coefficients in the binary mixture came out as a consequence of the constraint on molar concentrations, which can be generalized to

$$\sum_{\alpha=1}^{n} x_\alpha = 1 \quad \Rightarrow \quad \sum_{\alpha=1}^{n} \nabla x_\alpha = 0.$$

This relation, however, is not sufficient to prove the symmetry of diffusion coefficients in the multi-component mixtures. Nevertheless, more subtle arguments eventually lead to this conclusion, i.e. $D_{\alpha\beta} = D_{\beta\alpha}$ (see [**79**] for details). Finally, the Maxwell-Stefan relations (76) help us to close the diffusion problem. They provide the relation between the velocities of the constituents $\mathbf{v}_\alpha$ and field variables, which in conjunction with the mass balance laws form a complete system of governing equations. In such a way they represent the constitutive relations. Although we took into account mainly theoretical issues, the Maxwell-Stefan model is widely applied in practical calculations and presents a mathematically challenging problem [**16, 17**].

4.3.2 - Maxwell-Stefan model and extended thermodynamics

The first step in a comparative analysis of the Maxwell-Stefan model and extended thermodynamics of mixtures will be concerned with the binary mixture. Attention will be restricted to the isothermal processes in ideal gases, $T_\alpha = T = \text{const.}$, i.e assumption (A1) is fulfilled. Taking into account the source terms (60), the balance laws of momenta read:

$$\begin{aligned} &\frac{\partial(\rho_1 \mathbf{v}_1)}{\partial t} + \operatorname{div}(\rho_1 \mathbf{v}_1 \otimes \mathbf{v}_1) + \nabla p_1 = -\frac{\psi_{11}}{T}(\mathbf{u}_1 - \mathbf{u}_2), \\ &\frac{\partial(\rho_2 \mathbf{v}_2)}{\partial t} + \operatorname{div}(\rho_2 \mathbf{v}_2 \otimes \mathbf{v}_2) + \nabla p_2 = -\frac{\psi_{11}}{T}(\mathbf{u}_2 - \mathbf{u}_1). \end{aligned} \tag{77}$$

The comparison of (77) and (74) reveals a striking similarity – ET balance laws reduce to the Maxwell-Stefan relations if the inertial and convective contributions are neglected. Therefore, the Maxwell-Stefan relations can be regarded as a truncated form of the balance laws of momenta in extended thermodynamics of mixtures. In view of the remark given above, they can be regarded as valid for rather slow processes. However, the possibilities for comparative analysis are not exhausted in formal similarity of these models. The source terms in (77) determine the rate of change of momentum, just as the right-hand sides of (74). By a simple comparison, one may determine the phenomenological coefficient ψ_{11}:

$$\psi_{11} = pT\frac{x_1 x_2}{D_{12}}. \tag{78}$$

The main benefit of this relation is the possibility of calculation of the phenomenological coefficient in terms of the Maxwell-Stefan diffusivity, which can be determined by other means. In such a way, the main drawback of extended thermodynamics – indeterminacy of phenomenological coefficients – is removed.

Promising results obtained in the case of binary mixture motivate the study of the general case. There we meet a formal obstacle. Gradient of the partial pressure in Maxwell-Stefan relations (76) is balanced by the momentum exchanges due to collisions of the constituent α with all other constituents. On the other hand, under the isothermal assumption, the balance laws of momenta in ET read:

$$\frac{\partial(\rho_\alpha \mathbf{v}_\alpha)}{\partial t} + \operatorname{div}(\rho_\alpha \mathbf{v}_\alpha \otimes \mathbf{v}_\alpha) + \nabla p_\alpha = \mathbf{m}_\alpha = -\sum_{\beta=1}^{n-1} \frac{\psi_{\alpha\beta}}{T}(\mathbf{u}_\beta - \mathbf{u}_n), \tag{79}$$

for $\alpha = 1, \dots, n-1$, and $\mathbf{m}_n = -\sum_{\beta=1}^{n-1} \mathbf{m}_\beta$. Again, the Maxwell-Stefan relations (76) can be regarded as a truncated form of the balance laws (79) in which inertial and convective terms are neglected. However, to recast the source terms $\mathbf{m}_\alpha$ to the form comparable with the right-hand sides of (76), we have to rearrange the velocities:

$$\mathbf{u}_\beta - \mathbf{u}_n = (\mathbf{u}_\alpha - \mathbf{u}_n) - (\mathbf{u}_\alpha - \mathbf{u}_\beta).$$

In such a way, the source terms can be written as:

$$\mathbf{m}_\alpha = \sum_{\substack{\beta=1 \\ \beta\neq\alpha}}^{n-1} \frac{\psi_{\alpha\beta}}{T}(\mathbf{u}_\alpha - \mathbf{u}_\beta) - \left(\sum_{\beta=1}^{n-1} \frac{\psi_{\alpha\beta}}{T}\right)(\mathbf{u}_\alpha - \mathbf{u}_n). \tag{80}$$

By equalizing (80) with the right-hand side of (76), a simple calculation shows that phenomenological coefficients have the form:

$$\tag{81}\begin{aligned}\psi_{\alpha\beta} &= -\frac{x_\alpha x_\beta}{D_{\alpha\beta}} pT, \quad \alpha, \beta = 1, \ldots, n-1,\, \alpha \neq \beta, \\ \psi_{\alpha\alpha} &= \left(\sum_{\substack{\beta=1 \\ \beta\neq\alpha}}^{n} \frac{x_\alpha x_\beta}{D_{\alpha\beta}} \right) pT.\end{aligned}$$

Comparison of the Maxwell-Stefan diffusion model and extended thermodynamics of mixtures gave an efficient procedure for expressing the phenomenological coefficients in terms of the Maxwell-Stefan diffusivities. The procedure may be regarded as valid only if it gives positive definite matrix of phenomenological coefficients – the condition dictated by the entropy principle. In the case of binary mixture the result coming from (78) is trivial, $\psi_{11} > 0$, due to the positivity of diffusivity. In the case of ternary mixture, coefficients can be calculated using (81):

$$\begin{aligned}\psi_{11} &= \left(\frac{x_1 x_2}{D_{12}} + \frac{x_1 x_3}{D_{13}} \right) p\,T, \quad \psi_{12} = -\frac{x_1 x_2}{D_{12}}\, p\,T = \psi_{21}, \\ \psi_{22} &= \left(\frac{x_2 x_1}{D_{21}} + \frac{x_2 x_3}{D_{23}} \right) p\,T.\end{aligned}$$

Positive definiteness can be checked using the Sylvester's criterion – all the principal minors have to be positive – which leads to:

$$\begin{aligned}\Delta_1 &= \psi_{11} = \left(\frac{x_1 x_2}{D_{12}} + \frac{x_1 x_3}{D_{13}} \right) p\,T > 0, \\ \Delta_2 &= \psi_{11}\psi_{22} - \psi_{12}\psi_{21} \\ &= \left(\frac{x_1 x_3}{D_{13}} \frac{x_2 x_3}{D_{23}} + \frac{x_1 x_3}{D_{13}} \frac{x_2 x_1}{D_{21}} + \frac{x_1 x_2}{D_{12}} \frac{x_2 x_3}{D_{23}} \right) p^2 T^2 > 0,\end{aligned}$$

both inequalities being unconditionally satisfied as sums and products of positive quantities. This result strongly supports our idea to relate extended thermodynamics to the Maxwell-Stefan diffusion model. In the case of general multi-component mixture, this condition yet remains to be proved.

We would like to put this comparative analysis into a broader context. Namely, Ruggeri [**68**] showed that constitutive relations of the non-local type can be regarded as the truncated balance laws. This has been proven by direct calculation for Navier-Stokes relations for Newtonian fluids, Fourier's law of heat conduction, Darcy's law in porous media, and now for Maxwell-Stefan relations. It was also proved in [**68**] that the entropy inequality is satisfied as long as the state variables during the processes remain in some neighborhood of the local equilibrium state (in a generalized sense). This also motivates the calculation of the phenomenological coefficients in balance laws by the comparison with truncated balance laws, i.e. the constitutive relations. Possible objection could be made about the accuracy of the coefficients calculated in this manner – they obviously represent a kind of first approximation since the comparison is always made for the linearized source terms. However, these restrictive assumptions can be compensated by the nonlinearity of the source terms in general case. For example, we may take the coefficients (81) calculated for an isothermal process and use them in the analysis of non-isothermal ones, or even multi-temperature processes, with expectation that the nonlinearity of the source terms will capture the non-equilibrium effects that are missing in phenomenological coefficients. There is no general result which can support this observation. Nevertheless, it will be shown in the next Section that this could lead to satisfactory results confirmed through a comparison with experimental data.

Final remark is concerned with physical justification of extended models. In its development within ET, the mixture theory passed first through the multi-velocity stage. It helped to remove the paradox of infinite pulse speeds of diffusion, and recovered the Fick's law in classical limit. On the other hand, the Maxwell-Stefan relations appear as truncated form of the momentum balance equations for the constituents. One may justly ask for an experimental validation of the proposed model. We shall just mention the work of Kerkhof and Geboers [**48, 49**] who used the viscous multi-velocity model to describe the isothermal diffusion in a binary mixture. They assumed the steady flow, with negligible convected momentum through the long cylindrical capillary. They also assumed the velocity slip at the boundary. Their aim was to test the hypothesis of the presence of interspecies friction (momentum exchange between the constituents) through comparison with experimental data of Remick and Geankoplis [**63**]. As a matter of fact, they obtained an excellent agreement which supported the multi-velocity model.

5 - Shock structure in multi-temperature binary mixture

Shock waves are moving singular surfaces on which jump discontinuities of the field variables occur. In the physical reality, due to dissipative mechanisms they are observed as narrow transition regions with steep gradients of field variables within, i.e. shock waves are endowed with the structure. The shock structure problem consists of a mathematical description of this region through particular solutions of the appropriate mathematical models. This problem is challenging both from the mathematical and physical points of view. Mathematically, the questions of existence and uniqueness are very important for the solutions with jump discontinuities, as well as for the continuous ones. Physically, the continuum hypothesis becomes doubtful in this situation, thus limiting the range of validity of the continuum theories of fluids. On the other hand, the shock structure problem is a standard test for the models of non-equilibrium processes, through which they can be validated.

Theoretical studies of the shock structure problem in mixtures can be traced back to Sherman [**73**] where the continuum description was used. Although it contained some results which were refuted in the subsequent studies, this analysis drew attention to a lag of velocity profile of heavier constituent and triggered further investigations. Bird [**8**] applied the direct simulation Monte Carlo (DSMC) method in the analysis of binary mixture and observed some interesting phenomena: apart from the lag of velocity profiles, there is a difference in temperatures of the constituents; moreover, equilibration of the temperatures is the slowest relaxation process in the mixtures. In parallel, there were some experimental studies, although not much [**42, 19**], which gave a new insight into this problem. Certain theoretically predicted features were confirmed, and other carefully examined. Abe and Oguchi [**1**] made a careful comparison of the experiments with numerical simulations based upon the Boltzmann equations for mixtures. Their analysis confirmed the existence of the temperature overshoot of a heavier constituent – a region within a profile where the temperature increases above the terminal temperature of the mixture. They also gave an explanation using the heat conduction arguments. Recent studies within the framework of kinetic theory represent collections of valuable, yet particular results, mainly devoted to the development of deterministic numerical schemes for the solution of Boltzmann equations [**51, 62**]. However, the complexity of numerical schemes prevented massive calculations and systematic study of the shock structure.

In view of these facts, we shall first test the MT model against experimentally determined shock structure in Helium-Argon mixture [**42**]. This will be followed by the systematic analysis whose aim is to reveal the influence of the three parameters – the mass ratio, the Mach number and the equilibrium concentration – on global parameters of the shock structure – the shock thickness and the temperature overshoot of heavier constituent. The results of the analysis will show that the macroscopic MT model can be put at the same level of accuracy as more refined models of the kinetic theory [**1**], or the results of DSMC [**8**], at least for the weak shocks. However, the main advantage of the MT model is the possibility to apply it with only moderate numerical efforts and the use of standard numerical packages. Finally, the study will be completed with some results concerned with the influence of other dissipative properties on the shock structure, like viscosity and heat conductivity.

5.1 - *Formal aspects of the shock structure problem*

Although there are useful resources for the study of the shock structure problem [**24**], we shall give some general remarks about it to make the exposition self-contained. Consider the hyperbolic system of conservation laws in one space dimension:

$$\partial_t \mathbf{u} + \partial_x \mathbf{F}(\mathbf{u}) = \mathbf{0}, \tag{82}$$

where $\mathbf{u} \in \mathbf{R}^n$ is the vector of state variables and $\mathbf{F}(\mathbf{u}) \in \mathbf{R}^n$ is the vector of fluxes. To (82) one may adjoin the eigenvalue problem:

$$(- \lambda \mathbf{I} + D\mathbf{F}(\mathbf{u}))\mathbf{r} = \mathbf{0}, \tag{83}$$

where $\mathbf{I}$ is the identity matrix, $D\mathbf{F}(\mathbf{u})$ is Jacobian matrix of $\mathbf{F}$, $\lambda_i(\mathbf{u})$ are real eigenvalues – the characteristic speeds – and $\mathbf{r}_i \in \mathbf{R}^n$ are the corresponding eigenvectors.

The system of conservation laws (82) admits weak solutions with jumps, where the jumps of the state variables are determined as solutions of the Rankine-Hugoniot equations:

$$[\mathbf{F}(\mathbf{u})] = s[\mathbf{u}], \tag{84}$$

s being the shock speed and $[(\,)] = (\,)_1 - (\,)_0$, subscripts indicating the states in front (0) and behind (1) the shock. Nontrivial solutions of the Rankine-Hugoniot equations, which are of interest for our analysis, bifurcate from the characteristic speeds, i.e they exist in the neighborhood of $s = \lambda_i(\mathbf{u}_0)$. However, not all of them are admissible and one must take into account the appropriate selection rules. For our purposes, it will be sufficient to use the Lax condition (where we implicitly assumed that all the eigenvalues are distinct):

$$\lambda_1(\mathbf{u}_0) < \ldots < \lambda_i(\mathbf{u}_0) < s < \lambda_{i+1}(\mathbf{u}_0) < \ldots < \lambda_n(\mathbf{u}_0),$$
$$\lambda_1(\mathbf{u}_1) < \ldots < \lambda_{i-1}(\mathbf{u}_1) < s < \lambda_i(\mathbf{u}_1) < \ldots < \lambda_n(\mathbf{u}_1).$$

It can be combined into a single inequality for the so-called $i-$shock:

$$\lambda_i(\mathbf{u}_0) < s < \lambda_i(\mathbf{u}_1). \tag{85}$$

Classical continuum models introduce the dissipation through the non-local constitutive relations, which give rise to dissipative models with the diffusive terms:

$$\partial_t \mathbf{u} + \partial_x \mathbf{F}(\mathbf{u}) = \varepsilon \partial_x (\mathbf{B}(\mathbf{u}) \partial_{\mathrm{x}} \mathbf{u}), \tag{86}$$

where $\mathbf{B}(\mathbf{u})$ is the viscosity matrix and $\varepsilon > 0$ a small parameter. Shock waves in these systems are regularized, i.e. endowed with a continuous structure. When the traveling wave solution is assumed, the shock structure can be represented as a heteroclinic orbit in the phase space. Existence of the shock structure is naturally related to the Lax admissibility condition (85), but the existence of heteroclinic orbits is not a prerogative of the admissible equilibrium states – they exist even for the non-admissible solutions of Rankine-Hugoniot equations of (84) (see [**75**] for more details in the context of Navier-Stokes-Fourier model).

Dissipation can be introduced through the relaxation terms as well. If we extend the set of state variables, the source terms of relaxation type appear in the extended set of governing equations which have the form of balance laws:

$$\partial_t \mathbf{U} + \partial_x \hat{\mathbf{F}}(\mathbf{U}) = \frac{1}{\tau}\mathbf{Q}(\mathbf{U}), \tag{87}$$

with the following structure:

$$\mathbf{U} = \begin{pmatrix} \mathbf{u} \\ \mathbf{w} \end{pmatrix}, \quad \begin{matrix} \mathbf{u} \in \mathbf{R}^n, \\ \mathbf{w} \in \mathbf{R}^m \end{matrix}, \quad \hat{\mathbf{F}}(\mathbf{U}) = \begin{pmatrix} \mathbf{f}(\mathbf{u},\mathbf{w}) \\ \mathbf{g}(\mathbf{u},\mathbf{w}) \end{pmatrix}, \tag{88}$$
$$\mathbf{Q}(\mathbf{U}) = \begin{pmatrix} \mathbf{0} \\ \mathbf{q}(\mathbf{u},\mathbf{w}) \end{pmatrix}.$$

In (88) $\mathbf{U} \in \mathbf{R}^N$, $N = n + m$, is the extended set of state variables, $\hat{\mathbf{F}}(\mathbf{U})$ is the corresponding vector of fluxes, $\mathbf{Q}(\mathbf{U})$ is the vector of source terms and $\tau > 0$ a small parameter – the relaxation time. It is an important assumption that there exists an *equilibrium manifold* in the extended phase space, determined by the relation:

$$\mathbf{q}(\mathbf{u},\mathbf{w}) = \mathbf{0}. \tag{89}$$

We shall also assume that (89) can be solved for **v**, so that the equilibrium manifold is explicitly determined:

$$\mathbf{q}(\mathbf{u},\mathbf{w}) = \mathbf{0} \quad \Rightarrow \quad \mathbf{w}_{\mathrm{E}} = \mathbf{h}(\mathbf{u}) \text{ as } \tau \to 0. \tag{90}$$

On the equilibrium manifold, the system (87) is reduced to an *equilibrium subsystem*:

$$\partial_t \mathbf{u} + \partial_x \mathbf{f}(\mathbf{u}, \mathbf{h}(\mathbf{u})) = \mathbf{0}, \quad \mathbf{f}(\mathbf{u}, \mathbf{h}(\mathbf{u})) = \mathbf{F}(\mathbf{u}), \tag{91}$$

which coincides with the system of conservation laws (82). To the differential part of (87) one may adjoin the eigenvalue problem:

$$(-\Lambda \mathbf{I} + D\hat{\mathbf{F}}(\mathbf{U}))\mathbf{R} = \mathbf{0}, \tag{92}$$

whose eigenvalues $\Lambda_j(\mathbf{U})$, if they are real, ought to satisfy the subcharacteristic condition on the equilibrium manifold:

$$\min_{1\le j\le N} \Lambda_j(\mathbf{u}, \mathbf{h}(\mathbf{u})) \le \lambda_i(\mathbf{u}) \le \max_{1\le j\le N} \Lambda_j(\mathbf{u}, \mathbf{h}(\mathbf{u})). \tag{93}$$

The shock structure is assumed to be a traveling wave solution of (87) which asymptotically connects the equilibrium states. To that end we assume the solution in the form:

$$\mathbf{U} = \mathbf{U}(\xi), \quad \xi = \frac{x - st}{\tau}, \tag{94}$$

and reduce the system of balance laws (87) to a system of ODE's – the shock structure equations:

$$\frac{\mathrm{d}}{\mathrm{d}\xi}\left[-s\mathbf{U} + \hat{\mathbf{F}}(\mathbf{U})\right] = \mathbf{Q}(\mathbf{U}). \tag{95}$$

They are equipped with the boundary conditions:

$$\lim_{\xi \to -\infty} \mathbf{U}(\xi) = \mathbf{U}_0, \quad \lim_{\xi \to \infty} \mathbf{U}(\xi) = \mathbf{U}_1, \quad \lim_{\xi \to \pm\infty} \mathbf{U}'(\xi) = \mathbf{0}, \tag{96}$$

for which it is assumed:

$$\lim_{\xi \to -\infty} \mathbf{w}(\xi) = \mathbf{w}_{E0} = \mathbf{h}(\mathbf{u}_0), \quad \lim_{\xi \to \infty} \mathbf{w}(\xi) = \mathbf{w}_{E1} = \mathbf{h}(\mathbf{u}_1), \tag{97}$$

i.e. the solution approaches the equilibrium manifolds at infinity. By integrating the conservative part of the system (95), one obtains $-s\mathbf{u} + \mathbf{f}(\mathbf{u}, \mathbf{w}) = \mathrm{const}$. Using the boundary data (97), the Rankine-Hugoniot equations for the equilibrium subsystem (91) are recovered:

$$\mathbf{f}(\mathbf{u}_1, \mathbf{h}(\mathbf{u}_1)) - s\mathbf{u}_1 = \mathbf{f}(\mathbf{u}_0, \mathbf{h}(\mathbf{u}_0)) - s\mathbf{u}_0. \tag{98}$$

Therefore, we may conclude that shock structure connects the equilibrium states of the system (87), i.e. stationary points of (95), which correspond to the solution of the Rankine-Hugoniot equations of the equilibrium subsystem (91). In view of that fact, the critical value of the shock speed s ought to be the one from which nontrivial solution of the Rankine-Hugoniot equations bifurcate, i.e. the one which coincides with the characteristic speed of the equilibrium subsystem.

Linear stability analysis of the equilibrium states (stationary points), through the spectral analysis of linearized variational equations of (95), yields that there are exactly n eigenvalues (corresponding to the conservative part of the system) which are identical zeros:

$$\lambda^{(i_k)}(\mathbf{U}_0) = \lambda^{(i_k)}(\mathbf{U}_1) \equiv 0, \quad k = 1, \ldots, n. \tag{99}$$

The remaining m eigenvalues (corresponding to the non-equilibrium part of the system) obey the following relations:

$$\begin{aligned} &\lambda^{(j_1)}(\mathbf{U}_0) < \lambda^{(j_2)}(\mathbf{U}_0) < \ldots < \lambda^{(j_{m-1})}(\mathbf{U}_0) < 0 < \lambda^{(j_m)}(\mathbf{U}_0), \\ &\lambda^{(j_1)}(\mathbf{U}_1) < \lambda^{(j_2)}(\mathbf{U}_1) < \ldots < \lambda^{(j_{m-1})}(\mathbf{U}_1) < \lambda^{(j_m)}(\mathbf{U}_1) < 0, \end{aligned} \tag{100}$$

i.e. the highest eigenvalue has different signs at the upstream and the downstream equilibria. Moreover, it is the only eigenvalue which changes the sign, and it occurs when the shock speed crosses the highest characteristic speed of the equilibrium subsystem:

$$\lambda^{(j_m)}(\mathbf{U}_0, \lambda_n(\mathbf{u}_0)) = 0, \quad \frac{\mathrm{d}\lambda^{(j_m)}}{\mathrm{d}s}(\mathbf{U}_0, \lambda_n(\mathbf{u}_0)) \neq 0. \tag{101}$$

This result, drawn from several convincing particular cases, which indicates the occurrence of transcritical bifurcation pattern, is rather a conjecture than a genuine theorem. The proof of this statement, as well as a proper bifurcation analysis, is still an open problem for the hyperbolic systems of balance laws. In [**74, 76**] one may find a good collection of examples which confirm the conjecture stated above. In the case of viscous dissipative systems one may refer to a recent result of Achleitner and Szmolyan [**2**].

The promising aspect of the inequalities (100) is that the stationary points $\mathbf{U}_0$ and $\mathbf{U}_1$ behave like the saddle and the stable node, respectively, albeit in a generalized sense since they are non-hyperbolic. This permits the numerical solution of the shock structure problem (95)-(96) as an initial value problem [83].

5.2 - *Shock structure equations in MT binary mixture*

Shock structure problem will be analyzed as a stationary problem, i.e. the shock structure is considered as a plane traveling wave, moving at a constant speed s. Considering the problem in a binary mixture, we shall choose governing equations in the mixed form (51), with state variables $(\rho, \mathbf{v}, T, \rho_1, \mathbf{v}_1, T_1)$.

First step in the analysis will be the choice of state variables and the recognition of parameters. The constituents are assumed to be ideal gases, with the thermal and caloric equations of state (55). The average temperature of the MT mixture will be defined by means of the intrinsic (thermal) part of internal energy in equilibrium (65):

$$(\rho_1 c_{V_1} + \rho_2 c_{V_2})T = \rho_1 c_{V_1} T_1 + \rho_2 c_{V_2} T_2. \tag{102}$$

By restricting the analysis to the binary mixture of monatomic gases, $\gamma_1 = \gamma_2 = \gamma = 5/3$, we may express the total pressure and the intrinsic part of internal energy in the same form as in the case of a single component gas:

$$p = p_1 + p_2 = \rho \frac{k_B}{m} T, \quad \rho\varepsilon_I = \rho_1\varepsilon_1 + \rho_2\varepsilon_2 = \rho \frac{k_B}{(\gamma - 1)m} T,$$

provided we introduce the average mass $m = m(c)$, and the average temperature T of the mixture in the following form:

$$\frac{1}{m(c)} = \frac{c}{m_1} + \frac{1-c}{m_2}, \quad T = c\frac{m(c)}{m_1} T_1 + (1-c)\frac{m(c)}{m_2} T_2, \tag{103}$$

where c is the concentration variable related to the mass densities in the following way:

$$\rho_1 = \rho c, \quad \rho_2 = \rho(1-c).$$

In the sequel, we will introduce the difference of temperatures $\Theta = T_2 - T_1$, the so-called *diffusion temperature*, and the ratio of masses of the constituents:

$$\mu = \frac{m_1}{m_2}, \quad 0 < \mu \leq 1,$$

where we assumed $m_1 \leq m_2$. The temperatures of the constituents can now be expressed in terms of the new variables T, Θ and c, using μ as a parameter:

$$T_1 = T - f(c)\Theta, \quad T_2 = T + (1 - f(c))\Theta,$$

where the auxiliary function $f(c)$ reads:

$$f(c) = \frac{\mu(1-c)}{c + \mu(1-c)}.$$

Finally, we will also use the diffusion flux $\mathbf{J}$ of the constituent, instead of its velocity $\mathbf{v}_1$. Since the relative velocities obey the relation $\rho_1\mathbf{u}_1 + \rho_2\mathbf{u}_2 = \mathbf{0}$, due to (50), the diffusion flux of constituent 1 is defined as:

$$\mathbf{J} = \rho_1\mathbf{u}_1 = -\rho_2\mathbf{u}_2.$$

Therefore, we take the change of variables:

$$(\rho, \mathbf{v}, T, \rho_1, \mathbf{v}_1, T_1) \to (\rho, \mathbf{v}, T, c, \mathbf{J}, \Theta),$$

and rewrite the system of the governing equations in terms of them. The complete set of equations can be found in [**69**]. We shall be restricted here only to the shock structure equations.

The source terms (58) in the case of non-reacting ($\tau_\alpha = 0$) binary mixture have the following form:

$$\hat{\mathbf{m}}_1 = -\psi_{11}\left(\frac{\mathbf{u}_1}{T_1} - \frac{\mathbf{u}_2}{T_2}\right), \quad \hat{e}_1 = -\theta_{11}\left(-\frac{1}{T_1} + \frac{1}{T_2}\right), \tag{104}$$

where ψ_{11} and θ_{11} are the phenomenological coefficients. They can be related to the state variables and relaxation times for diffusion τ_D and temperature τ_T [**55**]:

$$\psi_{11} = \frac{1}{\tau_D}\frac{\rho_1\rho_2}{\rho}T, \quad \theta_{11} = \frac{1}{\tau_T}\frac{\rho_1 c_{V_1}\rho_2 c_{V_2}}{\rho_1 c_{V_1} + \rho_2 c_{V_2}}T^2. \tag{105}$$

We have already seen that ET does not possess an inherent method to determine the phenomenological coefficients completely. However, by the methods of kinetic theory of gases one can relate the relaxation times τ_D and τ_T to the diffusivity D_{12} of the binary mixture of monatomic gases [**22**, **9**]:

$$\tau_D = \frac{cm_2 + (1-c)m_1}{k_B T}D_{12}, \quad \tau_T = \frac{m_1 + m_2}{k_B T}D_{12}. \tag{106}$$

In fact, kinetic theory establishes the relation $(106)_1$ between τ_D and D_{12}, while the other one comes as a consequence of the ratio between the relaxation times in the case of monatomic gases [**14, 72, 55**]:

$$\frac{\tau_T}{\tau_D} = \frac{m_1 + m_2}{c\, m_2 + (1-c)\, m_1} > 1. \tag{107}$$

Diffusivity of the binary mixture, derived from the model of hard spheres, is determined as [**22, 9**]:

$$D_{12} = \frac{3}{8nd_{12}^2} \left(\frac{k_{\mathrm{B}}T}{2\pi} \frac{m_1 + m_2}{m_1 m_2} \right)^{1/2}, \tag{108}$$

where $n = \rho/m$ is the mixture number density, $n = n_1 + n_2 = \rho_1/m_1 + \rho_2/m_2$, and $d_{12} = (d_1 + d_2)/2$ is the average atomic diameter of the mixture constituents, whose diameters are d_1 and d_2.

For the shock structure related to plane shocks, i.e. to the shock waves whose singular surface is plane, one space variable, say x, will suffice for the description of the problem. The shock structure will be assumed in the form of a traveling wave, moving at constant speed s in the direction x orthogonal to the singular surface, and asymptotically connecting the equilibrium states in front and behind the shock wave. Under these assumptions, the shock structure will depend on a single variable $\xi = x - st$, and the model is transformed into a set of ordinary differential equations where the velocity, the diffusion flux and the source term (momentum exchange) are described by a single component, i.e. $\mathbf{v} = (v, 0, 0)$, $\mathbf{J} = (J, 0, 0)$ and $\hat{\mathbf{m}}_1 = (\hat{m}_1, 0, 0)$, in Cartesian coordinates. The shock structure equations then read:

$$\begin{aligned}
&\frac{\mathrm{d}}{\mathrm{d}\xi}(\rho u) = 0, \\
&\frac{\mathrm{d}}{\mathrm{d}\xi}\left(\rho u^2 + p + \frac{J^2}{\rho c(1-c)} \right) = 0, \\
&\frac{\mathrm{d}}{\mathrm{d}\xi}\left\{ \left(\frac{1}{2}\rho u^2 + \rho\varepsilon + p \right) u + \left(\frac{uJ}{\rho c(1-c)} + \frac{1}{\beta} \right) J \right\} = 0, \\
&\frac{\mathrm{d}}{\mathrm{d}\xi}(\rho c u + J) = 0, \\
&\frac{\mathrm{d}}{\mathrm{d}\xi}\left\{ \rho c u^2 + \frac{J^2}{\rho c} + 2uJ + p_1 \right\} = \hat{m}_1, \\
&\frac{\mathrm{d}}{\mathrm{d}\xi}\left\{ \left(\frac{1}{2}\rho c \left(u + \frac{J}{\rho c} \right)^2 + \rho c \varepsilon_1 + p_1 \right) \left(u + \frac{J}{\rho c} \right) \right\} = \hat{m}_1 u + \hat{e}_1,
\end{aligned} \tag{109}$$

where β determines the so-called thermal inertia:

$$\beta = \frac{1}{g_1 - g_2}, \quad g_\alpha = \varepsilon_\alpha + \frac{p_\alpha}{\rho_\alpha} + \frac{u_\alpha^2}{2}.$$

The problem of the shock structure will be studied in the dimensionless form. For that purpose, we shall introduce the dimensionless variables by scaling the state variables and the independent variable ξ with the appropriate upstream equilibrium values, indicated by the subscript 0:

$$\tilde{\rho} = \frac{\rho}{\rho_0},\ \tilde{u} = \frac{u}{a_0},\ \tilde{T} = \frac{T}{T_0},\ \tilde{J} = \frac{J}{\rho_0 a_0},\ \tilde{\Theta} = \frac{\Theta}{T_0},\ \tilde{\xi} = \frac{\xi}{l_0},\ M_0 = \frac{u_0}{a_0}, \tag{110}$$

where $u = v - s$ is the relative mixture velocity with respect to the shock wave, l_0 is the upstream reference length and $a_0 = \{\gamma(k_B/m_0)T_0\}^{1/2}$ is the upstream speed of sound; $m_0 = m(c_0)$ is the equilibrium average mass of the mixture and M_0 is the upstream Mach number. For the sake of simplicity, tilde will be dropped in the sequel.

The upstream reference length l_0 is usually taken as the mean free path of the atoms. The average mean free path in the mixture will be expressed in terms of the other, more primitive properties of the constituents [**9**]:

$$\begin{aligned} l_0 &= \frac{n_1}{n}(l_1)_0 + \frac{n_2}{n}(l_2)_0, \\ (l_\alpha)_0 &= \frac{1}{\pi d_{12}^2}\left[n_1\left(1+\frac{m_\alpha}{m_1}\right)^{1/2} + n_2\left(1+\frac{m_\alpha}{m_2}\right)^{1/2}\right]^{-1}, \end{aligned} \tag{111}$$

where n_α are number densities of the constituents, and $n = n_1 + n_2$ is the mixture number density.

Using the scaled variables (110), we obtain the following set of dimensionless equations:

$$\begin{aligned} &\frac{\mathrm{d}}{\mathrm{d}\xi}(\rho u) = 0, \\ &\frac{\mathrm{d}}{\mathrm{d}\xi}\left(\rho u^2 + \frac{1}{\gamma}\frac{m_0}{m}\rho T + \frac{J^2}{\rho c(1-c)}\right) = 0, \\ &\frac{\mathrm{d}}{\mathrm{d}\xi}\left\{\left(\frac{1}{2}\rho u^2 + \frac{1}{\gamma-1}\frac{m_0}{m}\rho T + \frac{J^2}{2\rho c(1-c)}\right)u \right. \\ &\qquad \left. + \left(\frac{uJ}{\rho c(1-c)} + \frac{1}{\beta}\right)J\right\} = 0, \\ &\frac{\mathrm{d}}{\mathrm{d}\xi}(\rho c u + J) = 0, \\ &\frac{\mathrm{d}}{\mathrm{d}\xi}\left\{\rho c u^2 + \frac{J^2}{\rho c} + 2uJ + \frac{1}{\gamma}\frac{m_0}{m_1}\rho c(T - f(c)\Theta)\right\} \\ &\qquad = -\frac{l_0}{\tau_D a_0} m_\mu(T, c, \Theta)J, \\ &\frac{\mathrm{d}}{\mathrm{d}\xi}\left\{\left(\frac{1}{2}\rho c\left(u + \frac{J}{\rho c}\right)^2 + \frac{1}{\gamma-1}\frac{m_0}{m_1}\rho c(T - f(c)\Theta)\right)\left(u + \frac{J}{\rho c}\right)\right\} \\ &\qquad = -\frac{l_0}{\tau_D a_0} m_\mu(T, c, \Theta)Ju + \frac{l_0}{\tau_T a_0} e_\mu(\rho, T, c, \Theta)\Theta. \end{aligned} \tag{112}$$

Auxiliary functions in the source terms read:

$$m_\mu(T,c,\Theta)=\frac{T+[1-c-f(c)]\Theta}{[T-f(c)\Theta][T+(1-f(c))\Theta]}T,$$

$$e_\mu(\rho,T,c,\Theta)=\frac{1}{\gamma(\gamma-1)}\frac{m_0}{m_1}\frac{m}{m_2}\frac{\rho c(1-c)T^2}{[T-f(c)\Theta][T+(1-f(c))\Theta]},$$

and the ratios of masses can be expressed as:

$$\frac{m_0}{m}=\frac{c+\mu(1-c)}{c_0+\mu(1-c_0)},\quad \frac{m_0}{m_1}=\frac{1}{c_0+\mu(1-c_0)},\quad \frac{m}{m_2}=\frac{\mu}{c+\mu(1-c)}.$$

In (112), the dimensionless thermal inertia has the following form:

$$\frac{1}{\beta}=\frac{1}{\gamma-1}\left[\frac{m_0}{m_1}(1-\mu)T-\frac{m_0}{m_1}\frac{m}{m_2}\Theta\right]+\frac{J^2}{2\rho^2}\left[\frac{1}{c^2}-\frac{1}{(1-c)^2}\right].$$

One may note that the shock structure equations (112) comprise only two dimensionless groups:

$$\Pi_D=\frac{l_0}{\tau_D a_0},\quad \Pi_T=\frac{l_0}{\tau_T a_0}.$$

The shock structure equations (110) obviously have the structure (95). There still remains to determine the boundary conditions. Mere observation of the source terms in (112) yields that the diffusion flux and the diffusion temperature vanish both in upstream and downstream stationary points, i.e. $J_0=J_1=0$, $\Theta_0=\Theta_1=0$. Thus, for a given upstream equilibrium state $\mathbf{U}_0=(\rho_0,u_0,T_0,c_0,J_0,\Theta_0)$ one may determine the downstream equilibrium state $\mathbf{U}_1=(\rho_1,u_1,T_1,c_1,J_1,\Theta_1)$ by integration of the conservative part of the system $(112)_{1-4}$. The nontrivial solution in dimensionless form reads:

$$\mathbf{U}_0=\begin{bmatrix}1\\ M_0\\ 1\\ c_0\\ 0\\ 0\end{bmatrix},\quad \mathbf{U}_1=\begin{bmatrix}\dfrac{4M_0^2}{3+M_0^2}\\ \dfrac{3+M_0^2}{4M_0}\\ \dfrac{1}{16}\left(14-\dfrac{3}{M_0^2}+5M_0^2\right)\\ c_0\\ 0\\ 0\end{bmatrix}. \tag{113}$$

Note that relations between the mixture state variables ρ_1, u_1, T_1 and ρ_0, u_0, T_0, correspond to the solution of the usual Rankine-Hugoniot equations between the state variables at the shock wave for a single fluid. On the other hand, the constituent-related state variables c, J and Θ have the same equilibrium values in front of and behind the shock. Since the diffusion flux J and the diffusion temperature Θ vanish in equilibrium, they can be regarded as genuine non-equilibrium variables. Also, the concentration is the same in both equilibrium states, $c_1 = c_0$, and in the sequel it will be termed equilibrium concentration, without special regard to the upstream or the downstream state. Finally, the downstream equilibrium can be regarded as a one-parameter family of states, parametrized by the Mach number (i.e. the shock speed), $\mathbf{U}_1 = \mathbf{U}_1(\mathbf{U}_0, M_0)$.

After complete analysis of the mathematical model of the shock structure, we may conclude that three parameters distilled after the scaling procedure: M_0 – the upstream Mach number, μ – the mass ratio of the constituents and c_0 – the equilibrium concentration. First parameter measures the strength of the shock and it is omnipresent in all shock structure problems. The other two parameters are peculiar for the mixtures. Our aim is to analyze the influence of these parameters on the structure of shocks in the binary MT mixture.

The shock structure equations (110), along with boundary conditions (113), will be solved numerically. The details of numerical procedure are thoroughly explained in [**56**]. We shall give only two important remarks. First, the idea to analyze the shock structure problem by the methods of dynamical systems theory was proposed by Gilbarg and Paolucci [**29**]. It can be formalized and efficiently applied as long as the numerical procedure does not meet any kind of singularity. This question was raised as early as Grad [**36**] faced the problem of appearance of the non-smooth profiles in 13 moments equations. Later on Weiss [**83**] offered an answer using the singularity analysis. Finally, Boillat and Ruggeri [**13**] proved that a continuous shock structure does not exist if the shock speed is greater than the highest characteristic speed of the full system in the upstream equilibrium. In the case of mixtures, the problem of non-existence becomes more delicate because of several parameters which influence the solution. We shall restrict the analysis to the weak shocks for which the existence of smooth solutions is imminent.

5.3 - *Comparison with experimental data*

Our first aim is to compare the predictions of the hyperbolic MT model with the experimental data reported by Harnett and Muntz [**42**]. Measurement of the data was based upon electron beam fluorescence technique for three different mixture compositions. We shall make a comparison between the numerical solution and the experimental data for the upstream Argon mole fraction $\chi_{\mathrm{Ar}} = 0.247$ and the upstream Mach number $M_0 = 1.63$. These data correspond to the Helium upstream concentration (mass fraction) $c_0 = 0.234$. To make the comparison with experiments feasible, it is needed to choose the unique length scale. In [**42**] the mean free path was determined using the viscosity of the mixture at sonic conditions, $l_{\text{HM}} = \mu^*/(\rho_0 u_0)$. Consequently, the conversion rule $\tilde{\xi} = (l_{\text{HM}}/l_0)\tilde{\xi}_{\text{HM}}$ will be applied to the experimental data, where $\tilde{\xi}_{\text{HM}}$ is the dimensionless length used in [**42**]. The results given here were presented with more details in [**55**].

Figures 1 show the numerically obtained profiles of the velocities and the temperatures for the MT model, superposed with the experimental data of Harnett and Muntz [**42**]. In the case for which the comparison is made, the Argon velocity profile is obtained directly from experiment, while the Helium velocity profile and both temperature profiles are obtained indirectly. Also, we compare only the so-called average temperatures of the constituents, as defined in the kinetic theory of gases, since parallel and orthogonal temperatures are indistinguishable in our MT model.

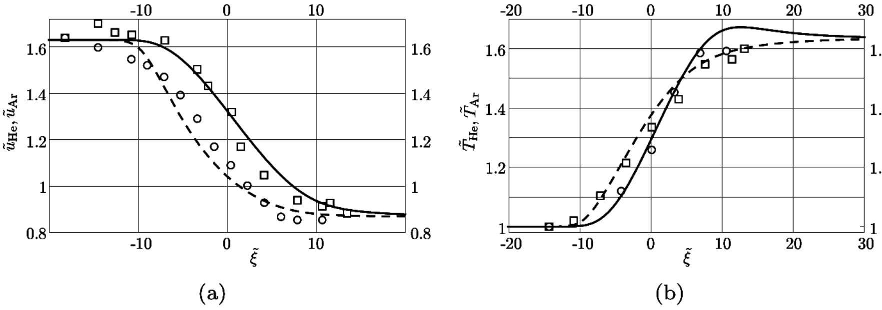


Fig. 1. Dimensionless velocity (a) and temperature (b) profiles. MT model: solid line – Ar, dashed line – He. Experiment: squares – Ar, circles – He.

Velocity profile of Argon has a very good agreement with the experiment, while slight discrepancy can be observed in the Helium velocity profile. This can be attributed to the fact that experimental Helium profile is determined indirectly. However, the tendency and the gradients of velocities are in satisfactory agreement. The diffusive separation in numerical solution is of the same kind as in the experiment.

In the case of temperature profiles, certain discrepancies between the MT model and the experimental results can be observed. The first discrepancy is concerned with opposite sense of temperature diffusion Θ in numerical simulation and experiment: there is a lag in the Helium temperature rise in experimental data, while the Argon temperature has a lag in numerically calculated profile for the MT model. The same discrepancy was observed in the numerical simulations of Abe and Oguchi [**1**], the discrete velocity models by Monaco [**57**] and the DSMC by Bird [8]. The same pattern is observed also in more recent studies of the shock structure in binary mixtures of hard spheres [**51**]. Therefore, our profiles seem to agree with other theoretically obtained ones.

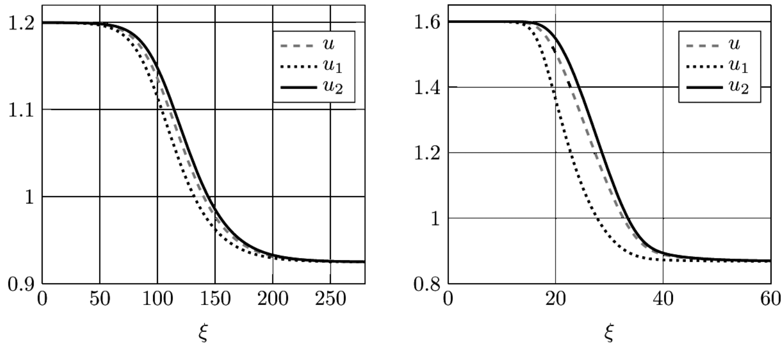
The second discrepancy in the temperature profile is concerned with a temperature overshoot of Argon – existence of an interval within a profile where the temperature becomes higher than the terminal one. In our calculation, the maximum relative temperature overshoot is $((T_{\mathrm{Ar}})_{\max} - T_1)/(T_1 - T_0) \approx 0.06$. Harnett and Muntz [**42**] observed that the parallel temperature of Argon has an overshoot in the case of $\chi_{\mathrm{Ar}} = 0.115$ upstream Argon molar fraction, although it is within the uncertainty of the temperature measurement. On the other hand, mean Argon temperature does not exhibit an overshoot. These observations were supported by the asymptotic analysis [**43**]. Since the overshoot of mean Argon temperature occurred also in simulations with low Argon concentration [**8**], they conjectured that an overshoot of the parallel Argon temperature represents an onset of the mean temperature overshoot phenomenon, since it competes with the influence of cross collisions between the two species, and prevails in the case of low Argon mole fraction. These observations were confirmed in other profiles obtained numerically from the Boltzmann equations, e.g. in [**1**] for the low Argon concentration and in [**51**] for the low concentration of heavier constituent.

5.4 - *Detailed analysis of the shock structure*

Systematic analysis of the shock structure is clearly motivated by the satisfactory agreement of numerical simulation with experimental data. The results presented in the sequel can be found in [**56**] in the expanded form. The analysis will commence with two particular cases: (a) $M_0 = 1.2$, $c_0 = 0.35$, $\mu = 0.05$; (b) $M_0 = 1.6$, $c_0 = 0.21$, $\mu = 0.1$.

In both cases a monotonicity of the mixture state variables u (Figure 2) and T (Figure 3) can be observed. Also, there is a lag in the velocity profile of heavier component in either case, and the shock thickness is obviously different. It is important to note that the temperature overshoot does not exist unconditionally. Therefore, we need a conspicuous analysis of the influence of parameters M_0, c_0 and μ on the shock structure. We shall analyze their influence on the two quantities – the shock thickness and the temperature overshoot. Shock thickness measures the region within the shock structure where the most significant variation of state variable u occurs:

$$\delta = \left| \frac{u_1 - u_0}{(du/d\xi)_{\max}} \right|.$$



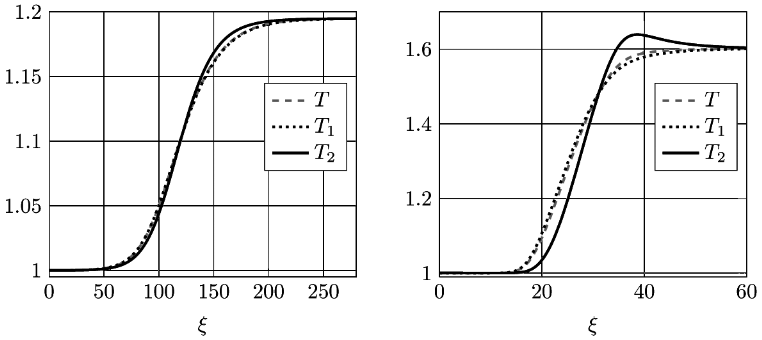
(a) (b)

Fig. 2. Velocity profiles in the shock structure (u – average velocity of the mixture, u_1 – velocity of the lighter constituent, u_2 – velocity of the heavier constituent): (a) $M_0 = 1.2$, $c_0 = 0.35$, $\mu = 0.05$; (b) $M_0 = 1.6$, $c_0 = 0.21$, $\mu = 0.1$.

We shall take the average velocity of the mixture to calculate the thickness. It is important to notice that the dimensionless shock thickness is equal to the reciprocal of the Knudsen number

$$\tilde{\delta} = \frac{\delta}{l_0} = \frac{1}{\mathrm{Kn}}. \tag{114}$$

Its value will help us to distinguish between the different flow regimes. Temperature overshoot (TO) measures the relative increase of the temperature of heavier con-



(a) (b)

Fig. 3. Temperature profiles in the shock structure (T – average temperature of the mixture, T_1 – temperature of the lighter constituent, T_2 – temperature of the heavier constituent): (a) $M_0 = 1.2$, $c_0 = 0.35$, $\mu = 0.05$; (b) $M_0 = 1.6$, $c_0 = 0.21$, $\mu = 0.1$.

stituent above the downstream temperature of the mixture:

$$\mathrm{TO} = \frac{\mathrm{T}_2^{\max} - \mathrm{T}_1}{\mathrm{T}_1 - \mathrm{T}_0},$$

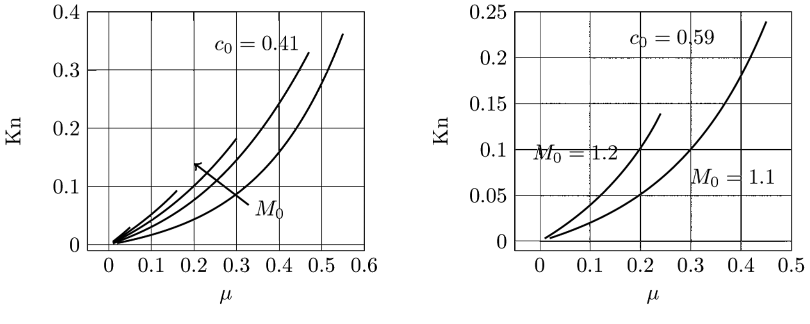
where $T_2^{\max}$ denotes the maximum temperature of the heavier constituent within the profile, whereas T_0 and T_1 are upstream and downstream equilibrium temperatures of the mixture, respectively.

The results presented in the sequel are based upon numerical calculations of the shock profiles for 4394 combinations of parameters M_0, c_0 and μ. For these values of the parameters, Knudsen number is bounded $0.002 \leq \mathrm{Kn} \leq 0.48$, which leads to the conclusion that the slip flow and the transition regime dominate.

5.4.1 - Analysis of the shock thickness

The dependence of the Knudsen number (shock thickness) on Mach number is monotonous for the fixed mass ratio and upstream concentration (Figure 4). It increases with the increase of Mach number, which amounts to a decrease of the shock thickness. This is rather expected result which resonates with the behaviour of a single-component gas in the range $M_0 \leq 2.0$. For larger Mach numbers in the single-component gases Kn decreases with M_0, but we cannot proceed to them since the continuity of the profile will be lost.

The Knudsen number increases monotonically also with the increase of the mass ratio, for the fixed Mach number and upstream concentration (Figure 4). In other words, the smaller the mass difference, the smaller the shock thickness. On the other hand, in mixtures with larger mass discrepancy between the constituents (smaller μ)

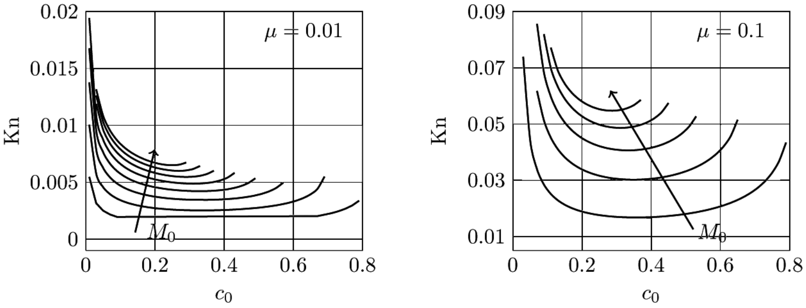


(a) $M_0 = 1.1 - 1.5$ (b)

Fig. 4. Dependence of Kn on mass ratio μ for fixed mass concentration c_0. Mach number is increased from $M_0 = 1.1$ with an increment 0.1. Arrow indicates graphs for increasing values of M_0.

the thickness is increased. This observation will be of interest in the analysis of the temperature overshoot.

Quite intriguing results were obtained when the Knudsen number is calculated in terms of equilibrium concentration, for the fixed values of M_0 and μ. For different combinations of M_0 and μ it was observed that Knudsen number increases when c_0 tends to extreme values, i.e. to 0 or to 1, whereas it has a single local minimum in between (Figure 5). One may say that the shock thickness decreases when one of the constituents dominates, i.e when the mixture behaves like a single-component gas. On the other hand, when a genuine mixture is at hand, the shock thickness is increased, i.e. the shock profile becomes wider.



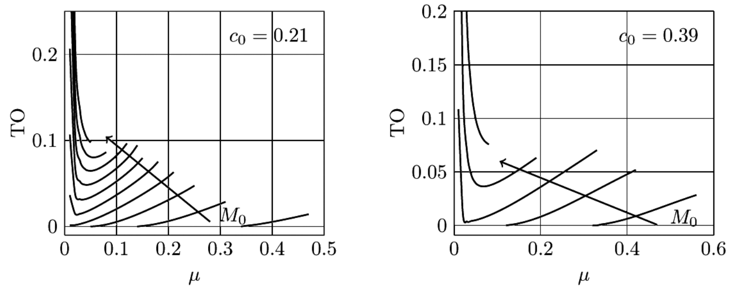
(a) $M_0 = 1.1 - 1.8$ (b) $M_0 = 1.1 - 1.5$

Fig. 5. Dependence of Kn on mass concentration c_0 for fixed mass ratio μ. Mach number is increased from $M_0 = 1.1$ with an increment 0.1. Arrow indicates graphs for increasing values of M_0.

This result can be attributed to the fact that, for c_0 far from lower or upper bound, the cross-collisions between the molecules of different species cause the intense exchange of the momentum and energy between the constituents, described by the source terms. This mechanism becomes equally important as self-collisions among the molecules of the same specie. It causes the endurance of relaxation of the state variables towards the equilibrium, so that more time (and space) is needed in a traveling wave to attain the equilibrium state, which increases the shock thickness.

5.4.2 - Analysis of the temperature overshoot

Temperature overshoot is a phenomenon peculiar for mixtures. In binary mixtures it is the most significant in the case of small molar fraction of heavier component. Abe and Oguchi [1] offered physical explanation of this phenomenon. They stated that in the case of vanishingly small mole fraction of the heavier component, the main structure of the shock wave is determined by the lighter one. This causes the deceleration of heavier component and, at the same time, conversion of the kinetic into the thermal energy. Nevertheless, the dissipation through conduction is a slow process, which cannot diffuse the thermal energy gained by deceleration. As a consequence, the internal energy (temperature) of the heavier component is raised above the terminal one.

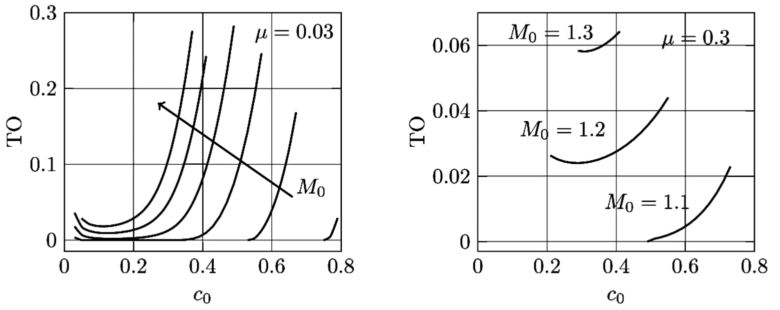


(a) $M_0 = 1.1 - 2.1$ with increment 0.1 (b) $M_0 = 1.1 - 1.5$ with increment 0.1

Fig. 6. Dependence of TO on mass ratio μ for fixed mass concentration c_0. Mach number is increased from $M_0 = 1.1$ with an increment 0.1. Arrow indicates graphs for increasing values of M_0.

In our model, the momentum and the energy transfer through viscosity and heat conduction are neglected. We are focused on dissipation caused by the mutual exchange of momentum and energy between the constituents, where the most prominent role is played by their mass ratio μ. Vast amount of numerical simulations revealed the two typical patterns (Figure 6). The first one is characterized by the existence of the minimal value of the mass ratio, below which the temperature overshoot does not occur. For mass ratios above this value, the temperature overshoot increases with the increase of μ. This pattern is common for low values of the Mach number.

Different pattern appears when the Mach number is increased: TO varies non-monotonically and there exists a value μ^* of the mass ratio which determines the local minimum of the temperature overshoot. This phenomenon is observed in this study thanks to a huge amount of numerical simulations, not performed previously. The outstanding feature of the non-monotonic behaviour of temperature overshoot can be given an explanation within the simplicity of our model, albeit in conjunction with the results of the shock thickness analysis. For $\mu < \mu^*$ the temperature overshoot is increased due to the large mass difference and low Kn. The flow is between the hy-



(a) $M_0 = 1.1 - 1.6$ with increment 0.1 (b) $M_0 = 1.1 - 1.3$ with increment 0.1

Fig. 7. Dependence of TO on mass concentration c_0 for fixed mass ratio μ. Mach number is increased from $M_0 = 1.1$ with an increment 0.1. Arrow indicates graphs for increasing values of M_0.

drodynamic and the slip flow regime, but the mass ratio is too small to yield sufficient exchange of the energy between the constituents which could attenuate TO. For $\mu > \mu^*$ the Knudsen number is increased, which puts the flow into the transition regime. Although the masses of the constituents become comparable, the exchange of energy is prevented by the rarefaction of the mixture, i.e. the small number of cross-collisions which could cause it. Consequently, the temperature of heavier constituent cannot be attenuated, and the temperature overshoot is increased.

Therefore, in a simplified model of MT mixtures, where the viscosity and the heat conductivity are neglected, the small mutual exchange of energy between the constituents can be pointed out as the main physical reason for the increase of temperature overshoot. It can occur for two reasons: (a) either there is a large mass discrepancy between the constituents (small μ), or (b) the mixture became more rarefied.

The temperature overshoot can also be analyzed in terms of equilibrium concentration c_0, for the fixed mass ratio μ. It is obvious that TO increases with c_0, which corresponds to the low fraction of heavier component (Figure 7). This is in sound agreement with the known results obtained by other methods. Interestingly enough, there is also a region of low values of c_0, i.e. high fraction of heavier component, for which TO exhibits a slight increase.

5.4.3 - Remark about the average temperature

In the previous discussion we introduced the average temperature of the mixture T according to the definition of the mixture internal energy, by using only its intrinsic (thermal) part:

$$\rho\varepsilon_I = \rho_1\varepsilon_1 + \rho_2\varepsilon_2.$$

This assumption is equivalent to the fact that intrinsic internal energy of the multi-component mixture must correspond to the intrinsic internal energy of the mixture with a single macroscopic temperature [**72**]. In the kinetic theory [**10**] average temperature of the mixture T_{kin} can also be based upon the complete internal energy, where the kinetic energy of diffusion is also taken into account:

$$\rho\varepsilon = \rho\varepsilon_I + \sum_{\alpha=1}^{2} \frac{1}{2}\rho_\alpha u_\alpha^2.$$

This kinetic temperature T_{kin} can be expressed in the dimensionless form:

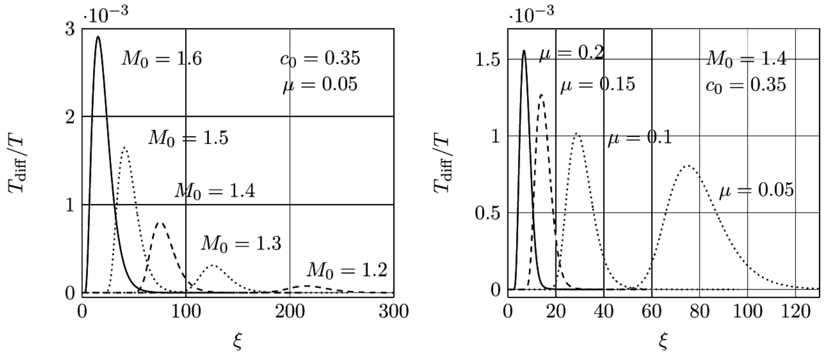
$$T_{\text{kin}} = c\frac{m}{m_1}T_1 + (1-c)\frac{m}{m_2}T_2 + \frac{1}{2}\frac{\gamma-1}{\gamma}\frac{J^2}{\rho^2 c(1-c)}, \tag{115}$$

where the following structure can be recognized:

$$T_{\text{kin}} = T + T_{\text{diff}}, \qquad \frac{T_{\text{diff}}}{T} = \frac{1}{2}\frac{\gamma-1}{\gamma}\frac{J^2}{\rho^2 c(1-c)T}.$$

Our aim is to estimate the relative contribution of the diffusive part of kinetic temperature in the shock structure.

From Figure 8 we can observe that the influence of the T_{diff} increases with the increase of the strength of the shock wave (i.e. Mach number M_0). The diffusive part



(a) (b)

Fig. 8. Influence of the diffusion part T_{diff} on the average temperature T: (a) different Mach numbers M_0; (b) different mass ratios μ.

T_{diff} increases also with the increase of the mass ratio. However, in the case of a weak shock waves the fraction of the diffusion part in the mixture temperature remains less then 0.3% . This result shows that relative contribution of the kinetic energy of diffusion to the average temperature is small, under the conditions stated above, and permits determination of the average mixture temperature from the intrinsic part of internal energy.

5.4.4 - Shock structure in viscous multi-temperature model

Final remark is concerned with the influence of viscosity and heat conductivity on the shock structure. To that end we shall use the classical NSF constitutive relations for the stress tensor and the heat flux of the constituents:

$$\begin{aligned} &\mathbf{t}_\alpha = -p_\alpha \mathbf{I} + \boldsymbol{\sigma}_\alpha, \quad \boldsymbol{\sigma}_\alpha = 2\mu_\alpha \mathbf{D}_\alpha, \quad \mathbf{D}_\alpha = \frac{1}{2}\left(\nabla \mathbf{v}_\alpha + (\nabla \mathbf{v}_\alpha)^T\right), \\ &\mathbf{q}_\alpha = -\kappa_\alpha \nabla T_\alpha, \end{aligned} \tag{116}$$

where μ_α is the viscosity, and κ_α the thermal conductivity. In one-dimensional setting, the dimensionless stresses and heat flow rates are determined by the following relations:

$$\tilde{\sigma}_\alpha = \frac{\sigma_\alpha}{\rho_0 \dfrac{k_B}{m_\alpha} T_0}, \quad \tilde{q}_\alpha = \frac{q_\alpha}{\rho_0 \dfrac{k_B}{m_\alpha} T_0 a_0}.$$

As in the inviscid case, the tilde will be omitted when writing the dimensionless equations. The shock structure equations (112) have to be adjoined with the constitutive relations written in dimensionless form:

$$\begin{aligned} &\frac{\mathrm{d}}{\mathrm{d}\xi}\left(u - \frac{J}{\rho c}\right) = \frac{3}{4}\frac{\rho_0 a_0 \lambda_0}{\gamma \mu_{10}} \frac{\sigma_1}{\sqrt{T - f(c)\Theta}}, \\ &\frac{\mathrm{d}}{\mathrm{d}\xi}\left(u - \frac{J}{\rho(1-c)}\right) = \frac{3}{4}\frac{\rho_0 a_0 \lambda_0}{\gamma \mu_{20}} \frac{\sigma_2}{\sqrt{T + (1-f(c))\Theta}}, \\ &\frac{\mathrm{d}}{\mathrm{d}\xi}(T - f(c)\Theta) = -\frac{\rho_0 a_0^3 \lambda_0}{\gamma T_0 \kappa_{10}} \frac{q_1}{\sqrt{T - f(c)\Theta}}, \\ &\frac{\mathrm{d}}{\mathrm{d}\xi}(T + (1-f(c))\Theta) = -\frac{\rho_0 a_0^3 \lambda_0}{\gamma T_0 \kappa_{20}} \frac{q_2}{\sqrt{T + (1-f(c))\Theta}}. \end{aligned} \tag{117}$$

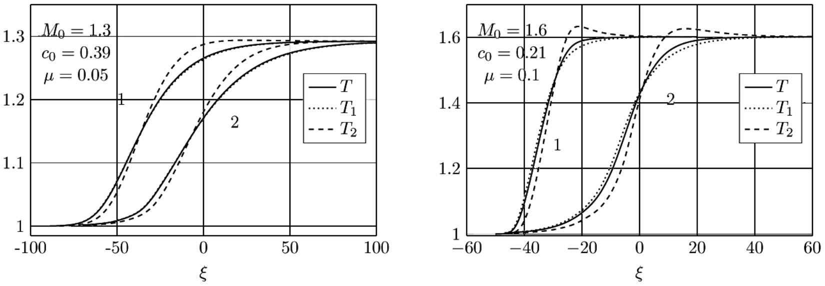
In further analysis, the viscosity and the thermal conductivity of the constituents, which appear in previous equations, will be expressed using the relations of kinetic theory of gases for the model of hard spheres:

$$\mu_{10} = \frac{5}{16}\frac{a_0}{\sqrt{\pi}d_1^2}\sqrt{\frac{m_0 m_1}{\gamma}}, \quad \mu_{20} = \frac{5}{16}\frac{a_0}{\sqrt{\pi}d_2^2}\sqrt{\frac{m_0 m_2}{\gamma}},$$

$$\kappa_{10} = \frac{15}{4}\frac{k}{m_1}\mu_{10}, \quad \kappa_{20} = \frac{15}{4}\frac{k}{m_2}\mu_{20},$$

where, as we mentioned before, d_1 and d_2 are the atomic diameters of the mixture constituents. Therefore, the presence of the viscosity and the thermal conductivity in the model implicitly introduces the atomic diameters of the constituents as new parameters. This fact entails another very important problem: with the change of the mass ratio, the ratio $\mathrm{DR} = d_1/d_2$ also changes. Our analysis will be restricted to the mixture of Helium and Argon, $\mathrm{DR} = d_{\mathrm{He}}/d_{\mathrm{Ar}} = 0.4366$.

Our main concern is the influence of the additional dissipative mechanisms on the temperature overshoot. On the basis of individual results (Figure 9) it can be concluded that the introduction of new dissipative mechanisms is not enough to completely exclude the occurrence of TO. Specifically, in relation to the values of TO in the inviscid case, the values of TO are considerably lower here. This also implies the increase of the minimal value of the Mach number at which TO occurs. In comparison with the inviscid case, TO is reduced but still present. Moreover, newly introduced dissipative mechanisms also increase the width of the shock wave. Preliminary study also shows that non-monotonic dependence of TO on the mass ratio μ persists. However, the systematic study is not performed yet, and it is a matter of ongoing research.



(a) (b)

Fig. 9. Temperature profiles: 1 – inviscid model, 2 – viscous model; T - average temperature of the mixture, T_1 - temperature of the lighter component, T_2 - temperature of the heavier component.

6 - Kinetic theory of mixtures

Main part of this study was devoted to extended thermodynamics of mixtures, particularly to the multi-temperature model. Although ET is regarded as a macroscopic theory, it was shown in Section 2 that it presents a bridge between the two levels of description – classical macroscopic level and mesoscopic level. Therefore, the kinetic approach to mixture theory cannot be disregarded if we want to get a proper impression about the accuracy of the multi-temperature model developed within ET. This Section will not bring thorough analysis of the kinetic theory of mixtures, but rather a sketch of the main issues and reveal the arguments which lead to the multi-temperature approximation of the kind we advocated in the previous Sections. Although the arguments are quite easy to follow, interested reader may take [**22**] or [**52**] for reference.

6.1 - *Kinetic modelling of mixtures*

State of the monatomic gas is determined by the velocity distribution function $f(t, \mathbf{x}, \xi)$. In the case of mixture, to every constituent we ascribe its own velocity distribution function $f_\alpha(t, \mathbf{x}, \xi)$, $\alpha = 1, \ldots, n$. Restricting our attention to monatomic gases only, the fundamental macroscopic quantity – the number density of the constituent – is then defined as:

$$n_\alpha(t, \mathbf{x}) = \int_{\mathbb{R}^3} f_\alpha(t, \mathbf{x}, \xi) \, \mathrm{d}\xi. \tag{118}$$

The rate of change of the distribution functions is then described by the system of Boltzmann equations, one for each constituent. However, the collision operators have more complex structure now. They comprise two mechanisms which cause the change of distribution functions:

(1) elastic collisions – they describe mechanical interactions between the particles;
(2) reactive collisions – they describe chemical reactions which occur in the mixture.

In the sequel we shall assume that no chemical reactions occur, i.e. the change of distribution function is only due to mechanical collisions and the Boltzmann equations read:

$$\frac{\partial f_\alpha}{\partial t} + \sum_{i=1}^{3} \xi_i \frac{\partial f_\alpha}{\partial x_i} = \sum_{\beta=1}^{n} Q_{\alpha\beta}(f_\alpha, f_\beta). \tag{119}$$

To describe the interactions of particles at atomic level, let (ξ, ξ_*) denote outgoing velocities of the particles in collision, and (ξ', ξ'_*) denote their incoming velocities. Interactions of the particles is governed by the conservation laws of momentum and energy during the collision:

$$\begin{aligned} & m_\alpha \xi' + m_\beta \xi'_* = m_\alpha \xi + m_\beta \xi_*, \\ & \frac{m_\alpha}{2}|\xi'|^2 + \frac{m_\beta}{2}|\xi'_*|^2 = \frac{m_\alpha}{2}|\xi|^2 + \frac{m_\beta}{2}|\xi_*|^2. \end{aligned} \tag{120}$$

Using these equations, the following velocity transformation is obtained, which expresses the incoming velocities in terms of the outgoing velocities and the unit vector ω:

$$\begin{aligned} \xi' &= \frac{m_\alpha \xi + m_\beta \xi_*}{m_\alpha + m_\beta} + \frac{m_\beta}{m_\alpha + m_\beta} T_\omega[\xi - \xi_*], \\ \xi'_* &= \frac{m_\alpha \xi + m_\beta \xi_*}{m_\alpha + m_\beta} - \frac{m_\alpha}{m_\alpha + m_\beta} T_\omega[\xi - \xi_*], \end{aligned}$$

where the transformation operator reads $T_\omega \mathbf{z} = \mathbf{z} - 2(\omega \cdot \mathbf{z})\mathbf{z}$.

The collision operators which describe elastic collisions are bilinear operators of the similar kind as in the single-component gas:

$$Q_{\alpha\beta}(f,g) = \int\limits_{\mathbb{R}^3} \int\limits_{S^2} (f' g'_* - f g_*) \breve{\mathcal{B}}_{\alpha\beta}(\xi, \xi_*, \omega) \mathrm{d}\omega \mathrm{d}\xi_*. \tag{121}$$

The cross section must obey the properties of Galilean invariance:

$$\breve{\mathcal{B}}_{\alpha\beta}(\xi, \xi_*, \omega) = \mathcal{B}_{\alpha\beta}\left(|\xi - \xi_*|, \left| \omega \cdot \frac{\xi - \xi_*}{|\xi - \xi_*|} \right| \right),$$

and micro-reversibility:

$$\mathcal{B}_{\alpha\beta}\left(|\xi - \xi_*|, \left| \omega \cdot \frac{\xi - \xi_*}{|\xi - \xi_*|} \right| \right) = \mathcal{B}_{\beta\alpha}\left(|\xi - \xi_*|, \left| \omega \cdot \frac{\xi - \xi_*}{|\xi - \xi_*|} \right| \right).$$

Proper relation to the macroscopic equations and the hydrodynamic approximation can be established only if we know the collision invariants, i.e. the conditions which secure the macroscopic equilibrium. In the case of mixtures without reactive collisions the following relations hold:

$$\begin{aligned} & \int\limits_{\mathbb{R}^3} Q_{\alpha\beta}(f,g)(\xi)\, \mathrm{d}\xi = 0, \\ & \int\limits_{\mathbb{R}^3} Q_{\alpha\beta}(f,g)(\xi) \begin{pmatrix} m_\alpha \xi \\ m_\alpha |\xi|^2 \end{pmatrix} \mathrm{d}\xi + \int\limits_{\mathbb{R}^3} Q_{\beta\alpha}(f,g)(\xi) \begin{pmatrix} m_\beta \xi \\ m_\beta |\xi|^2 \end{pmatrix} \mathrm{d}\xi = 0. \end{aligned} \tag{122}$$

They have the following implications on macroscopic description: (a) the mass density of each constituent is conserved and (b) the momentum and energy densities are conserved only for the whole mixture. These consequences are in a full accordance with the basic principles of extended thermodynamics applied to the non-reacting mixtures.

Finally, dissipative character of the kinetic model of mixtures is described by the appropriate form of the $H-$theorem. To that end the entropy production functional is defined as:

$$D(f_1,\dots,f_n) := \sum_{\alpha=1}^{n}\sum_{\beta=1}^{n}\int_{\mathbb{R}^3} Q_{\alpha\beta}(f_\alpha,f_\beta)(\xi)\log f_\alpha(\xi)\,\mathrm{d}\xi.$$

Theorem 6.1. *Assume that the cross-sections $\mathcal{B}_{\alpha\beta}$ are positive a.e. and that all $f_\alpha := f_\alpha(\xi) \geq 0$ are such that the collision operators $Q_{\alpha\beta}$ and the entropy production functional are well-defined. Then:*

1. *the entropy production is non-positive*
$$D(f_1,\dots,f_n) \leq 0;$$
2. *the following three properties are equivalent:*
   (a) *for any $1 \leq \alpha,\beta \leq n$ and $\xi \in \mathbb{R}^3$*
   $$Q_{\alpha\beta}(f_\alpha,f_\beta)(\xi) = 0;$$
   (b) *the entropy production vanishes*
   $$D(f_1,\dots,f_n) = 0;$$
   (c) *there exist $T > 0$, $\mathbf{v} \in \mathbb{R}^3$ and $n_\alpha \geq 0$ such that*
   $$f_{E\alpha}(\xi) = n_\alpha\left(\frac{m_\alpha}{2\pi k_B T}\right)^{3/2}\exp\left(-\frac{m_\alpha}{2k_B T}|\xi-\mathbf{v}|^2\right).$$

Note that the $H-$theorem determines the form of constituent equilibrium functions, that are Maxwellian–like and have common macroscopic velocity $\mathbf{v}$ and temperature T.

Standard issue in kinetic modelling is the derivation of macroscopic equations. In the single-constituent case it was rather straightforward. In the case of mixtures, the macroscopic quantities can be defined in different ways, especially the ones determined by the central moments, and certain attention has to be paid. We shall start with the definitions of mass, momentum and energy densities of the constituents:

$$\begin{pmatrix} \rho_\alpha \\ \rho v_{\alpha i} \\ \rho|\mathbf{v}_\alpha|^2 + 2\rho_\alpha\varepsilon_\alpha \end{pmatrix} = \int_{\mathbb{R}^3} m_\alpha \begin{pmatrix} 1 \\ \xi_i \\ |\xi|^2 \end{pmatrix} f_\alpha\,\mathrm{d}\xi. \tag{123}$$

The macroscopic quantities of the mixture can then be defined in the usual manner:

$$\rho = \sum_{\alpha=1}^{n} \rho_\alpha, \quad \rho \mathbf{v} = \sum_{\alpha=1}^{n} \rho_\alpha \mathbf{v}_\alpha, \quad \mathbf{u}_\alpha = \mathbf{v}_\alpha - \mathbf{v},$$

where $\mathbf{u}_\alpha$ is the diffusion velocity. Possible cause of confusion could lie in the fact that we may define two different kinds of the peculiar velocities – one with respect to the constituent velocities ($\mathbf{C}_\alpha$), and another one with respect to the mixture velocity ($\mathbf{C}$):

$$\mathbf{C}_\alpha = \boldsymbol{\xi} - \mathbf{v}_\alpha, \quad \mathbf{C} = \boldsymbol{\xi} - \mathbf{v}. \tag{124}$$

Both of them can be used, in a proper way, to define the internal energy density, the pressure tensor and the heat flux. When $\mathbf{C}_\alpha$ is used, these central moments are related to the constituents:

$$\rho_\alpha \varepsilon_\alpha = \int_{\mathbb{R}^3} \frac{1}{2} m_\alpha |\mathbf{C}_\alpha|^2 f_\alpha \mathrm{d}\mathbf{C}, \tag{125}$$

$$p_{\alpha ij} = \int_{\mathbb{R}^3} m_\alpha C_{\alpha i} C_{\alpha j} f_\alpha \mathrm{d}\mathbf{C} = -t_{\alpha ij}, \tag{126}$$

$$q_{\alpha i} = \int_{\mathbb{R}^3} \frac{1}{2} m_\alpha |\mathbf{C}_\alpha|^2 C_{\alpha i} f_\alpha \mathrm{d}\mathbf{C}, \tag{127}$$

while the use of $\mathbf{C}$ leads to the central moments related to the mixture:

$$\rho \varepsilon = \sum_{\alpha=1}^{n} \int_{\mathbb{R}^3} \frac{1}{2} m_\alpha |\mathbf{C}|^2 f_\alpha \mathrm{d}\mathbf{C}, \tag{128}$$

$$p_{ij} = \sum_{\alpha=1}^{n} \int_{\mathbb{R}^3} m_\alpha C_i C_j f_\alpha \mathrm{d}\mathbf{C} = -t_{ij}, \tag{129}$$

$$q_i = \sum_{\alpha=1}^{n} \int_{\mathbb{R}^3} \frac{1}{2} m_\alpha |\mathbf{C}|^2 C_i f_\alpha \mathrm{d}\mathbf{C}. \tag{130}$$

In this way (125) and (128) can be related through the same relations proposed in rational thermodynamics (50):

$$\rho \varepsilon = \sum_{\alpha=1}^{n} \rho_\alpha \left(\varepsilon_\alpha + \frac{1}{2} |\mathbf{u}_\alpha|^2 \right), \quad p_{ij} = \sum_{\alpha=1}^{n} p_{\alpha ij} + \rho_\alpha u_{\alpha i} u_{\alpha j},$$

$$q_i = \sum_{\alpha=1}^{n} q_{\alpha i} + \rho_\alpha \left(\varepsilon_\alpha + \frac{1}{2} |\mathbf{u}_\alpha|^2 \right) u_{\alpha i} + p_{\alpha ij} u_{\alpha j}.$$

With these relations one can derive the macroscopic equations:

$$\begin{aligned}\int_{\mathbb{R}^3} m_\alpha f_\alpha \begin{pmatrix} 1 \\ \xi \\ \xi^2/2 \end{pmatrix} \mathrm{d}\xi + \sum_{i=1}^{3} \int_{\mathbb{R}^3} m_\alpha \xi_i \frac{\partial f_\alpha}{\partial x_i} \begin{pmatrix} 1 \\ \xi \\ \xi^2/2 \end{pmatrix} \mathrm{d}\xi \\ = \sum_{\beta=1}^{n} \int_{\mathbb{R}^3} m_\alpha \begin{pmatrix} 1 \\ \xi \\ \xi^2/2 \end{pmatrix} Q_{\alpha\beta}(f_\alpha, f_\beta)\, \mathrm{d}\xi,\end{aligned}$$

to obtain the balance laws for the constituents:

$$\begin{aligned} &\frac{\partial \rho_\alpha}{\partial t} + \mathrm{div}(\rho_\alpha \mathbf{v}_\alpha) = 0, \\ &\frac{\partial (\rho_\alpha \mathbf{v}_\alpha)}{\partial t} + \mathrm{div}(\rho_\alpha \mathbf{v}_\alpha \otimes \mathbf{v}_\alpha - \mathbf{t}_\alpha) = \mathbf{m}_\alpha, \quad \mathbf{t}_\alpha = -\mathbf{p}_\alpha, \\ &\frac{\partial \left(\frac{1}{2}\rho_\alpha v_\alpha^2 + \rho_\alpha \varepsilon_\alpha\right)}{\partial t} + \mathrm{div}\left\{ \left(\frac{1}{2}\rho_\alpha v_\alpha^2 + \rho_\alpha \varepsilon_\alpha\right)\mathbf{v}_\alpha - \mathbf{t}_\alpha \mathbf{v}_\alpha + \mathbf{q}_\alpha \right\} = e_\alpha, \end{aligned} \tag{131}$$

that were postulated within the context of rational thermodynamics (47). Note that only the mass density of the constituents is conserved, as anticipated by the collision invariant $(122)_1$. Conservation of momentum and energy can be recovered by summation of the balance laws for the constituents, in accordance with $(122)_2$, and thus conserved only for the whole mixture. These results provide a different view on the metaphysical principles of rational thermodynamics – they become macroscopic consequences of the relations established at mesoscopic level.

6.2 - *Kinetic framework for multi-temperature mixtures*

The $H-$theorem for the mixtures determines the equilibrium distribution functions in the form where all the constituents have common velocity $\mathbf{v}$ and temperature T. This corresponds to the macroscopic equilibrium conditions derived in the MT model in extended thermodynamics. We also know that macroscopic fields in the local Maxwellian distribution (17), obtained as a first approximation in the Chapman-Enskog expansion, satisfy Euler gas dynamics equations (26). However, at this moment we do not have an appropriate counterpart of the local Maxwellian in the case of mixtures which will produce the macroscopic equations of Euler type. It is our goal to find the kinetic framework which will lead to the macroscopic multi-temperature model at Euler level.

The key for derivation of the MT model at Euler level is a proper scaling of the Boltzmann equations for mixtures. Natural attempt is to scale the Boltzmann equations as follows (see e.g. [**50**]):

$$\frac{\partial f_\alpha}{\partial t} + \sum_{i=1}^{3} \xi_i \frac{\partial f_\alpha}{\partial x_i} = \frac{1}{\varepsilon} \sum_{\beta=1}^{n} Q_{\alpha\beta}(f_\alpha, f_\beta). \tag{132}$$

It is easy to show that in the limit we have:

$$\varepsilon \to 0 \quad \Rightarrow \quad Q_{\alpha\beta}(f_\alpha, f_\beta) = 0,$$

and that the local equilibrium distribution reads:

$$f_{E\alpha}(\xi) = n_\alpha \left(\frac{m_\alpha}{2\pi k_B T} \right)^{3/2} \exp\left(-\frac{m_\alpha}{2k_B T} |\xi - \mathbf{v}|^2 \right),$$

where $n_\alpha = n_\alpha(t, \mathbf{x})$, $\mathbf{v} = \mathbf{v}(t, \mathbf{x})$ and $T = T(t, \mathbf{x})$. Obviously, under the scaling given in (132), the velocities and the temperatures of the constituents cannot be distinguished at the Euler level. Equivalent result was also obtained in the case of kinetic model for mixtures of polyatomic gases [**26**]. Therefore, some other scaling with a proper motivation has to be found.

It was (again) Harold Grad who conjectured in 1960 that in a binary mixture, consisted of species with disparate masses, the approach to equilibrium exhibits an epochal relaxation: first convergence to the local Maxwellians with independent temperatures, then equilibration between the species. In a more formal way, the approximate local Maxwellian distributions are reached by the species in times of the order of different self-collision times τ_{11} and τ_{22}, while equilibration between the species is reached after that, in time of order $\tau_{\Delta T}$:

$$\frac{\tau_{11}}{\tau_{22}} \approx \frac{\tau_{22}}{\tau_{\Delta T}} \approx \left(\frac{m_1}{m_2} \right)^{1/2},$$

where m_1 and m_2 ($m_1 < m_2$) are the molecular masses. Goldman and Sirovich [**32**] supported this idea and divided the approach to equilibrium in binary mixtures in the two phases: (1) Maxwellization – the approach of the distribution functions towards the local Maxwellians with different velocities and temperatures and (2) equilibration – vanishing of differences in velocities and temperatures in the local Maxwellians. These observations recognize the local Maxwellians, with different velocities and temperatures, as an intermediate phase in the process of equilibration towards common velocity and temperature.

The idea of sequential (epochal) relaxation led to the formal reordering in the Boltzmann equations for the binary mixture [**31**]. There were different reordering strategies with the common property that collision process in one species is weakly affected by the presence of other species. Therefore, the dominant term in the Boltzmann equation for constituent α should be the collision integral $Q_{\alpha\alpha}(f_\alpha,f_\alpha)$, describing the collisions of the molecules of the same species. This (formally) gives rise to another, species-dependent scaling of the Boltzmann equations:

$$\frac{\partial f_\alpha^\varepsilon}{\partial t}+\sum_{i=1}^{3}\xi_i\frac{\partial f_\alpha^\varepsilon}{\partial x_i}=\frac{1}{\varepsilon}Q_{\alpha\alpha}(f_\alpha^\varepsilon,f_\alpha^\varepsilon)+\sum_{\substack{\beta=1\\(\beta\neq\alpha)}}^{n}Q_{\alpha\beta}(f_\alpha^\varepsilon,f_\beta^\varepsilon). \tag{133}$$

This scaling obviously leads to the following limiting behaviour:

$$\varepsilon\to 0 \quad\Rightarrow\quad Q_{\alpha\alpha}(f_\alpha,f_\alpha)=0,$$

and the new local equilibrium approximation of the distribution function:

$$f_{E\alpha}(\xi)=n_\alpha\left(\frac{m_\alpha}{2\pi k_B T_\alpha}\right)^{3/2}\exp\left(-\frac{m_\alpha}{2k_B T_\alpha}|\xi-\mathbf{v}_\alpha|^2\right), \tag{134}$$

where $n_\alpha=n_\alpha(t,\mathbf{x})$, $\mathbf{v}_\alpha=\mathbf{v}_\alpha(t,\mathbf{x})$ and $T_\alpha=T_\alpha(t,\mathbf{x})$. This equilibrium approximation determines the local equilibrium with different velocities $\mathbf{v}_\alpha$ and temperatures T_α for the constituents. The macroscopic fields are not arbitrary, but satisfy Euler gas dynamics equations for mixtures (131), with:

$$p_\alpha=\rho_\alpha\frac{k_B}{m_\alpha}T_\alpha,\quad \varepsilon_\alpha=\frac{3}{2}\frac{p_\alpha}{\rho_\alpha},$$
$$p_{\alpha ij}^{(E)}=p_\alpha\,\delta_{ij},\quad q_{\alpha i}^{(E)}=0.$$

The source terms in (131) are calculated as the moments of the collision operator at the Euler level:

$$\mathbf{m}_\alpha=\sum_{\substack{\beta=1\\(\beta\neq\alpha)}}^{n}\int_{\mathbb{R}^3}m_\alpha\xi\,Q_{\alpha\beta}(f_{E\alpha},f_{E\beta})\,\mathrm{d}\xi, \tag{135}$$

$$e_\alpha=\sum_{\substack{\beta=1\\(\beta\neq\alpha)}}^{n}\int_{\mathbb{R}^3}\frac{1}{2}m_\alpha\xi^2\,Q_{\alpha\beta}(f_{E\alpha},f_{E\beta})\,\mathrm{d}\xi.$$

The scaling with dominated self-collisions (133) was used to derive the hydrodynamic closure of kinetic equations for mixtures [**10, 11**]. There were analyzed also reactive collisions. It is important to note that the source terms, derived from elastic collision integral, have the form which matches the form of the source terms derived in ET in the limit $|\mathbf{v}_\alpha-\mathbf{v}_\beta|\to 0$, $T_\alpha-T_\beta\to 0$, i.e in the case of small deviations from equilibrium. This result encourages further parallel studies of kinetic and macroscopic aspects of the multi-temperature mixtures.

Although the hydrodynamic closure at the Euler level, obtained by particular scaling (133), gave promising results, there are still open questions. Namely, it formally matches the multi-temperature mixture model of ET, but its physical justification is not inevitable. Formally, there is a way out of this problem if one takes the scaling:

$$\frac{\partial f_\alpha^\varepsilon}{\partial t} + \sum_{i=1}^{3} \xi_i \frac{\partial f_\alpha^\varepsilon}{\partial x_i} = \frac{1}{\varepsilon^{k_\alpha}} Q_{\alpha\alpha}(f_\alpha^\varepsilon, f_\alpha^\varepsilon) + \sum_{\substack{\beta=1 \\ (\beta\neq\alpha)}}^{n} \frac{1}{\varepsilon^{k_{\alpha\beta}}} Q_{\alpha\beta}(f_\alpha^\varepsilon, f_\beta^\varepsilon),$$

with $k_\alpha > k_{\alpha\beta}$. This scaling preserves the assumption that self-collision process is the fastest one among all elastic collisions. The presence of non-dominating small parameters in the collision operators will certainly influence the macroscopic source terms, determining their order of magnitude. This study, which has to be adjoined with a careful dimensional analysis and estimates of reference quantities, is still work in progress.

7 - Final remarks

It is not possible to cover all important or interesting topics in the survey of this kind. The choice of subjects always depends on personal preferences and research interests. There are a lot of open problems in the domain covered by these lecture notes. We would like to mention some of them at the end.

At the very beginning, we put extended thermodynamics in juxtaposition with classical continuum modelling and kinetic theory of gases, and we saw the paradigmatic model of 13 moments. On the other hand, in the multi-temperature modelling of mixtures we made a closure at the Euler level. Is there a counterpart of 13 moments model in the context of mixtures? So far the answer was given through the moments method of kinetic theory [**31**], or in the single-temperature case [**44**]. Deeper analysis within the context of extended thermodynamics has not been preformed, yet.

Another group of problems which remained out of the scope is concerned with the chemically reacting mixtures. First, in the context of kinetic theory one has to take into account operator of reactive (inelastic) collisions. Consequently, two kinds of processes can be identified: (a) processes driven by elastic scattering (slow chemical reaction) and (b) processes driven by elastic scattering and chemical reaction (fast chemical reaction). This distinction leads to the different hydrodynamic limits, as well. This group of problems is still almost completely open in the context of extended thermodynamics.

Finally, the question of model equations and asymptotic analysis in the kinetic theory of mixtures remained completely beyond the limits of these notes. Interested reader could take [3] or [**18**] as good sources of information.

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SRBOLJUB SIMIĆ
Department of Mechanics
University of Novi Sad
Trg Dositeja Obradovića 6
21000 Novi Sad, Serbia
e-mail: ssimic@uns.ac.rs

MILANA PAVIĆ-ČOLIĆ
Department of Mathematics and Informatics
University of Novi Sad
Trg Dositeja Obradovića 4
21000 Novi Sad, Serbia
e-mail: milana.pavic@dmi.uns.ac.rs

DAMIR MADJAREVIĆ
Department of Mechanics
University of Novi Sad
Trg Dositeja Obradovića 6
21000 Novi Sad, Serbia
e-mail: damirm@uns.ac.rs