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# An extended thermodynamics description of stationary heat transfer in binary gas mixtures confined in radial symmetric bounded domains

Received: 19 August 2011 / Accepted: 12 September 2011 / Published online: 11 October 2011  
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**Abstract** In this paper, we describe the stationary heat transfer problem in non-reacting gas mixtures confined between two coaxial cylinders or two concentric spheres kept at different temperatures. For the description of this phenomenon, we refer to the extended thermodynamics 13-moments single temperature system and we compare its predictions with those obtained by the classical Navier–Stokes–Fourier–Fick approximations. In contrast with the classical theory, we show that extended thermodynamics takes over also thermodiffusion effects, predicts boundary layers for the common temperature and non-vanishing stress tensors. Furthermore, we compare the results with those already obtained in the planar case, in order to point out the effects of the radial dependence.

**Keywords** Extended thermodynamics · Gas mixtures · Heat transfer · Thermal diffusion

## 1 Introduction

In a gas mixture, the presence of a temperature gradient gives rise to a gradient of the relative concentration of the constituents [1]. This effect is known as thermal diffusion and was theoretically discovered and described by Enskog [2,3] and, independently, by Chapman some years later [4]. The experimental demonstration of the existence of such a phenomenon is due to Chapman and Dootson [5]. After its discovery, very soon thermal diffusion was used for the mixture separation and a wide literature appeared on this topic, with analysis both from the theoretical and from the experimental point of view, see for example [6–14]. At the beginning, all the theoretical treatments were restricted by the assumption that the mixture was confined between two parallel plates [6,11–14], one hot and the other cold. Nevertheless, in experiments of mixture separations (in particular isotope separations) and in devices for the experimental determination of physical coefficients such an assumption was not correct [7–10]. In fact, the separation columns used in practice consists usually of two concentric cylinders. So, from 1940 many authors studied the heat transfer problem and the isotope separation in cylindrical symmetry [15–23].

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Dedicated to Professor Ingo Müller on the occasion of his 75th birthday.

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Communicated by Manuel Torrilhon.

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The description of gas mixture effects through mathematical models is an appealing problem studied by many authors in the last century. There are basically two different theoretical approaches to this subject: a microscopic description of the phenomena through kinetic theory and Boltzmann equations [1] and macroscopic models from continuum mechanics [24–27]. We have to recall that the first theory for homogeneous gas mixtures within the framework of rational thermodynamics was proposed by Truesdell [28–31] and Müller [32,33] and in what follows we will follow their approach to the problem. Phenomenological macroscopic models are often less accurate but extremely more simple to be used. Unfortunately, in the stationary case the most simple equations, that are the ones obtained through the Fourier, Navier-Stokes and Fick approximations with the assumption of a common temperature (classical thermodynamics), fail to take into account thermal diffusion [34]. Very recently, it was shown [35–37] that in the planar stationary case, thermal diffusion is qualitatively and quantitatively well described by the extended thermodynamics (ET) model for mixture with 13 moments and the single temperature assumption due to Heckl and Müller [38] with the BGK approximation [39]. For the planar case, the same heat transfer problem has been studied by Kosuge, Aoki and Takata [40] through the numerical integration of the full Boltzmann equation. They found that the common temperature exhibits boundary layers in the neighborhood of the two boundaries. As already remarked, this behavior cannot be described by the field equations of classical thermodynamics. Indeed, the classical temperature field in the planar case is practically the linear function which connects the two boundary temperatures. Instead, it has been found that the field equations of 13 moments extended thermodynamics appropriate to the planar case are able to describe these boundary layers [35–37]. In particular, in [36] the solutions of the non-linearized field equations of extended thermodynamics are directly compared with the results obtained in [40] through kinetic theory. The comparison shows a very good agreement for the temperature field. Furthermore, the same equations imply a non-constant mass concentration for the two constituents. In fact, if a temperature gradient is applied to a monoatomic gas mixture, the lighter molecules tend to move toward the hot side, while the heavier ones toward the cold side.

For the cylindrical and the spherical domains, there are no results in the literature about the field variables obtained from the numerical integration of the Boltzmann equation or from experimental measurement, but also in these geometries, we expect a behavior similar to the classical solution combined with boundary layers. The aim of this paper is precisely to test these equations in non-planar domains and to study the effect of domain geometry on the thermodiffusion.

In this framework, also the comparison between classical and 13 moments extended thermodynamics description of heat transfer problems plays a relevant role. In the literature, previous comparisons were already presented for single gases [41–45]. In that case, it was clearly shown that for heat transfer in non-planar geometries, there were differences between classical and extended thermodynamics models: in the temperature behavior and also in the presence of non-vanishing stress tensor components. So, what will we expect for heat transfer problems in binary mixtures confined in radial domains? Of course, as for a single gas, stress tensors do not vanish and the temperature presents a profile with boundary layers that cannot be predicted by the classical theory. Moreover, thermodiffusion is well described by ET, and it is possible to show how this phenomenon depends on the geometry of the problem. In particular, the curvature of the domain enhances the thermal diffusion effect.

In this paper, we have extended the model by Heckl and Müller to non-Cartesian coordinates with BGK approximation (see Sect. 2 and the “Appendix”). Furthermore, in Sect. 3, the Navier–Stokes–Fourier–Fick model is briefly recalled. In order to get analytical solutions (Sect. 4), we have focused on the linearized equation system and in Sect. 5 we have used fluctuation principle [46] to prescribe the non-observable boundary data. In Sect. 6, the solutions are analyzed and compared.

## 2 Extended thermodynamics field equations

In this paper, we refer to the field equations derived by Heckl and Müller [38] in the context of extended thermodynamics. In the Appendix, one can find some details about the determination of the field equations. We will focus here on binary inert mixtures of classical ideal gases confined between two cylinders or two spheres maintained at different temperatures. We assume that one boundary is permeable, while the other is impermeable, so that the diffusion flux of each component vanishes (see “Appendix”). Moreover, the process is supposed to be stationary, the velocity of the mixture (barycentric velocity) vanishes and the fields depend only on the radial coordinate  $r$ . From now on,  $r$  will denote the radial coordinate in the case of coaxial cylinders or concentric spheres and the Cartesian coordinate orthogonal to the walls in the planar domains. Explicitly, the equations read

$$\begin{aligned}
\frac{d}{dr} [\rho_{(rr)}^1 + \underline{p}^1] + \frac{j}{r} [\rho_{(rr)}^1 - \rho_{(\vartheta\vartheta)}^1] &= \underline{0}, \\
\frac{8}{15} \frac{dq^1}{dr} - \frac{4}{15} j \frac{q^1}{r} &= -\frac{\rho_{(rr)}^1}{\tau}, \\
\frac{d}{dr} \left[ 5p^1 \frac{k_B}{m_1} T + 7 \frac{k_B}{m_1} T \rho_{(rr)}^1 \right] + \frac{7}{r} j \frac{k_B}{m_1} T [\rho_{(rr)}^1 - \rho_{(\vartheta\vartheta)}^1] &= -2 \frac{q^1}{\tau},
\end{aligned} \tag{1}$$

for the first constituent

$$\begin{aligned}
\frac{d}{dr} [p^1 + p^2] &= 0, \\
\frac{d}{dr} [q^1 + q^2] + \frac{j}{r} [q^1 + q^2] &= 0, \\
-\frac{4}{5} \frac{j}{r} [q^1 + q^2] &= -\frac{\rho_{(rr)}^1 + \rho_{(rr)}^2}{\tau}, \\
\frac{d}{dr} \left[ 5 \left( \frac{k_B}{m_1} p^1 + \frac{k_B}{m_2} p^2 \right) T + 7 \left( \frac{k_B}{m_1} \rho_{(rr)}^1 + \frac{k_B}{m_2} \rho_{(rr)}^2 \right) T \right] \\
+ \frac{7}{r} j \left[ \frac{k_B}{m_1} (\rho_{(rr)}^1 - \rho_{(\vartheta\vartheta)}^1) + \frac{k_B}{m_2} (\rho_{(rr)}^2 - \rho_{(\vartheta\vartheta)}^2) \right] T &= -2 \frac{q^1 + q^2}{\tau},
\end{aligned} \tag{2}$$

for the whole mixture, together with the algebraic relations

$$\begin{aligned}
\rho_{(\vartheta\vartheta)}^1 &= \frac{2}{5} \tau (\Gamma_{31}^3 - \Gamma_{21}^2) q^1 - \frac{1}{2} \rho_{(rr)}^1, \\
\rho_{(33)}^1 &= -\rho_{(rr)}^1 - \rho_{(\vartheta\vartheta)}^1, \\
\rho_{(\vartheta\vartheta)}^1 + \rho_{(\vartheta\vartheta)}^2 &= -\frac{4}{5} \tau \Gamma_{21}^2 (q^1 + q^2), \\
\rho_{(33)}^1 + \rho_{(33)}^2 &= -\frac{4}{5} \tau \Gamma_{31}^3 (q^1 + q^2).
\end{aligned} \tag{3}$$

This system consists of eleven equations in the eleven fields  $p^\alpha$ ,  $\rho_{(rr)}^\alpha$ ,  $\rho_{(\vartheta\vartheta)}^\alpha$ ,  $\rho_{(33)}^\alpha$ ,  $q^\alpha$  (with  $\alpha = 1, 2$ ) and  $T$ , which represent, respectively, the pressure, the traceless<sup>1</sup> parts of the stress tensor, the radial component of the heat flux appropriate to the  $\alpha$ -constituent and the common temperature<sup>2</sup>. Instead of the usual contra- or co-variant components of the vectors and tensors, here we have used the physical components (for details, see [25,47] or the ‘‘Appendix’’).  $k_B$  denotes the Boltzmann constant and  $m_\alpha$  are the atomic masses.  $\Gamma_{lk}^i$  represents the Christoffel symbols and the index  $j$  characterizes the three different geometries: we have  $j = 0$  for the planar case,  $j = 1$  for cylindrical domains and  $j = 2$  for the spherical geometry. Finally,  $\tau$  is the constant relaxation time appropriate to the BGK approximations [39] used in this paper.

Equations (1)<sub>1</sub> and (2)<sub>1</sub> are the conservation laws of momentum for the first constituent and for the whole mixture. Equation (2)<sub>2</sub> is the conservation law of energy for the whole mixture. While, the other equations are the balance laws for the traceless parts of the stress tensor and for the heat flux.

The equations for the whole mixture (2) coincide with those of extended thermodynamics with thirteen moments for a single gas in cylindrical and spherical coordinates, derived and studied by Müller and Ruggeri [41]. The underlined terms in system (1–3) give the field equations of classical thermodynamics. This last system will be discussed in detail in the next section.

For further purposes, we introduce the mass concentration  $c^\alpha$ , defined in terms of the mass density  $\rho^\alpha$ , as

$$c^\alpha = \frac{\rho^\alpha}{\rho} \quad \text{where} \quad \rho = \rho^1 + \rho^2. \tag{4}$$

These quantities can be easily computed with respect to the field variables through the thermal equations of state,  $p^\alpha = k_B/m_\alpha \rho^\alpha T$ .

The field Eqs. (1–3) require six boundary conditions to be integrated. Unfortunately, we can associate to this problem only four boundary values that are the temperature, the total pressure and the mass concentration at the external permeable boundary and the temperature at the internal impermeable wall:

<sup>1</sup> Angular brackets refer to the traceless part of a symmetric tensor.

<sup>2</sup> See the ‘‘Appendix’’ for the definition of the common temperature.

$$\begin{aligned} \text{at } r = r_e \quad T &= T_e, \quad p^1 + p^2 = P, \quad c^1 = c_e^1, \\ \text{at } r = r_i \quad T &= T_i. \end{aligned} \quad (5)$$

Later on, we will prescribe the remaining boundary values through a fluctuation principle [46].

To avoid misunderstandings, we underline that the boundary temperatures  $T_e$  and  $T_i$  are the temperatures of the gas at the walls, not the wall temperatures. Our analysis does not incorporate the temperature jumps at the walls.

We proceed here introducing the dimensionless fields

$$\tilde{r} = \frac{r}{r_e}, \quad \tilde{T} = \frac{T}{T_e}, \quad \tilde{p}^\alpha = \frac{p^\alpha}{P}, \quad \tilde{q}^\alpha = \frac{q^\alpha}{P\sqrt{\frac{k_B}{m_2}T_e}}, \quad \tilde{\rho}_{(ij)}^\alpha = \frac{\rho_{(ij)}^\alpha}{P} \quad (6)$$

and the parameters

$$r_m = \frac{m_1}{m_2}, \quad \text{Kn} = \frac{\tau\sqrt{\frac{k_B}{m_2}T_e}}{r_e}. \quad (7)$$

We assume that  $m_2 > m_1$  and so Kn plays the role of the Knudsen number related to the heaviest component of the mixture.

With respect to the dimensionless variables, the system<sup>3</sup> is rewritten as

$$\begin{aligned} \frac{d}{d\tilde{r}} \left[ \tilde{\rho}_{(rr)}^1 + \tilde{p}^1 \right] + \frac{j}{\tilde{r}} \left[ \tilde{\rho}_{(rr)}^1 - \tilde{\rho}_{(\vartheta\vartheta)}^1 \right] &= 0, \\ \frac{8}{15} \frac{d\tilde{q}^1}{d\tilde{r}} - \frac{4}{15} j \frac{\tilde{q}^1}{\tilde{r}} &= -\frac{\tilde{\rho}_{(rr)}^1}{\text{Kn}}, \\ \frac{d}{d\tilde{r}} \left[ 5\tilde{p}^1\tilde{T} + 7\tilde{T}\tilde{\rho}_{(rr)}^1 \right] + \frac{7}{\tilde{r}} j \tilde{T} \left[ \tilde{\rho}_{(rr)}^1 - \tilde{\rho}_{(\vartheta\vartheta)}^1 \right] &= -2r_m \frac{\tilde{q}^1}{\text{Kn}}, \\ \frac{d}{d\tilde{r}} \left[ \tilde{p}^1 + \tilde{p}^2 \right] &= 0, \\ \frac{d}{d\tilde{r}} \left[ \tilde{q}^1 + \tilde{q}^2 \right] + \frac{j}{\tilde{r}} \left[ \tilde{q}^1 + \tilde{q}^2 \right] &= 0, \\ -\frac{4}{5} \frac{j}{\tilde{r}} \left[ \tilde{q}^1 + \tilde{q}^2 \right] &= -\frac{\tilde{\rho}_{(rr)}^1 + \tilde{\rho}_{(rr)}^2}{\text{Kn}}, \\ \frac{d}{d\tilde{r}} \left[ 5(\tilde{p}^1 + r_m\tilde{p}^2)\tilde{T} + 7(\tilde{\rho}_{(rr)}^1 + r_m\tilde{\rho}_{(rr)}^2)\tilde{T} \right] \\ + \frac{7}{\tilde{r}} j \left[ \tilde{\rho}_{(rr)}^1 - \tilde{\rho}_{(\vartheta\vartheta)}^1 + r_m(\tilde{\rho}_{(rr)}^2 - \tilde{\rho}_{(\vartheta\vartheta)}^2) \right] \tilde{T} &= -2r_m \frac{\tilde{q}^1 + \tilde{q}^2}{\text{Kn}} \end{aligned} \quad (8)$$

and the mass concentrations become

$$c^1 = \frac{r_m\tilde{p}^1}{r_m\tilde{p}^1 + \tilde{p}^2}, \quad c^2 = 1 - c^1. \quad (9)$$

Equation (8) cannot be solved analytically and, therefore, in order to get analytical solutions, we linearize system (8) around the constant state  $\tilde{T} = \tilde{T}_e = 1$ ,  $\tilde{p}^\alpha = \tilde{p}_e^\alpha$ ,  $\tilde{\rho}_{(ij)}^\alpha = 0$  and  $\tilde{q}^\alpha = 0$ , where the values  $\tilde{p}_e^\alpha$  in terms of the boundary concentration  $c_e^1$  are given by

$$\tilde{p}_e^1 = \frac{c_e^1}{r_m + c_e^1(1 - r_m)}, \quad \tilde{p}_e^2 = 1 - \tilde{p}_e^1. \quad (10)$$

In the linearized case, all Eq. (8) remain unchanged, since they contain only linear terms, except for (8)<sub>3,7</sub> that become

$$\begin{aligned} \frac{d}{d\tilde{r}} \left[ 5\tilde{p}_e^1\tilde{T} + 5\tilde{p}^1 + 7\tilde{\rho}_{(rr)}^1 \right] + \frac{7}{\tilde{r}} j \left[ \tilde{\rho}_{(rr)}^1 - \tilde{\rho}_{(\vartheta\vartheta)}^1 \right] &= -2r_m \frac{\tilde{q}^1}{\text{Kn}}, \\ \frac{d}{d\tilde{r}} \left[ 5(\tilde{p}_e^1 + r_m\tilde{p}_e^2)\tilde{T} + 5\tilde{p}^1 + 5r_m\tilde{p}^2 + 7\tilde{\rho}_{(rr)}^1 + 7r_m\tilde{\rho}_{(rr)}^2 \right] \\ + \frac{7}{\tilde{r}} j \left[ \tilde{\rho}_{(rr)}^1 - \tilde{\rho}_{(\vartheta\vartheta)}^1 + r_m(\tilde{\rho}_{(rr)}^2 - \tilde{\rho}_{(\vartheta\vartheta)}^2) \right] &= -2r_m \frac{\tilde{q}^1 + \tilde{q}^2}{\text{Kn}}. \end{aligned} \quad (11)$$

<sup>3</sup> The dimensionless form of the algebraic relations (3) is not presented here, since it is trivial.

After some rearrangements, the field equations read

$$\begin{aligned}
\frac{d}{d\bar{r}} \left[ \tilde{\rho}_{(rr)}^1 + \tilde{p}^1 \right] + \frac{j}{\bar{r}} \left[ \tilde{\rho}_{(rr)}^1 - \tilde{\rho}_{(\vartheta\vartheta)}^1 \right] &= 0, \\
\frac{8}{15} \frac{d\tilde{q}^1}{d\bar{r}} - \frac{4}{15} j \frac{\tilde{q}^1}{\bar{r}} &= -\frac{\tilde{\rho}_{(rr)}^1}{\text{Kn}}, \\
\frac{d}{d\bar{r}} \left[ 5\tilde{p}_c^1 \tilde{T} - 2\tilde{p}^1 \right] &= -2r_m \frac{\tilde{q}^1}{\text{Kn}}, \\
\tilde{p}^1 + \tilde{p}^2 &= 1, \\
\tilde{q}^1 + \tilde{q}^2 &= \frac{Q}{\bar{r}^j}, \\
\tilde{\rho}_{(rr)}^1 + \tilde{\rho}_{(rr)}^2 &= \frac{4}{5} j \text{Kn} \frac{Q}{\bar{r}^{j+1}}, \\
\frac{d}{d\bar{r}} \left[ 5(r_m + \tilde{p}_c^1(1-r_m)) \tilde{T} - 2(1-r_m)\tilde{p}^1 \right] &= -2r_m \frac{\tilde{q}^1 + \tilde{q}^2}{\text{Kn}},
\end{aligned} \tag{12}$$

together with

$$\begin{aligned}
\tilde{\rho}_{(\vartheta\vartheta)}^1 &= \frac{2}{5} \text{Kn} \frac{j(j-2)}{\bar{r}} \tilde{q}^1 - \frac{1}{2} \tilde{\rho}_{(rr)}^1, \\
\tilde{\rho}_{(33)}^1 &= -\tilde{\rho}_{(rr)}^1 - \tilde{\rho}_{(\vartheta\vartheta)}^1, \\
\tilde{\rho}_{(\vartheta\vartheta)}^1 + \tilde{\rho}_{(\vartheta\vartheta)}^2 &= -\frac{2}{5} \text{Kn} \frac{j(3-j)}{\bar{r}} (\tilde{q}^1 + \tilde{q}^2), \\
\tilde{\rho}_{(33)}^1 + \tilde{\rho}_{(33)}^2 &= -\frac{2}{5} \text{Kn} \frac{j(j-1)}{\bar{r}} (\tilde{q}^1 + \tilde{q}^2),
\end{aligned} \tag{13}$$

where  $Q$  is a dimensionless constant to be determined and we have already used the boundary condition (5)<sub>2</sub>. In the linear approximation, the mass concentrations are expressed as

$$\begin{aligned}
c^1 &= \frac{r_m}{1-(1-r_m)\tilde{p}_c^1} \left[ \tilde{p}^1 + \tilde{p}_c^1 \frac{1-r_m}{1-(1-r_m)\tilde{p}_c^1} (\tilde{p}^1 - \tilde{p}_c^1) \right], \\
c^2 &= 1 - c^1.
\end{aligned} \tag{14}$$

The use of fluctuation principle requires the explicit expression of the entropy density. In this case, the entropy density reads (see [38] and ‘‘Appendix’’)

$$\rho\eta = \sum_{\alpha=1}^2 \left[ \rho^\alpha \eta_E^\alpha - \frac{1}{4} \frac{\rho_{(ij)}^\alpha \rho_{(ij)}^\alpha}{p^\alpha T} - \frac{1}{5} \frac{q^\alpha q^\alpha}{p^\alpha \frac{k_B}{m_\alpha} T^2} \right], \tag{15}$$

where the symbol E refers to the equilibrium value. So, in terms of the dimensionless variables and parameters (6, 7) it becomes

$$\tilde{\rho}\tilde{\eta} = \sum_{\alpha=1}^2 \left[ \tilde{\rho}^\alpha \tilde{\eta}_E^\alpha - \frac{1}{4} \frac{\tilde{\rho}_{(ij)}^\alpha \tilde{\rho}_{(ij)}^\alpha}{\tilde{p}^\alpha \tilde{T}} \right] - \frac{r_m}{5} \frac{\tilde{q}^1 \tilde{q}^1}{\tilde{p}^1 \tilde{T}^2} - \frac{1}{5} \frac{\tilde{q}^2 \tilde{q}^2}{\tilde{p}^2 \tilde{T}^2} \quad \text{with} \quad \tilde{\rho}\tilde{\eta} = \frac{T_c}{\bar{P}} \rho\eta. \tag{16}$$

Since here we consider the linearized field equations, it is reasonable to neglect in expression (16) all the terms of third or higher orders in the fluxes, so that  $\tilde{\rho}\tilde{\eta}$  reads

$$\tilde{\rho}\tilde{\eta} = \sum_{\alpha=1}^2 \left[ \tilde{\rho}^\alpha \tilde{\eta}_E^\alpha - \frac{1}{4} \frac{\tilde{\rho}_{(ij)}^\alpha \tilde{\rho}_{(ij)}^\alpha}{\tilde{p}_c^\alpha} \right] - \frac{r_m}{5} \frac{\tilde{q}^1 \tilde{q}^1}{\tilde{p}_c^1} - \frac{1}{5} \frac{\tilde{q}^2 \tilde{q}^2}{\tilde{p}_c^2}. \tag{17}$$

This expression will be used in Sect. 5 for the evaluation of the remaining unknown boundary values.

In this paper, we will refer to system (12) and compare its solutions with the results already known in the literature. To this aim, in the next section, we will briefly recall the results concerning the planar case and the classical Navier–Stokes–Fourier–Fick approximations for the cylindrical and spherical cases.

### 3 The Navier–Stokes–Fourier–Fick model for heat transfer in binary mixtures

We present here a brief summary of the Navier–Stokes–Fourier–Fick (NSFF) approximations.

The field equations of classical thermodynamics for a single gas are based on the conservation laws of mass, momentum and energy. These conservation equations are closed through the Navier–Stokes and Fourier laws, which assume the stress tensor and the heat flux proportional respectively to the gradient of velocity and temperature.

In the case of mixtures, the equations of classical thermodynamics are introduced in two different ways. A possible manner is to consider the classical equations for both components of the mixtures, as it was made in [38] for the extended thermodynamics description (see also the ‘‘Appendix’’). The field equations coincide with those of a single fluid except for the production terms that must take into account the interactions between the components. Here we follow this method. The field equations are given by the underlined terms in systems (1–3, 8, 12). In particular, for the linearized dimensionless case, we have

$$\begin{aligned}
 \frac{d\tilde{p}^1}{d\tilde{r}} &= -\frac{\tilde{J}_1^1}{\text{Kn}} = 0, \\
 5\tilde{p}_e^1 \frac{d\tilde{T}}{d\tilde{r}} &= -2r_m \frac{\tilde{q}^1}{\text{Kn}}, \\
 \tilde{p}^1 + \tilde{p}^2 &= 1, \\
 \tilde{q}^1 + \tilde{q}^2 &= \frac{Q_F}{\tilde{r}_j}, \\
 5[r_m + \tilde{p}_e^1(1 - r_m)] \frac{d\tilde{T}}{d\tilde{r}} &= -2r_m \frac{\tilde{q}^1 + \tilde{q}^2}{\text{Kn}}, \\
 \tilde{\rho}_{(ij)}^\alpha &= 0.
 \end{aligned} \tag{18}$$

Another possible way to introduce the classical field equations for mixtures is to consider only the conservation laws of mass, momentum and energy for the whole mixture and to close them with the Navies-Stokes, Fourier and the generalized Fick’s laws. Under the assumptions previously made for the heat transfer problem, the conservation law of mass for the whole mixture is identically satisfied, the conservation law of momentum is given by (18)<sub>3</sub> in terms of the total pressure  $p = p^1 + p^2$ , while Eq. (18)<sub>4</sub>, with the total first component of the heat flux  $q = q^1 + q^2$ , corresponds to the conservation law of energy. Then, Eq. (18)<sub>5,6</sub> represent, respectively, the Fourier and Navier–Stokes laws for the whole mixture, and (18)<sub>1</sub> recovers the generalized Fick law.  $\tilde{J}_1^1$  is the dimensionless first component of the diffusion flux for the first constituent which vanishes identically in the presence of an impermeable wall (see ‘‘Appendix’’ for more details).

If we determine the field equations of classical thermodynamics in the first way, Eq. (18)<sub>1</sub> follows as the conservation law of momentum for the first constituent, while in the second way, the same equation must be assumed as a constitutive law.

More commonly, Eq. (18)<sub>1</sub> is expressed in terms of the concentration of the first constituent. Indeed, taking into account the definition of the mass concentration (4) and the two thermal equations of state, Eq. (18)<sub>1</sub> becomes

$$\frac{r_m}{[r_m(1 - c^1) + c^1]^2} \frac{dc^1}{d\tilde{r}} = -\frac{\tilde{J}_1^1}{\text{Kn}} = 0. \tag{19}$$

Hence, the NSFF approximations imply in this case that the mass concentration is constant, so that no thermal diffusion can be described by these equations. This conclusion obviously contradicts the empirical and theoretical expectations and motivated our analysis of an alternative macroscopic description of mixtures.

Equation system (18) can be integrated referring to the boundary conditions (5). We have  $\tilde{p}^1 = \tilde{p}_e^1$ , where  $\tilde{p}_e^1$  is determined by relation (10), or  $c^1 = c_e^1$ , furthermore the temperature field reads

$$\tilde{T}_F = H_F - \frac{3}{4} \frac{Q_F r_m}{\text{Kn} \lambda} F(\tilde{r}) \tag{20}$$

with

$$F(\tilde{r}) = \frac{\tilde{r}^{1-j}}{1-j} \quad \text{for } j = 0, 2, \quad \text{while } F(\tilde{r}) = \ln(\tilde{r}) \quad \text{for } j = 1 \tag{21}$$

and  $\lambda = 15/8 [r_m + \tilde{p}_c^1 (1 - r_m)]$ . Then, through the two boundary conditions for the temperature (5)<sub>1,4</sub>, we get

$$\begin{aligned} Q_F &= -\frac{4}{3} \text{Kn} \frac{\lambda}{r_m} (1 - \tilde{T}_i), & H_F &= \tilde{T}_i, \\ Q_F &= +\frac{4}{3} \text{Kn} \frac{\lambda}{r_m} \frac{1 - \tilde{T}_i}{\ln \tilde{r}_i}, & H_F &= 1, \\ Q_F &= -\frac{4}{3} \text{Kn} \frac{\lambda}{r_m} \tilde{r}_i \frac{1 - \tilde{T}_i}{1 - \tilde{r}_i}, & H_F &= \frac{1 - \tilde{r}_i \tilde{T}_i}{1 - \tilde{r}_i}, \end{aligned} \quad (22)$$

for the planar<sup>4</sup>, cylindrical and spherical case, respectively. The other fields follow easily from system (18).

#### 4 ET analytical solutions

For the sake of completeness, we present here the results for the planar cases together with the radial one. We recall once more that for binary mixtures the planar case was already studied in [35] in the linear approximation and in [36] in the non-linear case.

From (12), a differential equation in the only temperature field is easily deduced. Taking into account that  $j = 0, 1, 2$ , the differential equation for the common temperature reads

$$\frac{d^3 \tilde{T}}{d\tilde{r}^3} + \frac{j}{\tilde{r}} \frac{d^2 \tilde{T}}{d\tilde{r}^2} - \frac{j}{\tilde{r}^2} \frac{d\tilde{T}}{d\tilde{r}} - \frac{\lambda}{\text{Kn}^2} \frac{d\tilde{T}}{d\tilde{r}} = \frac{3}{4} \frac{Q}{\text{Kn}^3} \frac{r_m}{\tilde{r}^j}. \quad (23)$$

Through its integration, the other field variables are completely determined, since it holds

$$\begin{aligned} \tilde{q}^1 &= \frac{Q}{(1 - r_m) \tilde{r}^j} + \frac{5}{2} \frac{\text{Kn}}{1 - r_m} \frac{d\tilde{T}}{d\tilde{r}}, \\ \tilde{\rho}_{(rr)}^1 &= \frac{4}{5} \frac{\text{Kn}}{1 - r_m} \frac{jQ}{\tilde{r}^{j+1}} - \frac{2}{3} \frac{\text{Kn}^2}{1 - r_m} \left( 2 \frac{d^2 \tilde{T}}{d\tilde{r}^2} - \frac{j}{\tilde{r}} \frac{d\tilde{T}}{d\tilde{r}} \right), \\ \tilde{p}^1 &= \Pi^1 + \frac{r_m Q}{\text{Kn}(1 - r_m)} F(\tilde{r}) + \frac{4}{3} \frac{\lambda}{1 - r_m} \tilde{T}, \end{aligned} \quad (24)$$

if  $F(r)$  is the function defined in (21) and  $\Pi^1$  is an unknown dimensionless constant. The other fields can be algebraically determined from the remaining equations of (12).

From (23), the explicit solution for the temperature field can be determined as a function of  $\tilde{r}$ , that is

$$\tilde{T}(\tilde{r}) = H - \frac{3Qr_m}{4\text{Kn}\lambda} F(\tilde{r}) + \frac{C_1}{\tilde{r}^{j(j-1)/2}} G_1 \left( \frac{\sqrt{\lambda} \tilde{r}}{\text{Kn}} \right) + \frac{C_2}{\tilde{r}^{j(j-1)/2}} G_2 \left( \frac{\sqrt{\lambda} \tilde{r}}{\text{Kn}} \right) \quad (25)$$

where

$$\begin{aligned} G_1(x) &= \cosh(x), & G_2(x) &= \sinh(x), & \text{for } j &= 0, 2, \\ G_1(x) &= I_0(x), & G_2(x) &= K_0(x), & \text{for } j &= 1, \end{aligned} \quad (26)$$

and  $H, C_1$  and  $C_2$  are three integration constants, while  $I_n$  and  $K_n$  are the modified Bessel functions of the first and second kind<sup>5</sup>.

From (25), it is evident that the unknown constants  $C_1$  and  $C_2$  play an important role since they are responsible for the deviation of the temperature field from the classical Fourier solution  $\tilde{T}_F(\tilde{r})$ .

<sup>4</sup> In the planar case, we have considered as integration domain  $[\tilde{r}_i = 0, \tilde{r}_c = 1]$ .

<sup>5</sup> The modified Bessel function of the first and second kind,  $I_n$  and  $K_n$ , are the solutions of the differential equation  $z^2 y'' + zy' - (z^2 + n^2)y = 0$ .

#### 4.1 Cylindrical case

Through (25), it is easily deduced the explicit form for the field variables  $\tilde{q}^1$ ,  $\tilde{\rho}_{(rr)}^1$  and  $\tilde{p}^1$  appropriate to the cylindrical case, that is

$$\begin{aligned}\tilde{q}^1 &= \frac{Q}{\tilde{r}} \frac{\lambda - \frac{15}{8}r_m}{\lambda(1-r_m)} + \frac{5}{2} \frac{\sqrt{\lambda}}{1-r_m} \left[ C_1 I_1 \left( \frac{\sqrt{\lambda}\tilde{r}}{\text{Kn}} \right) - C_2 K_1 \left( \frac{\sqrt{\lambda}\tilde{r}}{\text{Kn}} \right) \right], \\ \tilde{\rho}_{(rr)}^1 &= \frac{4 \text{Kn} Q}{5} \frac{\lambda - \frac{15}{8}r_m}{\tilde{r}^2 \lambda(1-r_m)} + \frac{2C_1}{1-r_m} \left[ \frac{2}{3} \lambda I_0 \left( \frac{\sqrt{\lambda}\tilde{r}}{\text{Kn}} \right) - \frac{\text{Kn}\sqrt{\lambda}}{\tilde{r}} I_1 \left( \frac{\sqrt{\lambda}\tilde{r}}{\text{Kn}} \right) \right] \\ &\quad + \frac{2C_2}{1-r_m} \left[ \frac{2}{3} \lambda K_0 \left( \frac{\sqrt{\lambda}\tilde{r}}{\text{Kn}} \right) + \frac{\text{Kn}\sqrt{\lambda}}{\tilde{r}} K_1 \left( \frac{\sqrt{\lambda}\tilde{r}}{\text{Kn}} \right) \right], \\ \tilde{p}^1 &= \Pi^1 + \frac{4\lambda}{3(1-r_m)} \left[ C_1 I_0 \left( \frac{\sqrt{\lambda}\tilde{r}}{\text{Kn}} \right) + C_2 K_0 \left( \frac{\sqrt{\lambda}\tilde{r}}{\text{Kn}} \right) \right],\end{aligned}\tag{27}$$

and, as already stressed, the remaining fields can be computed algebraically from system (3, 12).

In this way, the complete analytical solution is known if the values of five integration constants  $\Pi^1$ ,  $Q$ ,  $H$ ,  $C_1$  and  $C_2$  are prescribed. Through the three boundary conditions (5)<sub>1,3,4</sub>, it is only possible to recover the first three of them ( $\Pi^1$ ,  $Q$ ,  $H$ ) in terms of the remaining two ( $C_1$  and  $C_2$ ).

As a matter of fact, from the boundary conditions on the temperature field (5)<sub>1,4</sub> and the solution (25), the two integration constants  $H$  and  $Q$  are given by

$$\begin{aligned}H &= 1 - C_1 I_0 \left( \frac{\sqrt{\lambda}}{\text{Kn}} \right) - C_2 K_0 \left( \frac{\sqrt{\lambda}}{\text{Kn}} \right), \\ Q &= \frac{4}{3} \frac{\text{Kn} \lambda}{r_m \ln \tilde{r}_i} \left[ 1 - \tilde{T}_i - C_1 I_0 \left( \frac{\sqrt{\lambda}}{\text{Kn}} \right) + C_1 I_0 \left( \frac{\tilde{r}_i \sqrt{\lambda}}{\text{Kn}} \right) - C_2 K_0 \left( \frac{\sqrt{\lambda}}{\text{Kn}} \right) + C_2 K_0 \left( \frac{\tilde{r}_i \sqrt{\lambda}}{\text{Kn}} \right) \right].\end{aligned}\tag{28}$$

Furthermore, from the boundary value for the concentration (5)<sub>3</sub> and from (27)<sub>3</sub> evaluated at  $\tilde{r}_e$ , it holds

$$\Pi^1 = \tilde{p}_e^1 - \frac{4\lambda}{3(1-r_m)} \left[ C_1 I_0 \left( \frac{\sqrt{\lambda}}{\text{Kn}} \right) + C_2 K_0 \left( \frac{\sqrt{\lambda}}{\text{Kn}} \right) \right].\tag{29}$$

We have only to assign the last two integration constants, but it is not possible to prescribe any other boundary conditions, so this will be done in the next section through the fluctuation principle.

#### 4.2 Spherical case

For the bounded domains between two concentric spheres, we start from (25) in order to get the explicit expression for the non-vanishing fields, so we get

$$\begin{aligned}\tilde{q}^1 &= \frac{Q}{\tilde{r}^2} \frac{\lambda - \frac{15}{8}r_m}{\lambda(1-r_m)} + \frac{5}{2(1-r_m)\tilde{r}^2} \left[ (C_2 \tilde{r} \sqrt{\lambda} - C_1 \text{Kn}) \cosh \left( \frac{\sqrt{\lambda}\tilde{r}}{\text{Kn}} \right) + (C_1 \tilde{r} \sqrt{\lambda} - C_2 \text{Kn}) \sinh \left( \frac{\sqrt{\lambda}\tilde{r}}{\text{Kn}} \right) \right], \\ \tilde{\rho}_{(rr)}^1 &= \frac{8 \text{Kn} Q}{5} \frac{\lambda - \frac{15}{8}r_m}{\tilde{r}^3 \lambda(1-r_m)} - \frac{4}{3(1-r_m)\tilde{r}^3} \left[ (3C_1 \text{Kn}^2 - 3C_2 \text{Kn} \sqrt{\lambda}\tilde{r} + C_1 \lambda \tilde{r}^2) \cosh \left( \frac{\sqrt{\lambda}\tilde{r}}{\text{Kn}} \right) \right. \\ &\quad \left. + (3C_2 \text{Kn}^2 - 3C_1 \text{Kn} \sqrt{\lambda}\tilde{r} + C_2 \lambda \tilde{r}^2) \sinh \left( \frac{\sqrt{\lambda}\tilde{r}}{\text{Kn}} \right) \right], \\ \tilde{p}^1 &= \Pi^1 + \frac{4\lambda}{3(1-r_m)\tilde{r}} \left[ C_1 \cosh \left( \frac{\sqrt{\lambda}\tilde{r}}{\text{Kn}} \right) + C_2 \sinh \left( \frac{\sqrt{\lambda}\tilde{r}}{\text{Kn}} \right) \right].\end{aligned}\tag{30}$$



From the boundary conditions on the temperature field (5)<sub>1,4</sub> and the solution (25),  $H$  and  $Q$  are given by

$$H = \frac{1 - \tilde{r}_i \tilde{T}_i}{1 - \tilde{r}_i} - \frac{C_1}{1 - \tilde{r}_i} \left[ \cosh\left(\frac{\sqrt{\lambda}}{\text{Kn}}\right) - \cosh\left(\frac{\sqrt{\lambda} \tilde{r}_i}{\text{Kn}}\right) \right] - \frac{C_2}{1 - \tilde{r}_i} \left[ \sinh\left(\frac{\sqrt{\lambda}}{\text{Kn}}\right) - \sinh\left(\frac{\sqrt{\lambda} \tilde{r}_i}{\text{Kn}}\right) \right],$$

$$Q = -\frac{4\text{Kn}\tilde{r}_i(1 - \tilde{T}_i)\lambda}{3r_m(1 - \tilde{r}_i)} + \frac{4C_1\text{Kn}\lambda}{3(1 - \tilde{r}_i)r_m} \left[ \tilde{r}_i \cosh\left(\frac{\sqrt{\lambda}}{\text{Kn}}\right) - \cosh\left(\frac{\sqrt{\lambda} \tilde{r}_i}{\text{Kn}}\right) \right] + \frac{4C_2\text{Kn}\lambda}{3(1 - \tilde{r}_i)r_m} \left[ \tilde{r}_i \sinh\left(\frac{\sqrt{\lambda}}{\text{Kn}}\right) - \sinh\left(\frac{\sqrt{\lambda} \tilde{r}_i}{\text{Kn}}\right) \right]. \quad (31)$$

Furthermore, from the boundary value for the concentration (5)<sub>3</sub> and from (30)<sub>3</sub> calculated at  $\tilde{r}_e$ ,  $\Pi^1$  reads

$$\Pi^1 = \tilde{p}_e^1 - \frac{4\lambda}{3(1 - r_m)} \left[ C_1 \cosh\left(\frac{\sqrt{\lambda}}{\text{Kn}}\right) + C_2 \sinh\left(\frac{\sqrt{\lambda}}{\text{Kn}}\right) \right]. \quad (32)$$

## 5 The fluctuation principle and its application

From (25), it is evident that the deviation of the temperature field from the classical Fourier solution  $\tilde{T}_F(\tilde{r})$  is due to non-vanishing values of  $C_1$  and  $C_2$ . So that, although we cannot prescribe them through boundary conditions, such values cannot be arbitrary. Indeed, we expect a solution not coincident with the classical one, but close to it. We imagine that the gas itself adjusts the values for these two constants. A possible manner by which this is done is the way proposed by the fluctuation principle in [46]. It assumes that the gas is subject to thermal fluctuations, together with the fields and the non-controllable data. The fluctuations are extremely rapid for the gas to adjust to their ever changing values. Therefore, the gas adjusts its field variables to the mean values of the fluctuating data. These mean values can be calculated by the Boltzmann formula

$$S = k_B \ln W. \quad (33)$$

In the following we show how this can be done.

The entropy density appropriate to this problem is (17). We insert the analytical solutions into (17) and we recover the explicit entropy density  $\tilde{\rho}\tilde{\eta}$  in terms of the dimensionless radial coordinate  $\tilde{r}$  and the two remaining integration constants  $C_1$  and  $C_2$ . By integration of  $\tilde{\rho}\tilde{\eta}(\tilde{r}, C_1, C_2)$  over the whole spatial domain, we get the total entropy density appropriate to the radial cases as an explicit function of  $C_1$  and  $C_2$ , namely

$$S(C_1, C_2) = \frac{2\pi j Pr_e^3}{T_e} \int_{\tilde{r}_i}^1 \tilde{\rho}\tilde{\eta}(\tilde{r}, C_1, C_2) \tilde{r}^j d\tilde{r}. \quad (34)$$

Hence, from the Boltzmann formula (33), it is possible to recover  $W(C_1, C_2) = \exp(S(C_1, C_2)/k_B)$ , that is the number of possibilities of realizing these two integration constants. Therefore, the probability of the occurrence of  $C_1$  and  $C_2$  during a thermal fluctuation is

$$P(C_1, C_2) = \frac{\exp\left(\frac{S(C_1, C_2)}{k_B}\right)}{\int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \exp\left(\frac{S(C_1, C_2)}{k_B}\right) dC_1 dC_2} \quad (35)$$

and, consequently, the mean values of the two remaining integration constants are

$$\langle C_i \rangle = \frac{\int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} C_i \exp\left(\frac{S(C_1, C_2)}{k_B}\right) dC_1 dC_2}{\int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \exp\left(\frac{S(C_1, C_2)}{k_B}\right) dC_1 dC_2} \quad \text{with } i = 1, 2. \quad (36)$$

**Table 1** Mean values

$j$	$\langle C_1 \rangle$	$\langle C_2 \rangle$
0	$-1.89093 \times 10^{-2}$	$1.89093 \times 10^{-2}$
1	$1.20995 \times 10^{-7}$	$-8.92045 \times 10^{-2}$
2	$-1.89395 \times 10^{-2}$	$1.89395 \times 10^{-2}$

Following the fluctuation principle, the quantities (36) are the values of  $C_1$  and  $C_2$  that the gas “chooses”. In this way, the solutions of the field equations (12) appropriate to the cylindrical and spherical geometries are completely determined.

We have computed these mean values for  $c_e^1 = 0.5$ ,  $r_m = 0.1$ ,  $\tilde{r}_i = 0.1$ ,  $\text{Kn} = 0.1$  and  $\tilde{T}_i = 0.9$ . The results are listed in Table 1, where, for the sake of completeness, the values for the planar case obtained for the same parameters are also presented. The corresponding solutions will be analyzed and commented in the next section.

From Table 1, it is evident that the mean values obtained for the constants  $C_1$  and  $C_2$  in the cylindrical case ( $j = 1$ ) are quite different from the other cases. The reason lies in the expression of the analytical solution of the cylindrical equations, which differs from the other ones because of the occurrence of the modified Bessel functions.

## 6 Results

In this section, we analyze and compare the results obtained by the classical and the extended thermodynamics models. To this aim, in Fig. 1, we consider the cylindrical case and show the behavior of the extended thermodynamics solutions (25, 27) (solid lines), comparing them with the classical NSFF ones (dashed lines). In particular, in Fig. 1a one can find the temperature field (25, 26) for  $j = 1$  (the values of the two constants  $C_1$  and  $C_2$  are prescribed by the fluctuation principle). The temperature behavior is the combination of classical solution and boundary layers. To highlight the differences between the two models, Fig. 1b presents their difference  $\tilde{T} - \tilde{T}_F$ . Obviously, the boundary layers are more pronounced in the neighborhood of the internal wall, where the curvature is higher. Figure 1c, d shows the behavior of the concentrations  $c^1$  and  $c^2$  of the two constituents and compares it with the classical solution (dashed lines). As already said, the classical NSFF theory is not able to predict the thermal diffusion. On the contrary, the extended thermodynamics solution for  $c^1$  is an increasing function of  $\tilde{r}$ , while for  $c^2$  is a decreasing one. Our model predicts that the concentration of the lighter monatomic gas is greater near  $\tilde{r}_e$ , where the temperature is higher, while the concentration of the heavier monatomic gas,  $c^2$ , increases in the neighborhood of  $\tilde{r}_i$ , where the common temperature is lower.

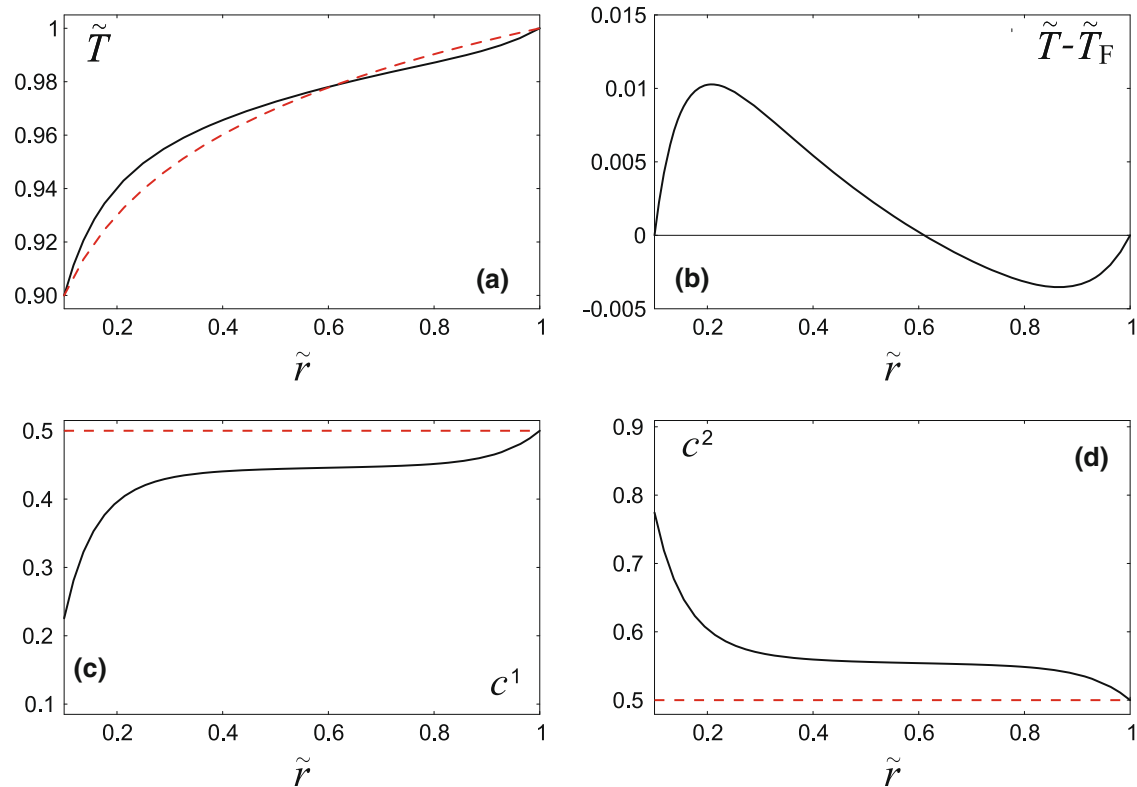
In Fig. 2, we present the same analysis for the spherical case. The solutions are actually of the same kind, but in the spherical domain, the effect of the curvature is visibly more pronounced.

In order to analyze the role of geometries, we have plotted in Fig. 3 the difference  $\tilde{T} - \tilde{T}_F$  and the normalized concentration  $\bar{c}^1 = c^1(\tilde{r}) - c^1((\tilde{r}_i + \tilde{r}_e)/2)$  relative to the cylindrical (solid lines), spherical (dotted lines) and planar (dashed lines) cases. We recall that in [35], the planar solution was studied for different choices of the parameters.

Figure 3 clearly shows that the “peak” in the temperature difference and the left boundary layer in  $\bar{c}^1$  are more evident in the spherical case, while the planar problem presents the weakest effects. From the comparison in Fig. 3, one could conclude that the mixture separation is stronger when the two components are confined between two spheres. On the contrary, the realization of an experiment for such problem in the spherical case is surely more complex.

In the subinterval  $[(\tilde{r}_i + \tilde{r}_e)/2, \tilde{r}_e]$ , the results for the planar and the spherical cases are more similar to each other than those of the cylindrical symmetry. Surely the reason of this effect lies in the analytical form of the solutions. In fact, the deviation of the temperature field obtained in (25, 26) from the corresponding classical solution for the spherical and planar cases differs by the factor  $1/\tilde{r}$ . Clearly, when the radius is increased, the differences between these two cases become less evident. In principle, the differences grow for small values of the radius, that is, to say in the neighborhood of the internal boundary. Of course this is not true at  $\tilde{r}_i$  where the two temperatures are forced to be equal. The cylindrical case, as it can be seen also from the analytical solution (25, 26) is somehow distinct.

From now on, we will restrict our attention to the cylindrical case. Obviously, analogous results could be obtained also in spherical symmetry.

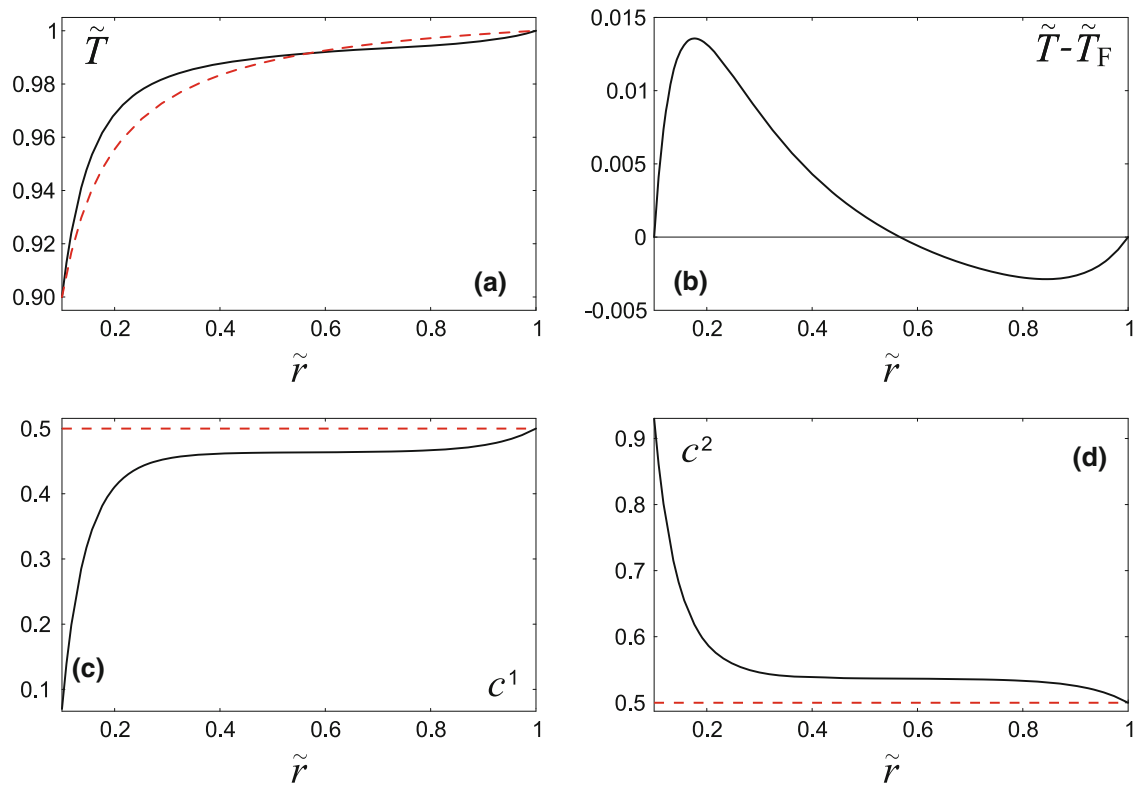


**Fig. 1** The cylindrical case with  $c_c^1 = 0.5$ ,  $r_m = 0.1$ ,  $\tilde{r}_i = 0.1$ ,  $\text{Kn} = 0.1$ ,  $\tilde{T}_i = 0.9$ : a comparison between the classical thermodynamics solutions (*dashed lines*) and the ones obtained by extended thermodynamics (*solid lines*) with the non-controllable boundary values prescribed by the fluctuation principle

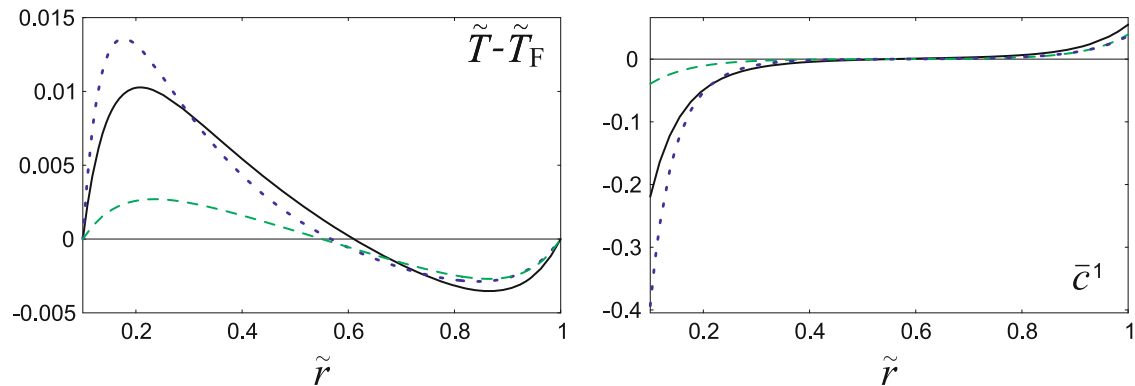
As already said in Sect. 3, the Navier–Stokes laws imply a vanishing stress tensor, since the mixture is at rest. On the contrary, the field equations of extended thermodynamics predict non-vanishing components for this field, also in accordance with the single fluid radial case [41]. As an example, in Fig. 4 we have plotted the behavior of  $\tilde{\rho}_{(rr)}^1$  which follows from (27) and, for completeness, the first component of the heat flux  $\tilde{q}^1$ , together with the corresponding classical fields (dashed lines). Also for stress tensor and heat flux, the curvature stresses the differences between classical and extended thermodynamics models. From (12)<sub>1</sub>, (18)<sub>1</sub> and (19), it can be seen that the field  $\tilde{\rho}_{(rr)}^1$ , together with  $\tilde{\rho}_{(\vartheta\vartheta)}^1 = -\tilde{\rho}_{(rr)}^1$ , are responsible for the deviation of the concentration  $c^1$  from the classical constant solution.

In Fig. 5, we analyze the effect of the gas rarefaction on the field behavior. For this purpose, we have used the same parameters already considered for the previous figures except for the Knudsen number. Some different values of Kn were chosen:  $\text{Kn} = 0.01$  (solid lines),  $\text{Kn} = 0.075$  (dashed-dotted lines),  $\text{Kn} = 0.05$  (dashed lines) and  $\text{Kn} = 0.025$  (dotted lines) and their effects are compared. It can be easily seen that the boundary layers in the temperature field and in the concentration of the first component  $\tilde{c}^1$  depend on the values of Kn and become more pronounced and broader for increasing Knudsen number, that is, in the case of more rarefied gases. In fact, the case of dense gases is close to the range of validity of classical thermodynamics. For small Kn, we expect only very little differences between classical and extended thermodynamics results, whereas the differences become more evident, for more rarefied single gases. A similar dependence on Kn was already observed in the planar geometry and in other problems of heat conduction for rarefied gases [35–37, 41, 43–46, 48, 49]. We have to stress that we cannot consider solutions for Knudsen number much greater than  $\text{Kn} = 0.1$ , since the equations of extended thermodynamics with only 13 moments are not sufficient for an accurate description of very rarefied cases. For larger Knudsen numbers, many moments have to be taken into account.

Finally, Fig. 6 presents the effect of the domain dimensions on the solutions. The parameters are the same as in Fig. 1, except for the value of the dimensionless internal radius. In particular, we have compared the

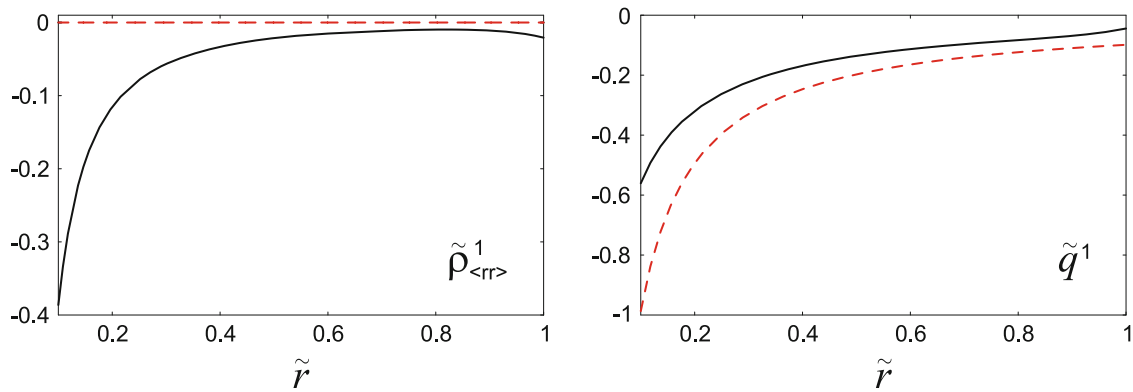


**Fig. 2** The spherical case with  $c_c^1 = 0.5$ ,  $r_m = 0.1$ ,  $\tilde{r}_i = 0.1$ ,  $\text{Kn} = 0.1$ ,  $\tilde{T}_i = 0.9$ : a comparison between the classical thermodynamics solutions (*dashed lines*) and the ones obtained by extended thermodynamics (*solid lines*) with the non-controllable boundary values prescribed by the fluctuation principle

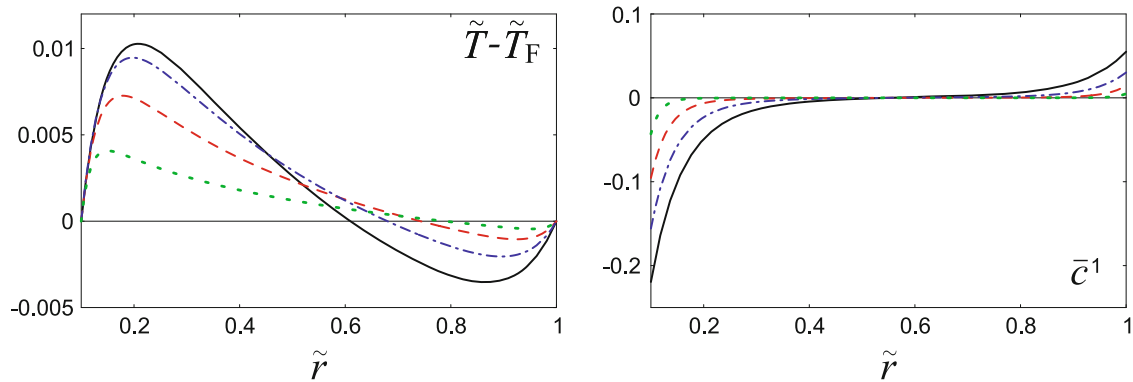


**Fig. 3** Comparison between the cylindrical (*solid lines*), spherical (*dotted lines*) and planar (*dashed lines*) solutions

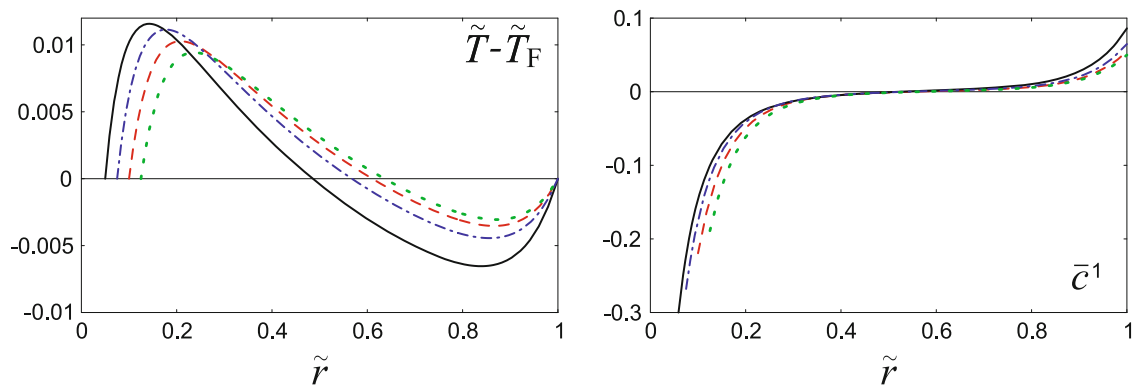
cases:  $\tilde{r}_i = 0.05$  (solid lines),  $\tilde{r}_i = 0.075$  (dashed-dotted lines),  $\tilde{r}_i = 0.1$  (dashed lines) and  $\tilde{r}_i = 0.125$  (dotted lines). These different values for  $\tilde{r}_i = r_i/r_c$  can be obtained fixing the internal radius and changing the external ones or vice versa. In both cases, when  $\tilde{r}_i$  decreases, the effects of the curvature become more evident. This effect is visible in the solutions illustrated in Fig. 6. In particular, the “peak” in  $\tilde{T} - \tilde{T}_F$  is less pronounced and broader for increasing  $\tilde{r}_i$ , and the difference tends to become skew-symmetric as in the planar domain. The field  $c_1$  is less influenced by the value of  $\tilde{r}_i$  in the whole range of  $\tilde{r}$  except in the neighborhood of the internal boundary, where significant differences in the values of the concentration can be observed.



**Fig. 4** The field variables  $\tilde{\rho}_{(rr)}^1$  and  $\tilde{q}^1$  for the cylindrical case, compared with the corresponding classical results (*dashed lines*)



**Fig. 5** Dependence of the solution on Kn



**Fig. 6** Dependence of the solution on  $\tilde{r}_1$

## 7 Conclusions and final remarks

In this paper, we have studied the potentiality of an extended thermodynamics description of gas mixtures for heat transfer problem between coaxial cylinders or concentric spheres. We have compared the results with those obtained by Navier–Stokes–Fourier–Fick approximations and with what is already known in the literature about this subject. The advantages of an extended thermodynamics model are evident also for radial geometries. In spite of all the simplifying hypothesis that we have introduced (only 13 moments, single temperature assumption, BGK approximation, linearization), the model is able to describe the thermal diffusion effects and to predict boundary layers in the temperature behavior. Moreover, in contrast with the classical thermodynamics, also the stress tensors present non-vanishing components. Referring to these results, we presuppose

that unlike the classical theory, thermodiffusion is well described by 13-moment extended thermodynamics models with single-temperature for any heat transfer problem of gas mixtures at rest confined in a bounded domain.

It is also interesting to underline that the 13-moment equations of extended thermodynamics are able to describe boundary layers in the case of a gas mixture but not for a single gas. This is due to the presence of non-vanishing stress tensors of the two components. In fact, to predict boundary layers in a single gas, more moments are needed (see for example [46,48–50]) or one can also refer to the regularized 13-moment equations [51–53].

We have to remark that in the present calculations, no temperature jumps at the walls have been taken into account. As already said, our boundary temperatures are the temperatures of the gas at the walls, not the wall temperatures. The jumps of the fields at the walls could be a further effect that can be added to the present calculations.

Finally, in order to focus on thermal diffusion phenomenon, in our system, we have neglected gravitation and thermal convection contribution. We believe that it would be interesting to consider also these effects that could play an important role, as in the separation columns. The problem is already under investigation, and it will be part of a further work.

**Acknowledgments** This paper was supported by GNFM-INdAM and partially by the GNFM project "Progetto giovani ricercatori 2010: Modelli classici e quantistici in Termodinamica Estesa e problemi di stabilità in fluidodinamica".

## Appendix

The field equations used in this paper are based on the model obtained in [38] for a multi-component mixture. In order to make this paper self-consistent, we summarize in this Appendix their determination in the case of a binary mixture.

The field variables of extended thermodynamic [27] for binary mixtures of classical, monatomic, ideal gases are moments of the distribution functions  $f_\alpha(\mathbf{x}, \mathbf{c}^\alpha, t)$  ( $\alpha = 1, 2$ ), where  $f_\alpha(\mathbf{x}, \mathbf{c}^\alpha, t) d\mathbf{x} d\mathbf{c}^\alpha$  indicates the average number of  $\alpha$  particles of velocity  $\mathbf{c}^\alpha$ , position  $\mathbf{x}$  and time  $t$ . The moment of rank  $N$  is defined as

$$F_{i_1, i_2, \dots, i_N}^\alpha = m_\alpha \int f_\alpha c_{i_1}^\alpha c_{i_2}^\alpha \dots c_{i_N}^\alpha d\mathbf{c}^\alpha, \quad (37)$$

where  $m_\alpha$  denotes the atomic mass of the  $\alpha$  constituent.

Usually, the fields  $F_{i_1, i_2, \dots, i_N}^\alpha$  are expressed in terms of the internal moments  $\rho_{i_1, i_2, \dots, i_N}^\alpha$ , defined as in (37) but with the peculiar velocity,  $C_i^\alpha = c_i^\alpha - v_i^\alpha$ , instead of  $c_i^\alpha$ , that is

$$\rho_{i_1, i_2, \dots, i_N}^\alpha = m_\alpha \int f_\alpha C_{i_1}^\alpha C_{i_2}^\alpha \dots C_{i_N}^\alpha d\mathbf{C}^\alpha, \quad (38)$$

if  $v_i^\alpha$  is the macroscopic velocity of the constituent  $\alpha$ .

Some of the internal moments can be expressed in terms of the usual physical variables. So, the moment of rank "0" is the density of the  $\alpha$  component,  $\rho^\alpha$ , and we have

$$\rho_i^\alpha = 0, \quad \rho_{ll}^\alpha = 3p^\alpha = 3\frac{k_B}{m_\alpha}\rho^\alpha T^\alpha, \quad \rho_{(ik)}^\alpha = -t_{(ik)}^\alpha, \quad \rho_{ill}^\alpha = 2q_i^\alpha, \quad (39)$$

where  $p^\alpha$ ,  $t_{(ik)}^\alpha$ ,  $q_i^\alpha$ ,  $T^\alpha$  represent, respectively, the pressure, the traceless part<sup>6</sup> of the stress tensor, the heat flux and the temperature of the constituent  $\alpha$ . Furthermore, in this paper, we consider only the case in which all the constituents of the mixture have the same temperature  $T$ , that is,  $T^\alpha = T$  for  $\alpha = 1, 2$ .

The relation between the  $F_{i_1, i_2, \dots, i_N}^\alpha$  and the  $\rho_{i_1, i_2, \dots, i_N}^\alpha$  reads<sup>7</sup>

$$F_{i_1 i_2 \dots i_N}^\alpha = \sum_{k=0}^N \binom{N}{k} \rho_{(i_1 i_2 \dots i_{N-k}}^\alpha v_{i_{N-k+1}}^\alpha \dots v_{i_N}^\alpha. \quad (40)$$

<sup>6</sup> Angular brackets denote symmetric trace-less tensors.

<sup>7</sup> Round brackets denote symmetric tensors.

In order to describe the behavior of the whole system, it could be useful to introduce the moments for the whole mixture. They are defined in terms of the  $\rho_{i_1, i_2, \dots, i_N}^\alpha$  as

$$\begin{aligned} F_{i_1 i_2 \dots i_N} &= \sum_{k=0}^N \binom{N}{k} \rho_{(i_1 i_2 \dots i_{N-k} v_{i_{N-k+1}} \dots v_{i_N})}, & \text{with} \\ \rho_{i_1 i_2 \dots i_N} &= \sum_{\alpha=1}^2 \left[ \sum_{k=0}^N \binom{N}{k} \rho_{(i_1 i_2 \dots i_{N-k} u_{i_{N-k+1}}^\alpha \dots u_{i_N}^\alpha)} \right]. \end{aligned} \quad (41)$$

Here  $v_i$ , called the velocity of the center of mass, represents the velocity of the whole mixture, while  $u_i^\alpha$ , defined as

$$u_i^\alpha = v_i^\alpha - v_i, \quad (42)$$

is the diffusion velocity of the constituent  $\alpha$ .

The field equations are obtained from the Boltzmann equation, which with the BGK approximation [39] reads

$$\frac{\partial f_\alpha}{\partial t} + c_k^\alpha \frac{\partial f_\alpha}{\partial x_k} = -\frac{f_\alpha - f_\alpha^E}{\tau}, \quad (43)$$

The symbol ‘‘E’’ refers to equilibrium, where the distribution function is a Maxwellian one, expressed as

$$f_\alpha^E = \frac{\rho^\alpha}{m_\alpha} \sqrt{\frac{m_\alpha}{2\pi k_B T}} \exp\left(-\frac{m_\alpha}{2k_B T} (\mathbf{c}^\alpha - \mathbf{v})^2\right). \quad (44)$$

$k_B$  represents the Boltzmann constant,  $\tau$  is a constant relaxation time.

Multiplying the Boltzmann equation by  $c_{i_1}^\alpha c_{i_2}^\alpha \dots c_{i_N}^\alpha$  and integrating it over  $\mathbf{c}^\alpha$ , one obtains the balance equations for the moments, that are

$$\frac{\partial F_{i_1, i_2, \dots, i_N}^\alpha}{\partial t} + \frac{\partial F_{i_1, i_2, \dots, i_N k}^\alpha}{\partial x_k} = -\frac{F_{i_1, i_2, \dots, i_N k}^\alpha - F_{i_1, i_2, \dots, i_N k}^E}{\tau} \quad \alpha = 1, 2, \quad (45)$$

while, the addition of these last equations in  $\alpha$  furnishes, thanks to the definitions (41), the balance equations for the moments relative to the whole mixture, namely

$$\frac{\partial F_{i_1, i_2, \dots, i_N}}{\partial t} + \frac{\partial F_{i_1, i_2, \dots, i_N k}}{\partial x_k} = -\frac{F_{i_1, i_2, \dots, i_N k} - F_{i_1, i_2, \dots, i_N k}^E}{\tau}. \quad (46)$$

One can use the balance equations (45) for the both components ( $\alpha = 1, 2$ ) or consider the set (45) relative to one component (for example  $\alpha = 1$ ) together with the set (46) for the whole mixture. This second choice is the one usually followed in extended thermodynamics.

Furthermore, the two infinite hierarchy of balance laws (45, 46) has to be truncated to a finite number of equations. A common choice in extended thermodynamics of a single gas is to use the first 13 moments. Here in the mixtures, this is equivalent to consider the first 25 field variables, that are  $\rho^\alpha, v_i^\alpha, T, \rho_{(ik)}^\alpha, q_i^\alpha$  with  $\alpha = 1, 2$ . Then, the field equations of the two hierarchies (45, 46) that we take are

$$\begin{array}{ll} \text{for the first component} & \text{for the whole mixture} \\ \frac{\partial \rho^1}{\partial t} + \frac{\partial \rho^1 v_k^1}{\partial x_k} = 0, & \frac{\partial \rho}{\partial t} + \frac{\partial \rho v_k}{\partial x_k} = 0, \\ \frac{\partial \rho^1 v_i^1}{\partial t} + \frac{\partial F_{ik}^1}{\partial x_k} = -\frac{\rho^1 u_i^1}{\tau}, & \frac{\partial \rho v_i}{\partial t} + \frac{\partial F_{ik}}{\partial x_k} = 0, \\ & \frac{\partial F_{ll}}{\partial t} + \frac{\partial F_{kll}}{\partial x_k} = 0, \\ \frac{\partial F_{(ij)}^1}{\partial t} + \frac{\partial F_{(ij)k}^1}{\partial x_k} = -\frac{F_{(ij)}^1 - F_{(ij)}^E}{\tau}, & \frac{\partial F_{(ij)}}{\partial t} + \frac{\partial F_{(ij)k}}{\partial x_k} = -\frac{F_{(ij)} - F_{(ij)}^E}{\tau}, \\ \frac{\partial F_{ill}^1}{\partial t} + \frac{\partial F_{ikll}^1}{\partial x_k} = -\frac{F_{ill}^1 - F_{ill}^E}{\tau}, & \frac{\partial F_{ill}}{\partial t} + \frac{\partial F_{ikll}}{\partial x_k} = -\frac{F_{ill} - F_{ill}^E}{\tau}. \end{array} \quad (47)$$

Equation (47)<sub>1,2</sub> are, respectively, the conservation laws of the mass of the first constituent and of the total mass. Clearly, the mass of the first constituent is conserved, since no reactions are taken into account. Equations (47)<sub>3,4</sub> are the balance law of momentum of the first constituent and the conservation law of total momentum. Equation (47)<sub>5</sub> is the conservation law of the total energy. The remaining equations are the balance laws of the stress tensor of the first constituent, the total stress tensor, the heat flux of the first constituent and the total heat flux, respectively.

Equation (47) form a not closed system because of the occurrence of the fields  $F_{(ij)k}^1$ ,  $F_{(ij)k}$ ,  $F_{ikll}^1$  and  $F_{ikll}$  or, from (40, 41), of the moments  $\rho_{(ij)k}^\alpha$  and  $\rho_{ikll}^\alpha$ .

They can be determined through the Grad's method [54,55]: the moments  $\rho_{(ij)k}^\alpha$  and  $\rho_{ikll}^\alpha$  can be obtained with the Grad's distribution function, which takes into account the first terms of an expansion of  $f_\alpha$  with respect to Hermit polynomials, that is

$$f_\alpha^G = f_\alpha^E \left[ 1 - \frac{u_\alpha^2}{2\theta^\alpha} + \frac{M_{(ij)}^\alpha C_i^\alpha C_j^\alpha}{2p^\alpha \theta^\alpha} + \frac{1}{2\theta^\alpha} \left( 7 - \frac{C_\alpha^2}{\theta^\alpha} \right) u_i^\alpha C_i^\alpha - \frac{Z_i^\alpha C_i^\alpha}{2p^\alpha \theta_\alpha^2} \left( 1 - \frac{C_\alpha^2}{5\theta_\alpha} \right) \right] \quad (48)$$

where

$$\begin{aligned} \theta^\alpha &= \frac{k_B}{m_\alpha} T, \quad M_{(ij)}^\alpha = \rho_{(ij)}^\alpha + \rho^\alpha u_i^\alpha u_j^\alpha, \\ Z_i^\alpha &= \rho_{ill}^\alpha + 2\rho_{(il)}^\alpha u_l^\alpha + 5p^\alpha u_i^\alpha + \rho^\alpha u_\alpha^2 u_i^\alpha. \end{aligned} \quad (49)$$

The combination of the Grad distribution (48) with the definition of the internal moments (38) yields the constitutive relations for the fields  $\rho_{(ij)k}^\alpha$  and  $\rho_{ikll}^\alpha$ , that, neglecting all the terms of quadratic or higher order in the variables  $u_i^\alpha$ ,  $\rho_{(ij)}^\alpha$  and  $\rho_{ill}^\alpha$ , read

$$\rho_{(ij)k}^\alpha = \frac{2}{5} \left( q_\alpha^i \delta_{jk} + q_\alpha^j \delta_{ik} - \frac{2}{3} q_\alpha^k \delta_{ij} \right), \quad \rho_{ikll}^\alpha = 5\rho^\alpha \left( \frac{k_B}{m_\alpha} T \right)^2 \delta_{ik} + 7 \frac{k_B}{m_\alpha} T \rho_{(ik)}^\alpha. \quad (50)$$

So, Eq. (47), together with the constitutive relations (50), form a closed system of 25 field equations in the 25 fields  $\rho^\alpha$ ,  $v_i^\alpha$ ,  $T$ ,  $\rho_{(ik)}^\alpha$ ,  $q_i^\alpha$ , with  $\alpha = 1, 2$ .

We use these equations in order to describe a stationary heat transfer problem in a binary inert mixture at rest between two infinite coaxial cylinders or two concentric spheres. Then, we can assume that the fields do not depend on time and that the velocity of the center of mass vanishes. Consequently, the field equations (47, 50), written in terms of the curvilinear coordinates  $z^k$ , become

$$\begin{aligned} &\text{for the first component:} && \text{for the whole mixture:} \\ &J_{1;k}^k = 0, && \text{identically satisfied} \\ &g^{ik} \frac{\partial p^1}{\partial z^k} + \rho_{1;k}^{(ik)} = -\frac{J_1^k}{\tau}, && \sum_{\alpha=1}^2 \left( g^{ik} \frac{\partial p^\alpha}{\partial z^k} + \rho_{\alpha;k}^{(ik)} \right) = 0, \\ & && \sum_{\alpha=1}^2 \left( 2q_{\alpha;k}^k + 5 \frac{k_B}{m_\alpha} T J_\alpha^i \right) = 0, \\ &\rho_{1;k}^{(ij)k} + M_{1;k}^{(ij)k} = -\frac{\rho_1^{(ij)}}{\tau}, && \sum_{\alpha=1}^2 \left( \rho_{\alpha;k}^{(ij)k} + M_{\alpha;k}^{(ij)k} \right) = -\frac{\sum_{\alpha=1}^2 \rho_\alpha^{(ij)}}{\tau}, \\ &\rho_{1n;k}^{ikn} = -\frac{2q_1^k + 5 \frac{k_B}{m_\alpha} T J_1^i}{\tau}, && \sum_{\alpha=1}^2 \rho_{\alpha n;k}^{ikn} = -\frac{\sum_{\alpha=1}^2 \left( 2q_\alpha^k + 5 \frac{k_B}{m_\alpha} T J_\alpha^i \right)}{\tau}, \end{aligned} \quad (51)$$



with

$$\begin{aligned}\rho_\alpha^{(ij)k} &= \frac{2}{5} \left( q_\alpha^i g^{jk} + q_\alpha^j g^{ki} - \frac{2}{3} q_\alpha^k g^{ij} \right) \\ M_\alpha^{(ij)k} &= \frac{k_B}{m_\alpha} T \left( J_\alpha^i g^{jk} + J_\alpha^j g^{ki} - \frac{2}{3} J_\alpha^k g^{ij} \right), \\ \rho_{\alpha n}^{ikn} &= 5 \frac{k_B}{m_\alpha} T p^\alpha g^{ik} + 7 \frac{k_B}{m_\alpha} T \rho^{(ik)}.\end{aligned}\quad (52)$$

In Eqs. (51, 52) upper and lower indices represent contra- and co-variant components of the tensors,  $g^{ik}$  is the metric tensor (as usual,  $g^{ik} g_{kj} = \delta_j^i$ , with  $\delta_j^i$  the Kronecker symbol) and the semicolon denotes covariant derivative with respect to  $z^k$ . For simplicity, the diffusion flux  $J_\alpha^k = \rho^\alpha u_k^\alpha = \rho^\alpha (v_k^\alpha - v_k)$  and the pressures of the two constituents  $p^\alpha = \frac{k_B}{m_\alpha} \rho^\alpha T$  are used as fields instead of  $v_k^\alpha$  and  $\rho^\alpha$ , respectively.

We will write Eqs. (51, 52) explicitly for the cases of heat transfer between two cylinders and two spheres. We assume that in both cases, the fields depend only on the radius  $r$ . Since the covariant derivative must be expressed in terms of the metric tensor and the Christoffel symbols, we recall that in cylindrical coordinates, they read

$$g^{ik} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & \frac{1}{r^2} & 0 \\ 0 & 0 & 1 \end{pmatrix}, \quad \Gamma_{22}^1 = -r, \quad \Gamma_{21}^2 = \Gamma_{12}^2 = \frac{1}{r}, \quad \Gamma_{kn}^m = 0 \quad \text{else}, \quad (53)$$

while in spherical coordinates, we have

$$\begin{aligned}g^{ik} &= \begin{pmatrix} 1 & 0 & 0 \\ 0 & \frac{1}{r^2 \sin^2 \vartheta} & 0 \\ 0 & 0 & \frac{1}{r^2} \end{pmatrix}, \quad \Gamma_{22}^1 = -r \sin^2 \vartheta, \quad \Gamma_{23}^2 = \Gamma_{32}^2 = \cot \vartheta, \quad \Gamma_{33}^1 = -r, \\ \Gamma_{21}^2 &= \Gamma_{12}^2 = \Gamma_{31}^3 = \Gamma_{13}^3 = \frac{1}{r}, \quad \Gamma_{22}^3 = -\sin \vartheta \cos \vartheta, \quad \Gamma_{kn}^m = 0 \quad \text{else}.\end{aligned}\quad (54)$$

Clearly, the equations are still valid in Cartesian coordinates, where  $r$  plays the role of  $x$  and  $g^{ik} = \delta^{ik}$ , while  $\Gamma_{kn}^m = 0$ .

In order to avoid useless calculations, it is better to consider the first Eq. (51)<sub>1</sub> separately. Indeed, it reads explicitly

$$\frac{dJ_1^1}{dr} + j \frac{J_1^1}{r} = 0, \quad \text{with } j = \begin{cases} 0 & \text{planar} \\ 1 & \text{for the cylindrical case.} \\ 2 & \text{spherical} \end{cases} \quad (55)$$

If we suppose that one boundary is impermeable,  $J_1^1$  vanishes there and from (55)<sub>1</sub>, we have  $J_\alpha^1 = 0 \forall r$ . Then, we obtain the field equations presented in system (1–3). They are written in terms of the physical components [25,47], defined as<sup>8</sup>

$$\hat{q}_\alpha^i = \sqrt{g_{ii}} q_\alpha^i, \quad \hat{\rho}_\alpha^{(ik)} = \sqrt{g_{ii}} \sqrt{g_{kk}} \rho_\alpha^{(ik)}. \quad (56)$$

But for simplicity, the hats in system (1–3) have been dropped. The field variables that do not appear in (1–3) vanish identically.

To the system of field equations, we can associate the entropy density  $\rho\eta$ . Indeed, the kinetic theory defines the entropy density in terms of the distribution function as

$$\rho\eta = \sum_{\alpha=1}^2 \rho^\alpha \eta^\alpha \quad \text{with} \quad \eta^\alpha = -\frac{k_B}{\rho^\alpha} \int f_\alpha \ln f_\alpha d\mathbf{c}^\alpha. \quad (57)$$

<sup>8</sup> The underlined indices are unsummed.

The Grad distribution function (48) together with (57) furnishes the expression of the entropy density in terms of the fields [38], that is,

$$\rho\eta = \sum_{\alpha=1}^2 \rho^{\alpha} \eta^{\alpha} \quad \text{with} \quad \eta^{\alpha} = \eta_{\text{E}}^{\alpha} - \frac{1}{4} \frac{\hat{\rho}_{(ij)}^{\alpha} \hat{\rho}_{(ij)}^{\alpha}}{\rho^{\alpha} p^{\alpha} T} - \frac{1}{5} \frac{\hat{q}_i^{\alpha} \hat{q}_i^{\alpha}}{p_{\alpha}^2 T}, \quad (58)$$

where  $\eta_{\text{E}}^{\alpha}$  represents the specific entropy density at equilibrium given by

$$\eta_{\text{E}}^{\alpha} = \frac{3}{2} \frac{k_{\text{B}}}{m_{\alpha}} \ln T - \frac{k_{\text{B}}}{m_{\alpha}} \ln \rho^{\alpha}. \quad (59)$$

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