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Average temperature and Maxwellian iteration in multitemperature mixtures of fluids

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This paper treats the nonequilibrium processes in mixtures of fluids under the assumption that each constituent is characterized by its own velocity and temperature field. First we discuss the concept of the average temperature of mixture based upon considerations that the internal energy of the mixture is the same as in the case of a single-temperature mixture. As a consequence, it is shown that the entropy of the mixture reaches a local maximum in equilibrium. An illustrative example of homogeneous mixtures is given to support the theoretical considerations. Through the procedure of Maxwellian iteration a new constitutive equation for nonequilibrium temperatures of constituents is obtained in a classical limit, together with the Fick's law for the diffusion flux. These results obtained for *n*-species are in perfect agreement with a recent classical approach of thermodynamics of irreversible processes in multitemperature case due to Gouin and Ruggeri and generalize our previous papers concerning the case of a binary mixture.

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I. INTRODUCTION

Modeling and analysis of mixtures is challenging and stimulating problem. In the case of gaseous mixtures, it can be successfully studied using the methods of kinetic theory of gases, but also by means of continuum theory of fluids. In either case, appropriate macroscopic equations can be derived. However, many questions are still open and are the fields of active research.

This study tends to provide some results concerned with the modeling problem of a mixture of gases. It is not only about derivation of a set of governing equations, but also about more subtle questions such as the definition of an average temperature, the entropy of the mixture and the comparison between the extended thermodynamic approach and the classic limit of thermodynamics of irreversible processes (TIP). These results can be regarded as a continuation of previous research in this field and a generalization of the results recently obtained by Ruggeri and Simić [1–3], and Gouin and Ruggeri [4].

The paper is organized as follows. First, the multitemperature model of homogeneous mixtures, established within the framework of extended thermodynamics, is reviewed. It is followed by the first principal result—the definition of an average temperature based upon the definition of the internal energy of the mixture [Eq. (6)]. As its natural consequence, it appears that the total entropy of the mixture reaches a local maximum in equilibrium [Eq. (14)]. These observations are supported by an example of spatially homogeneous mixtures which emphasizes the dissipative character of governing equations and the importance of multitemperature assumption through the asymptotic behavior of the solution.

In the second part of the paper we consider, for a mixture of n species, the so-called *Maxwellian iteration* [5], i.e., the limit equations when the relaxation times in the momentum equations and energy equations of each species are negligible. We obtain in this case the classic constitutive equation for mechanical diffusion [Fick law, Eq. (30)], together with a new constitutive equation that permit to determine also the nonequilibrium temperatures of the constituents [Eq. (34)]. These results are in perfect agreement with a recent classical TIP approach of multitemperature mixture given by Gouin and Ruggeri [4].

II. MULTITEMPERATURE MODEL OF HOMOGENEOUS MIXTURES

The theory of homogeneous mixtures was developed, within the framework of rational thermodynamics by Truesdell [6], under the assumption that each constituent obeys the same balance laws as a single fluid. A huge amount of literature appeared after that in the context of continuum approach, see e.g., [7–13]. The system of governing equations read,

$$\frac{\partial \rho_\alpha}{\partial t} + \mathrm{div}(\rho_\alpha \mathbf{v}_\alpha) = \tau_\alpha; \tag{1a}$$

$$\frac{\partial (\rho_\alpha \mathbf{v}_\alpha)}{\partial t} + \mathrm{div}(\rho_\alpha \mathbf{v}_\alpha \otimes \mathbf{v}_\alpha - \mathbf{t}_\alpha) = \mathbf{m}_\alpha; \tag{1b}$$

$$\frac{\partial \left(\frac{1}{2}\rho_\alpha v_\alpha^2 + \rho_\alpha \varepsilon_\alpha\right)}{\partial t} + \mathrm{div}\left\{\left(\frac{1}{2}\rho_\alpha v_\alpha^2 + \rho_\alpha \varepsilon_\alpha\right)\mathbf{v}_\alpha - \mathbf{t}_\alpha \mathbf{v}_\alpha + \mathbf{q}_\alpha\right\} = e_\alpha, \tag{1c}$$

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where $\alpha=1,\ldots,n$. On the left-hand side, ρ_α is the density, $\mathbf{v}_\alpha$ is the velocity, ε_α is the internal energy, $\mathbf{q}_\alpha$ is the heat flux and $\mathbf{t}_\alpha$ is the stress tensor. The stress tensor $\mathbf{t}_\alpha$ can be decomposed into a pressure part $-p_\alpha\mathbf{I}$ and a viscous part $\boldsymbol{\sigma}_\alpha$ as

$$\mathbf{t}_\alpha = -p_\alpha \mathbf{I} + \boldsymbol{\sigma}_\alpha .$$

Source terms τ_α, $\mathbf{m}_\alpha$, and e_α, which describe the interactions between constituents, satisfy the following relations:

$$\sum_{\alpha=1}^{n} \tau_\alpha = 0; \quad \sum_{\alpha=1}^{n} \mathbf{m}_\alpha = \mathbf{0}; \quad \sum_{\alpha=1}^{n} e_\alpha = 0.$$

The appropriate definitions of field variables for the whole mixture,

$$\rho = \sum_{\alpha=1}^{n} \rho_\alpha; \quad \rho\mathbf{v} = \sum_{\alpha=1}^{n} \rho_\alpha \mathbf{v}_\alpha; \quad \mathbf{u}_\alpha = \mathbf{v}_\alpha - \mathbf{v}; \tag{2a}$$

$$\rho\varepsilon_I = \sum_{\alpha=1}^{n} \rho_\alpha\varepsilon_\alpha; \quad \rho\varepsilon = \rho\varepsilon_I + \frac{1}{2}\sum_{\alpha=1}^{n} \rho_\alpha u_\alpha^2; \tag{2b}$$

$$\mathbf{t} = \sum_{\alpha=1}^{n} (\mathbf{t}_\alpha - \rho_\alpha \mathbf{u}_\alpha \otimes \mathbf{u}_\alpha); \tag{2c}$$

$$\mathbf{q} = \sum_{\alpha=1}^{n} \left\{ \mathbf{q}_\alpha + \rho_\alpha\left(\varepsilon_\alpha + \frac{1}{2}u_\alpha^2\right)\mathbf{u}_\alpha - \mathbf{t}_\alpha\mathbf{u}_\alpha \right\}, \tag{2d}$$

permit to obtain, by summation of Eqs. (1), the conservation laws of mass, momentum, and energy for the whole mixture in the same form as for a single fluid (ρ, $\mathbf{v}$, $\mathbf{u}_\alpha$, ε_I, ε, $\mathbf{t}$, and $\mathbf{q}$ are, respectively, the total mass density, the mixture velocity, the diffusion velocity of the component α, the intrinsic internal energy, the total internal energy, the stress tensor and the flux of internal energy). In such a way the balance laws for one constituent, say n, may be replaced by the conservation laws, leading to the following system of governing equations:

$$\frac{\partial \rho}{\partial t} + \mathrm{div}(\rho\mathbf{v}) = 0; \tag{3a}$$

$$\frac{\partial(\rho\mathbf{v})}{\partial t} + \mathrm{div}(\rho\mathbf{v}\otimes\mathbf{v} - \mathbf{t}) = \mathbf{0}; \tag{3b}$$

$$\frac{\partial\left(\frac{1}{2}\rho v^2 + \rho\varepsilon\right)}{\partial t} + \mathrm{div}\left\{\left(\frac{1}{2}\rho v^2 + \rho\varepsilon\right)\mathbf{v} - \mathbf{t}\mathbf{v} + \mathbf{q}\right\} = 0; \tag{3c}$$

$$\frac{\partial \rho_b}{\partial t} + \mathrm{div}(\rho_b \mathbf{v}_b) = \tau_b; \tag{3d}$$

$$\frac{\partial(\rho_b\mathbf{v}_b)}{\partial t} + \mathrm{div}(\rho_b\mathbf{v}_b\otimes\mathbf{v}_b - \mathbf{t}_b) = \mathbf{m}_b; \tag{3e}$$

$$\frac{\partial\left(\frac{1}{2}\rho_b v_b^2 + \rho_b\varepsilon_b\right)}{\partial t} + \mathrm{div}\left\{\left(\frac{1}{2}\rho_b v_b^2 + \rho_b\varepsilon_b\right)\mathbf{v}_b - \mathbf{t}_b\mathbf{v}_b + \mathbf{q}_b\right\} = e_b, \tag{3f}$$

with $b=1,\ldots,n-1$. The source terms are determined in accordance with the general principles of extended thermodynamics—Galilean invariance and entropy principle. The Galilean invariance [14] dictates the velocity dependence in the source terms [1]:

$$\tau_b = \hat{\tau}_b;$$

$$\mathbf{m}_b = \hat{\tau}_b\mathbf{v} + \hat{\mathbf{m}}_b; \quad (b = 1,\ldots,n-1),$$

$$e_b = \hat{\tau}_b\frac{v^2}{2} + \hat{\mathbf{m}}_b\cdot\mathbf{v} + \hat{e}_b,$$

where $\hat{\tau}_b$, $\hat{\mathbf{m}}_b$ and $\hat{e}_b$ are independent of $\mathbf{v}$. Their form can be determined through application of the entropy inequality. In particular, this was done in [1] for the mixture of Eulerian fluids,

$$\hat{\tau}_b = -\sum_{c=1}^{n-1} \varphi_{bc}\left(\frac{\mu_c - \frac{1}{2}u_c^2}{T_c} - \frac{\mu_n - \frac{1}{2}u_n^2}{T_n}\right); \tag{4a}$$

$$\hat{\mathbf{m}}_b = -\sum_{c=1}^{n-1} \psi_{bc}\left(\frac{\mathbf{u}_c}{T_c} - \frac{\mathbf{u}_n}{T_n}\right); \tag{4b}$$

$$\hat{e}_b = -\sum_{c=1}^{n-1} \theta_{bc}\left(-\frac{1}{T_c} + \frac{1}{T_n}\right), \tag{4c}$$

where T_α, $\alpha=1,\ldots,n$, are the temperatures of the constituents and

$$\mu_\alpha = \varepsilon_\alpha - T_\alpha S_\alpha + \frac{p_\alpha}{\rho_\alpha} \tag{5}$$

are their chemical potentials. Coefficients φ_{bc}, ψ_{bc}, and θ_{bc}, $(b,c=1,\ldots,n-1)$ are the elements of phenomenological symmetric positive definite matrices. In the sequel, our analysis will be restricted to a model of nonreacting mixtures, for which $\tau_b=0$.

III. AVERAGE TEMPERATURE

The theory of mixture of fluids in which each constituent has its own temperature seems to be more realistic than the models in which all the constituents have a common temperature. It is indispensable in some particular physical situations, such as plasma physics [15] and some recent questions of astrophysics [16]. Nevertheless, from the practical point of view, the main problem regards the measurement of the temperature of each constituent.

Modeling the mixtures of gases, in the way it is intended to be done here, calls for appropriate definition of an average temperature. It is not only the common temperature of all constituents in equilibrium, $T_\alpha = T = \text{const}$, $\alpha = 1, \ldots, n$, but also the temperature of the mixture expected to be identified during any thermodynamic process. In principle, $T_\alpha \neq T$ during the process ($T \neq \text{const}$), and this discrepancy can be described by nonequilibrium temperature difference $\Theta_\alpha = T_\alpha - T$. Therefore, a question of definition of an average temperature has to be posed.

The average temperature is not thoroughly discussed in the literature. In fact, in continuum approach the authors usually use the single-temperature (ST) theory, whereas multitemperature (MT) theory is mainly considered in the kinetic theory context. In the latter approach the temperature of a single constituent is evaluated by the knowledge of the distribution functions. Some previous definitions of the average temperature are proposed for a two-component system at kinetic level in terms of the algebraic average of the mean square velocities for the two distributions [17], or by the requirement that the total pressure of the mixture has the same form as in the ST theory, see, e.g., [18,19] and also [1].

In this paper we reconsider the definition of an average temperature proposed recently by Ruggeri and Simić [3] in the case of binary mixtures, and then implemented by Gouin and Ruggeri [4] in the context of classical thermodynamics of irreversible processes. The main idea is to exploit the definition of internal energy to introduce the (average) temperature T as a state variable for the mixture, and to do it in such a way that the intrinsic internal energy ε_I [see Eq. (2b)] of the multitemperature mixture resembles the structure of intrinsic internal energy of a single-temperature one. Therefore, *the following implicit definition of an average temperature is adopted*:

$$\rho\varepsilon_I(\rho_1, \ldots, \rho_n, T) = \sum_{\alpha=1}^{n} \rho_\alpha \varepsilon_\alpha(\rho_\alpha, T) = \sum_{\alpha=1}^{n} \rho_\alpha \varepsilon_\alpha(\rho_\alpha, T_\alpha). \tag{6}$$

By expanding this relation in the neighborhood of the average temperature we have:

$$T = \frac{\sum_{\alpha=1}^{n} \rho_\alpha c_V^{(\alpha)} T_\alpha}{\sum_{\alpha=1}^{n} \rho_\alpha c_V^{(\alpha)}}, \tag{7}$$

where

$$c_V^{(\alpha)} = \frac{\partial \varepsilon_\alpha(\rho_\alpha, T)}{\partial T_\alpha} \tag{8}$$

is specific heat at constant volume of constituent α. We observe that Eq. (7) gives the exact average temperature in the case of mixture of ideal gases. Furthermore, the following relation holds for non-equilibrium temperature difference in linear approximation close to equilibrium [4],

$$\Theta_n = -\frac{1}{\rho_n c_V^{(n)}} \sum_{b=1}^{n-1} \rho_b c_V^{(b)} \Theta_b. \tag{9}$$

Equation (6) uniquely determines the average temperature T, and there exist a one-to-one mapping of state variables $T_\alpha \leftrightarrow (T, \Theta_b)$, ($\alpha = 1, \ldots, n$; $b = 1, \ldots, n-1$). Therefore, as a consequence of definition (6) and of the aforementioned change of variables, the conservation law for the energy of the whole mixture [Eq. (3c)] becomes an evolution equation for the average temperature T and the energy Eqs. (3f) for the $n-1$ species become the evolution equations for the Θ_b. The Θ_b that can be regarded as nonequilibrium variables because when $\Theta_b = 0$ for all $b = 1, \ldots, n-1$, all the source terms $\hat{e}_b$ vanish [see Eq. (4c)]. The Θ_b's are the thermal counterpart of diffusion velocity fluxes $\mathbf{u}_b$, and for this reason we call them *diffusion temperature fluxes*.

A. Entropy of the mixture

The new definition of average temperature has several advantages. The first one is a consequence of definition (6) that the conservation law for the energy of mixture [Eq. (3c)] becomes an evolution equation for the average temperature T.

The second advantage is related to the entropy of the whole mixture defined as

$$\rho S = \sum_{\alpha=1}^{n} \rho_\alpha S_\alpha(\rho_\alpha, T_\alpha), \tag{10}$$

where S_α are the entropy densities of the constituents. It appears that Eq. (10) reaches its maximum value in equilibrium, i.e., when $\Theta_b = 0$ for all $b = 1, \ldots, n-1$, and it is a direct consequence of the definition (6). To prove this statement it is necessary to expand Eq. (10) in the neighborhood of $T_\alpha = T$,

$$\rho S = \sum_{\alpha=1}^{n} \rho_\alpha S_\alpha(\rho_\alpha, T) + \sum_{\alpha=1}^{n} \rho_\alpha \frac{\partial S_\alpha}{\partial T_\alpha}(\rho_\alpha, T)\Theta_\alpha + \frac{1}{2}\sum_{\alpha=1}^{n} \rho_\alpha \frac{\partial^2 S_\alpha}{\partial T_\alpha^2}(\rho_\alpha, T)\Theta_\alpha^2 + O(\Theta_\alpha^3). \tag{11}$$

However, only $n-1$ nonequilibrium variables Θ_α are independent because they are related through the definition of average temperature Eq. (6). Therefore, by expanding (6) in the neighborhood of $T_\alpha = T$ the following relation is obtained:

$$\sum_{\alpha=1}^{n} \rho_\alpha \frac{\partial \varepsilon_\alpha}{\partial T_\alpha}(\rho_\alpha, T)\Theta_\alpha = -\frac{1}{2}\sum_{\alpha=1}^{n} \rho_\alpha \frac{\partial^2 \varepsilon_\alpha}{\partial T_\alpha^2}(\rho_\alpha, T)\Theta_\alpha^2 + O(\Theta_\alpha^3). \tag{12}$$

From the Gibbs' equations for each constituent,

$$T_\alpha dS_\alpha = d\varepsilon_\alpha - \frac{p_\alpha}{\rho_\alpha^2} d\rho_\alpha, \tag{13}$$

we have

$$T_\alpha \frac{\partial S_\alpha}{\partial T_\alpha} = \frac{\partial \varepsilon_\alpha}{\partial T_\alpha}.$$

Starting from this equation, necessary relations in equilibrium can be derived,

$$\frac{\partial S_\alpha}{\partial T_\alpha}(\rho_\alpha, T) = \frac{1}{T}\frac{\partial \varepsilon_\alpha}{\partial T_\alpha}(\rho_\alpha, T);$$

$$\frac{\partial^2 S_\alpha}{\partial T_\alpha^2}(\rho_\alpha, T) = -\frac{1}{T^2}\frac{\partial \varepsilon_\alpha}{\partial T_\alpha}(\rho_\alpha, T) + \frac{1}{T}\frac{\partial^2 \varepsilon_\alpha}{\partial T_\alpha^2}(\rho_\alpha, T).$$

Putting them into Eq. (11) and exploiting the constraint (12), it can be shown that entropy of the mixture reads

$$\rho S = \sum_{\alpha=1}^{n} \rho_\alpha S_\alpha(\rho_\alpha, T) - \frac{1}{2T^2}\sum_{\alpha=1}^{n} \rho_\alpha c_V^{(\alpha)} \Theta_\alpha^2 + O(\Theta_\alpha^3). \tag{14}$$

Since $c_V^{(\alpha)} > 0$ there exist a neighborhood of equilibrium state $\Theta_\alpha = 0$ in which the nonequilibrium part of total entropy is a negative definite quadratic form of Θ_α, and thus *entropy of the mixture reaches its local maximum in equilibrium*. This result, which is a consequence of Eq. (6), is particularly interesting because such an estimate cannot be achieved in such a direct way with other definitions of average temperature.

B. Dynamical pressure

The total pressure of the mixture can be regarded as a sum of partial pressures,

$$p = \sum_{\alpha=1}^{n} p_\alpha(\rho_\alpha, T_\alpha).$$

Nevertheless, it can be viewed also as a sum of total pressure evaluated in equilibrium and an additional term, called *dynamical pressure*, which appears as a nonequilibrium pressure due to diffusion temperature flux Θ_b,

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

$$(\beta = 1, 2, \ldots, n; \quad b = 1, 2, \ldots, n-1). \tag{15}$$

In the first approximation dynamical pressure can be expressed as

$$\pi_\theta = \sum_{b=1}^{n-1} r_b \Theta_b, \tag{16}$$

where [4]

$$r_b = \frac{1}{\rho_n c_V^{(n)}} \left\{ \rho_n c_V^{(n)} \frac{\partial p_b}{\partial T_b}(\rho_b, T) - \rho_b c_V^{(b)} \frac{\partial p_n}{\partial T_n}(\rho_n, T) \right\}.$$

Two remarks have to be given about dynamical pressure. First, Eq. (16) represents exact expression for dynamical pressure in the case of mixture of ideal gases, for which

$$p_\alpha = \frac{k}{m_\alpha}\rho_\alpha T_\alpha,$$

and all higher order derivatives (greater than 1) of p_α with respect to T_α vanish. Therefore, for ideal gases, taking into account

$$\varepsilon_\alpha = c_V^{(\alpha)} T_\alpha, \quad c_V^{(\alpha)} = \frac{k}{m_\alpha(\gamma_\alpha - 1)},$$

(k and m_α and γ_α are, respectively, the Boltzmann constant, atomic mass, and ratio of specific heats of constituent α), we have

$$p = p_0 + \pi_\theta = p_0 + \sum_{b=1}^{n-1} \rho_b c_V^{(b)} (\gamma_b - \gamma_n)\Theta_b.$$

Second, when two ideal gases, say $\hat{b}$ and n, have the same ratio of specific heats, $\gamma_{\hat{b}} = \gamma_n$, then dynamical pressure does not depend on diffusion temperature flux $\Theta_{\hat{b}}$, since $r_{\hat{b}} = 0$. When all the constituents have the same ratio of specific heats, the total pressure of the mixture is equal to equilibrium one, regardless of possible diffusion temperature fluxes.

C. Alternative form of the differential system

In the context of multitemperature mixtures of nonreacting gases, the equilibrium field variables are ρ, $\mathbf{v}$, T, and ρ_b (or the concentration variables $c_b = \rho_b/\rho$). However, it is useful to introduce diffusion velocity flux $\mathbf{J}_\alpha$ related to diffusion velocity

$$\mathbf{J}_\alpha = \rho_\alpha \mathbf{u}_\alpha, \quad \left(\sum_{\alpha=1}^{n} \mathbf{J}_\alpha = \mathbf{0} \right),$$

so that $\mathbf{J}_b$ and Θ_b could be regarded as nonequilibrium variables. It is convenient for the following to rewrite the system (2e) using the material derivatives

$$\frac{d}{dt} = \frac{\partial}{\partial t} + \mathbf{v} \cdot \boldsymbol{\nabla}, \quad \frac{d_b}{dt} = \frac{\partial}{\partial t} + \mathbf{v}_b \cdot \boldsymbol{\nabla}$$

for $b = 1, \ldots, n-1$, and taking into account the definition of the average temperature given by Eq. (6),

$$\begin{cases} \dfrac{d\rho}{dt} + \rho\,\mathrm{div}\,\mathbf{v} = 0, \\ \rho\dfrac{d\mathbf{v}}{dt} - \mathrm{div}\,\mathbf{t} = 0, \\ \rho\dfrac{\partial \varepsilon_I}{\partial T}\dfrac{dT}{dt} = \rho^2\dfrac{\partial \varepsilon_I}{\partial \rho}\mathrm{div}\,\mathbf{v} + \sum_{b=1}^{n-1}\dfrac{\partial \varepsilon_I}{\partial c_b}\mathrm{div}\,\mathbf{J}_b + \mathbf{t}\,\mathrm{grad}\,\mathbf{v} - \mathrm{div}\,\ \mathbf{q}, \\ \dfrac{d_b\rho_b}{dt} + \rho_b\,\mathrm{div}\,\mathbf{v}_b = 0, \\ \rho_b\dfrac{d_b\mathbf{v}_b}{dt} - \mathrm{div}\,\mathbf{t}_b = \hat{\mathbf{m}}_b, \\ \rho_b\dfrac{d_b\varepsilon_b}{dt} - \mathbf{t}_b\cdot\boldsymbol{\nabla}\mathbf{v}_b + \mathrm{div}\,\mathbf{q}_b = \hat{e}_b. \end{cases} \tag{17}$$

The differential equations govern the evolution of ρ, $\mathbf{v}$, T, ρ_b, $\mathbf{J}_b$, and Θ_b, respectively, provided we assign the constitutive equations p_α, ε_α and for dissipative fluids also the heat fluxes $\mathbf{q}_\alpha$ and the viscous stress tensors $\boldsymbol{\sigma}_\alpha$, $(\alpha=1,2,\ldots,n)$. Moreover we have also to prescribe the matrices ψ_{bc} and θ_{bc}, $(b=1,\cdots n-1)$ that appear in Eq. (4).

IV. EXAMPLE OF SPATIALLY HOMOGENOUS MIXTURE

In this section a simple example will be provided in order to support previous theoretical considerations, and to stress the main features of multitemperature approach. To do it in the simplest possible way, a nonreacting mixture of gases will be considered in the special case of spatially homogeneous fields, i.e., the case in which field variables depend solely on time. The governing Eqs. (17) can be written in the following form:

$$\frac{d\rho}{dt} = 0; \quad \frac{d\mathbf{v}}{dt} = \mathbf{0}; \quad \frac{dT}{dt} = 0; \tag{18a}$$

$$\frac{d\rho_b}{dt} = 0; \quad \rho_b\frac{d\mathbf{v}_b}{dt} = \hat{\mathbf{m}}_b; \quad \rho_b\frac{d\varepsilon_b}{dt} = \hat{e}_b. \tag{18b}$$

where now $d/dt=\partial/\partial t$. From Eq. (18) it is easy to conclude

$$\rho = \text{const.}; \quad \mathbf{v} = \text{const.}; \quad T = \text{const.}; \tag{19a}$$

$$\rho_b = \text{const.}; \quad b = 1, \ldots, n, \tag{19b}$$

and due to Galilean invariance we may choose $\mathbf{v}=\mathbf{v}_0=\mathbf{0}$ without loss of generality. It is also remarkable that the average temperature of the mixture remains constant during the process: $T(t)=T_0$.

In the sequel we shall regard only small perturbations of equilibrium state, $\mathbf{v}_\alpha=\mathbf{v}_0=\mathbf{0}$, $T_\alpha=T_0$, $\alpha=1,\ldots,n$, and analyze their behavior. Therefore, the rhs of Eq. (18b) could be linearized in the neighborhood of equilibrium. Taking into account that solution depends only on time, and not on space variables, production terms given by Eqs. (4b) and (4c) that are valid for Eulerian gases, still remain valid also for viscous and heat conducting fluids. Therefore, in the linearized case we obtain

$$\rho_b\frac{d\mathbf{v}_b}{dt} = -\sum_{c=1}^{n-1}\frac{\psi_{bc}^0}{T_0}(\mathbf{v}_c - \mathbf{v}_n); \tag{20a}$$

$$\rho_b c_V^{(b)}\frac{dT_b}{dt} = -\sum_{c=1}^{n-1}\frac{\theta_{bc}^0}{T_0^2}(T_c - T_n), \tag{20b}$$

where ψ_{bc}^0 and θ_{bc}^0 are entries of positive definite matrices evaluated in equilibrium. Note that $\mathbf{v}_b-\mathbf{v}_n=\mathbf{u}_b-\mathbf{u}_n$ and $T_b-T_n=\Theta_b-\Theta_n$.

Although the system (20) is linear, the explicit solution would not give a suggestive answer about behavior of nonequilibrium variables. Instead, the results of qualitative nature can be obtained due to a fact that source terms have been constructed in accordance with the entropy principle. First note that we have

$$\sum_{b=1}^{n-1}\rho_b\frac{d\mathbf{v}_b}{dt} = -\rho_n\frac{d\mathbf{v}_n}{dt},$$

as a consequence of definition of mixture velocity and solutions (19a) and $\mathbf{v}=\mathbf{0}$. If we do a scalar multiplication of Eq. (20a) with $\mathbf{v}_b-\mathbf{v}_n$ and then sum up all the equations, the following result will be obtained

$$\frac{d}{dt}\sum_{\alpha=1}^{n}\left(\frac{1}{2}\rho_\alpha v_\alpha^2\right) = -\sum_{b,c=1}^{n-1}\frac{\psi_{bc}^0}{T_0}(\mathbf{v}_b - \mathbf{v}_n)\cdot(\mathbf{v}_c - \mathbf{v}_n) \leq 0,$$

the last inequality being a consequence of positive definiteness of the matrix $\boldsymbol{\psi}^0$. It can be concluded that the kinetic energy of the system, viewed as a measure of mechanical nonequilibrium in this example, is a decreasing function which asymptotically tends to zero. On the other hand, as a consequence of Eqs. (9) and (19a) we have

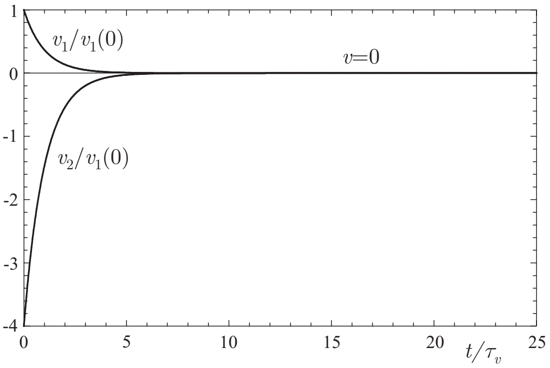

FIG. 1. Dimensionless velocities of the constituents versus dimensionless time.

$$\sum_{b=1}^{n-1} \rho_b c_V^{(b)} \Theta_b = - \rho_n c_V^{(n)} \Theta_n .$$

If we multiply Eq. (20b) with $\Theta_b - \Theta_n$ and then sum up all the equations, the following inequality is obtained,

$$\frac{d}{dt} \sum_{\alpha=1}^{n} \left(\frac{1}{2} \rho_\alpha c_V^{(\alpha)} \Theta_\alpha^2 \right) = - \sum_{b,c=1}^{n-1} \frac{\theta_{bc}^0}{T_0^2} (\Theta_b - \Theta_n)(\Theta_c - \Theta_n) \leq 0.$$

The first term—a positive definite quadratic form of Θ_α—can be regarded as a measure of thermal nonequilibrium. Its time derivative is a decreasing function due to definiteness of the matrix $\boldsymbol{\theta}^0$. Therefore, diffusion temperature fluxes asymptotically tend to zero.

In the particular case of a binary mixture the explicit solution of Eqs. (20) can be obtained and it reads

$$\mathbf{v}_1(t) = \mathbf{v}_1(0) e^{-t/\tau_v}; \quad T_1(t) = T_0 + (T_1(0) - T_0) e^{-t/\tau_T},$$

where τ_v and τ_T represent relaxation times that for ideal gas assume the expression

$$\tau_v = \frac{\rho_1 \rho_2 T_0}{\psi_{11}^0 \rho};$$

$$\tau_T = \frac{k \rho_1 \rho_2 T_0^2}{\theta_{11}^0 [\rho_1 m_2 (\gamma_2 - 1) + \rho_2 m_1 (\gamma_1 - 1)]}.$$

Starting from these solutions, other field variables can be obtained by means of defining equations

$$\rho_1 \mathbf{v}_1 + \rho_2 \mathbf{v}_2 = \rho \mathbf{v} = \mathbf{0};$$

$$\rho_1 c_V^{(1)} T_1 + \rho_2 c_V^{(2)} T_2 = (\rho_1 c_V^{(1)} + \rho_2 c_V^{(2)}) T = (\rho_1 c_V^{(1)} + \rho_2 c_V^{(2)}) T_0.$$

It is obvious that, due to dissipative character of the system, *all the nonequilibrium variables exponentially decay and converge to their equilibrium values* including also the dynamical pressure [Eq. (16)] which in this case reads

$$\pi_\theta = \rho_1 c_V^{(1)} (\gamma_1 - \gamma_2) \Theta_1 .$$

In order to compare the values of τ_v and τ_T for ideal gases, and also to compute the actual values of variables in numerical example, the relations from kinetic theory has to be recalled [15],

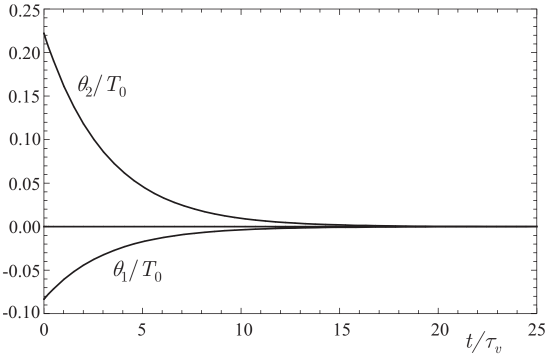

FIG. 2. Dimensionless diffusion temperature fluxes of the constituents versus dimensionless time.

$$\theta_{11}^0 = \frac{3 m_1 m_2}{(m_1 + m_2)^2} k T_0^2 \Gamma_{12}'; \quad \psi_{11}^0 = \frac{2 m_1 m_2}{m_1 + m_2} T_0 \Gamma_{12}',$$

where Γ_{12}' represents volumetric collision frequency, and the following estimate can be obtained:

$$\frac{\tau_T}{\tau_v} = \frac{2}{3} \frac{\rho (m_1 + m_2)}{\rho_1 m_2 (\gamma_2 - 1) + \rho_2 m_1 (\gamma_1 - 1)} > \frac{2}{3(\gamma_{\max} - 1)} \geq 1,$$

$$(\gamma_{\max} = \max\{\gamma_1, \gamma_2\} \leq 5/3). \tag{21}$$

With the aim to compare the thermal diffusion, associated with the multitemperature assumption, with the mechanical diffusion, in Figs. 1–3 we present the graphs of normalized velocities, diffusion temperature fluxes, and dynamical pressure are shown, respectively, in terms of scaled time variable t/τ_v, for the following choice of parameters of the mixture,

$$\frac{m_2}{m_1} = 0.4; \quad \frac{\rho_1}{\rho} = 0.8; \quad \frac{\rho_2}{\rho} = 0.2;$$

$$\gamma_1 = \frac{5}{3}; \quad \gamma_2 = \frac{7}{5}; \quad \frac{\tau_T}{\tau_v} = 3.18 \tag{22}$$

together with initial data: $T_1(0) = 300$ K; $T_2(0) = 400$ K. In such a way we have $T_0 = 327.3$ K.

It can be observed that, due to the inequality (21), *the*

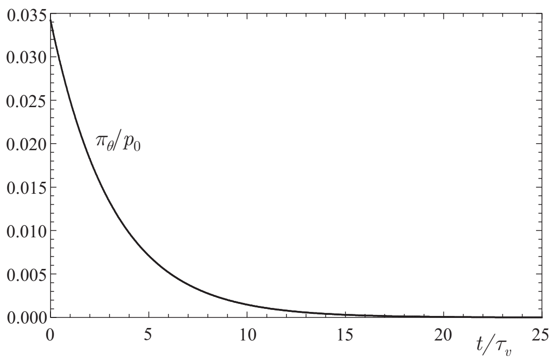

FIG. 3. Dimensionless dynamical pressure versus dimensionless time.

mechanical diffusion vanishes more rapidly than the thermal one. This is in sharp contrast with widely adopted approach which ignores the multitemperature assumption.

V. MAXWELLIAN ITERATION

The name and the procedure of the so-called *Maxwellian iteration* was first introduced in the paper by Ikenberry and Truesdell [5] (see also the book of Truesdell and Muncaster [20]) and was successfully applied in many circumstances in continuum mechanics as a sort of macroscopic Chapman-Enskog procedure, i.e., an expansion in power series in appropriate relaxation times. In this manner it is possible to recover TIP approach as a limit case of extended theories. For example, the Navier-Stokes-Fourier constitutive relations emerge as a first-order Maxwellian iteration of the Grad's 13 moments theory [21] in the context of extended thermodynamics [9]. Another example is the Fick's law obtained as a limiting case of momentum equations in ST theory [8,9].

Before proceeding to multitemperature mixture, the idea of Maxwellian iteration will be illustrated using the simplest system of 2×2 balance laws in one space dimension,

$$\partial_t u + \partial_x f(u,v) = 0; \tag{23a}$$

$$\partial_t v + \partial_x g(u,v) = \frac{1}{\tau}[v - h(u)], \tag{23b}$$

where τ denotes small parameter—relaxation time. In Eq. (23) u can be regarded as an equilibrium variable, whereas v is a nonequilibrium one, Eq. (23b) being its governing equation. Relation $v_E = h(u)$ determines equilibrium manifold on which source term in Eq. (23b) vanishes and the system is reduced to a conservation law,

$$\partial_t u + \partial_x F(u) = 0; \quad F(u) = f[u,h(u)]. \tag{24}$$

In this iterative procedure equilibrium value of v is treated as zeroth iterate, $v^{(0)} = v_E = h(u)$, and should be put into lhs of Eq. (23b). First iterate $v^{(1)}$ is then calculated form the rhs, i.e.,

$$\partial_t v^{(0)} + \partial_x g[u,v^{(0)}] = \frac{1}{\tau}[v^{(1)} - h(u)].$$

By a simple calculation, using Eq. (23a), one obtains the following expression for $v^{(1)}$:

$$\begin{aligned} v^{(1)} = h(u) + \tau\{&- h'(u)\{f_u[u,h(u)] + h'(u) f_v[u,h(u)] \\ &+ g_u[u,h(u)] + h'(u) g_v[u,h(u)]\}\}\partial_x u \end{aligned} \tag{25}$$

Putting $v^{(1)}$ into the lhs of Eq. (23b) one obtains in the same manner the second iterate $v^{(2)}$ from the rhs, etc. In such a way nonequilibrium variable is expanded in powers of relaxation time τ.

The iterative procedure being stopped at the first order, the limit of the evolution equations implies that the nonequilibrium variables $v^{(1)} - h(u)$ are proportional to the gradients of equilibrium variables $\partial_x u$. In the physical cases where this procedure was applied it was verified that expression (25) is equivalent to the constitutive equations of the corresponding TIP approach. We will see that, in the present case of mixture with multitemperature also, the Maxwellian iteration at the first order give the same result obtained earlier within the TIP framework of multitemperature mixture proposed by Gouin and Ruggeri [4].

As we are interested mainly in mechanical and thermal diffusion phenomena in mixtures, for the sake of simplicity we limit our calculation to the case of Euler gases for which Eqs. (4b) and (4c) hold. Nevertheless, our results remain confirmed also in the case of Navier-Stokes-Fourier fluids, as proved directly by extended TIP calculation given in [4].

Application of Maxwellian iterative procedure requires to put in the lhs of the system Eq. $(17)_{5,6}$ the zeroth iterate, i.e., the equilibrium state and in the rhs the first iterate. Taking into account that in zeroth iteration $\mathbf{v}_\alpha^{(0)} = \mathbf{v}$ and consequently $d_b^{(0)}/dt = d/dt$, $\mathbf{J}_b^{(0)} = \mathbf{u}_b^{(0)} = \mathbf{0}$, and moreover $\mathbf{T}_\alpha^{(0)} = T$, $\mathbf{q}^{(0)} = \mathbf{q}_b^{(0)} = 0$, $\mathbf{t}^{(0)} = -p^{(0)}\mathbf{I} = -p_0\mathbf{I}$, $\mathbf{t}_b^{(0)} = -p_b^{(0)}\mathbf{I}$, we obtain

$$\rho_b\left(\frac{d\mathbf{v}}{dt}\right)^{(0)} + \operatorname{grad} p_b^{(0)} = \hat{\mathbf{m}}_b^{(1)},$$

$$\begin{aligned} &\rho_b\left\{\left(\frac{\partial\varepsilon_b}{\partial\rho_b}\right)^{(0)}\left(\frac{d\rho_b}{dt}\right)^{(0)} + \left(\frac{\partial\varepsilon_b}{\partial T_b}\right)^{(0)}\left(\frac{dT}{dt}\right)^{(0)}\right\} + p_b^{(0)} \operatorname{div} \mathbf{v} \\ &\quad = \hat{e}_b^{(1)}, \quad (b = 1, \cdots n-1). \end{aligned} \tag{26}$$

On the other hand form the zero order of Eq. $(17)_{2,3,4}$ we have

$$\rho\left(\frac{d\mathbf{v}}{dt}\right)^{(0)} = -\operatorname{grad} p_0$$

$$\rho\frac{\partial\varepsilon_I}{\partial T}\left(\frac{dT}{dt}\right)^{(0)} = \left(\rho^2\frac{\partial\varepsilon_I}{\partial\rho} - p_0\right)\operatorname{div} \mathbf{v}$$

$$\left(\frac{d\rho_b}{dt}\right)^{(0)} = -\rho_b \operatorname{div} \mathbf{v}, \tag{27}$$

and therefore inserting Eq. (27) in Eq. (26) we obtain

$$-\frac{\rho_b}{\rho}\operatorname{grad} p_0 + \operatorname{grad} p_b^{(0)} = \hat{\mathbf{m}}_b^{(1)},$$

$$\Omega_b \operatorname{div} \mathbf{v} = \hat{e}_b^{(1)}, \quad (b = 1, \ldots, n-1), \tag{28}$$

where

$$\Omega_b = p_b^{(0)} + \rho_b\left\{-\rho_b\left(\frac{\partial\varepsilon_b}{\partial\rho_b}\right)^{(0)} + \left(\rho^2\frac{\partial\varepsilon_I}{\partial\rho} - p_0\right)\frac{\left(\dfrac{\partial\varepsilon_b}{\partial T_b}\right)^{(0)}}{\rho\dfrac{\partial\varepsilon_I}{\partial T}}\right\}. \tag{29}$$

These relations have to be transformed further in order to recognize terms which represent thermodynamic forces in the sense of TIP.

A. Diffusion velocity flux

Taking into account that $p^{(0)} = p_0 = \Sigma_{\alpha=1}^{n} p_\alpha(\rho_\alpha, T)$, Eq. $(28)_1$ can be rewritten as

$$\sum_{a=1}^{n-1}\left(\delta_{ab}\rho_b-\frac{\rho_a\rho_b}{\rho}\right)\times\left(\frac{1}{\rho_a}\text{grad }p_a^{(0)}-\frac{1}{\rho_n}\text{grad }p_n^{(0)}\right)=\hat{\mathbf{m}}_b^{(1)}$$

From the definition of chemical potential (5) one obtains the following relations:

$$\frac{\partial\mu_\alpha}{\partial\rho_\alpha}=\frac{1}{\rho_\alpha}\frac{\partial p_\alpha}{\partial\rho_\alpha};\quad \frac{\partial\mu_\alpha}{\partial T_\alpha}=\frac{1}{\rho_\alpha}\frac{\partial p_\alpha}{\partial T_\alpha}-S_\alpha.$$

Using the first of them, the following transformation could be done:

$$\begin{aligned}\frac{1}{\rho_b}\text{grad }p_b^{(0)}&=\frac{1}{\rho_b}\left(\frac{\partial p_b}{\partial\rho_b}\text{grad }\rho_b+\frac{\partial p_b}{\partial T_b}\text{grad }T_b\right)^{(0)}\\&=T\text{ grad}\left(\frac{\mu_b^{(0)}}{T}\right)+T^2\left\{T\frac{\partial}{\partial T}\left(\frac{\mu_b^{(0)}}{T}\right)\right.\\&\quad\left.-\frac{\partial}{\partial T}\left(\frac{p_b^{(0)}}{\rho_b}\right)\right\}\text{grad}\left(\frac{1}{T}\right)\end{aligned}$$

To reach the goal of this section, the rhs of Eq. $(28)_1$ has to be transformed in accordance with Eq. (4b). Taking into account that $\mathbf{u}_\alpha^{(1)}=\mathbf{J}_\alpha^{(1)}/\rho_\alpha$, and using the relation between diffusion fluxes $\mathbf{J}_n=-\Sigma_{a=1}^{n-1}\mathbf{J}_a$, the following relation is obtained,

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

where $F_{ad}=\delta_{ad}/\rho_a-1/\rho_n$. Since $\hat{\mathbf{m}}_b^{(1)}$ is a linear combination of $\mathbf{J}_a^{(1)}$, after some algebraic manipulations the explicit equation for the first iterate of diffusion flux reads

$$\mathbf{J}_a^{(1)}=\sum_{b=1}^{n-1}L_{ab}\text{ grad}\left(\frac{\mu_b-\mu_n}{T}\right)+L_a\text{ grad}\left(\frac{1}{T}\right),\qquad(30)$$

where phenomenological coefficients, evaluated in equilibrium, are

$$L_{ab}=-T^2[\mathbf{F}^{-1}\boldsymbol{\psi}^{-1}\mathbf{F}^{-1}]_{ab}^{(0)};$$

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

and $(\mathbf{F}^{-1})_{ad}=\delta_{ad}\rho_d-(\rho_a\rho_d)/\rho$. *Thus,* Eq. (30) *recovers the Fick's law well-known from classical thermodynamics of irreversible processes* and is in complete agreement with the result obtained trough the same procedure for single-temperature mixtures in extended thermodynamics [9].

B. Diffusion temperature flux in the multitemperature model

Concerning the Eq. $(28)_2$, we can put first Ω_b in a more convenient form taking into account that from the Gibbs equations for each species [Eq. (13)] we can deduce the well-known thermodynamical relations,

$$\left(\frac{\partial\varepsilon_b}{\partial T_b}\right)^{(0)}=T\left(\frac{\partial S_b}{\partial T_b}\right)^{(0)}$$

$$\left(\frac{\partial\varepsilon_b}{\partial\rho_b}\right)^{(0)}=\frac{p_b^{(0)}}{\rho_b^2}+T\left(\frac{\partial S_b}{\partial\rho_b}\right)^{(0)}.\qquad(31)$$

From the Gibbs equation of the whole mixture in equilibrium,

$$TdS=d\varepsilon_I-\frac{p_0}{\rho^2}d\rho-\sum_{b=1}^{n-1}(\mu_b-\mu_n)^{(0)}dc_b$$

and taking the map $\rho_\alpha\leftrightarrow(\rho,c_b)$, $\alpha=1,2,\ldots,n$; $b=1,2,\ldots,n-1$, we obtain

$$\left(\frac{\partial\varepsilon_I}{\partial T}\right)^{(0)}=T\left(\frac{\partial S}{\partial T}\right)^{(0)},$$

$$\left(\frac{\partial\varepsilon_I}{\partial\rho}\right)^{(0)}=\frac{p^{(0)}}{\rho^2}+T\left(\frac{\partial S}{\partial\rho}\right)^{(0)}.\qquad(32)$$

Inserting Eqs. (31) and (32) in Eq. (29), we have

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

The first iterate of the source term $\hat{e}_b$ is calculated through expansion of Eq. (4c) in the neighborhood of T, and using the relation between diffusion temperature fluxes,

$$\hat{e}_b^{(1)}=-\frac{1}{T^2}\sum_{c=1}^{n-1}\theta_{bc}^{(0)}\sum_{d=1}^{n-1}(\Phi_{cd}\Theta_d^{(1)}).\qquad(33)$$

where $\Phi_{cd}=\delta_{cd}+(\rho_dc_V^{(d)})/(\rho_nc_V^{(n)})$. By combining Eq. $(28)_2$ with Eq. (33), an expression for the first iterate of the diffusion temperature flux is obtained through a simple algebraic manipulation,

$$\Theta_a^{(1)}=-k_a\text{ div }\mathbf{v}.\qquad(34)$$

where

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

Equation (34), obtained by means of Maxwellian iteration, *gives the temperature of each species as a constitutive equation* in the same manner as the Fick law give the velocities of each species. The present result which is in complete accordance with the classical TIP approach to multitemperature mixtures, proposed recently by Gouin and Ruggeri [4].

For a mixture of ideal gases

$$\Omega_b=\rho_bTc_V^{(b)}\frac{\sum_{\alpha=1}^{n}\rho_\alpha c_V^{(\alpha)}(\gamma_b-\gamma_\alpha)}{\sum_{\alpha=1}^{n}\rho_\alpha c_V^{(\alpha)}}.$$

When all the constituents have the same ratio of specific heats we have $\Omega_b=0$, and consequently $\Theta_b^{(1)}=0$, $a=1,\ldots,n-1$. In this case the diffusion temperature flux cannot be observed in the first approximation. In the case of a binary mixture, these results reduce to the ones presented in [2].

VI. CONCLUSIONS

In this paper we have reconsidered the definition of an average temperature in the context of multitemperature approach to the theory of mixtures of fluids. It was based upon the assumption that internal energy of the mixture should retain the same form as in a single-temperature approach. The supremacy of this definition is supported by a simple derivation of entropy maximization result in equilibrium as its consequence and the result that the average temperature remains constant for spatially homogenous mixture.

Furthermore, by means of Maxwellian first iterative procedure we have derived constitutive equations for nonequilibrium variables, mechanical diffusion flux $\mathbf{J}_a$, and diffusion temperature flux Θ_a, in the neighborhood of equilibrium. It was shown that the first iterate of diffusion flux $\mathbf{J}_a^{(1)}$ coincides with the classical generalized Fick's laws which can be obtained in TIP.

However, diffusion temperature flux $\Theta_a^{(1)}$ is found to be proportional to div $\mathbf{v}$—a new result which is in accordance with recent observations within classical TIP framework of multitemperature mixture [4].

The result is particularly important: so, at least in first approximation, the temperature of each species can be evaluated as a constitutive equation in the same manner as the Fick law gives the velocity of each species. Unfortunately, in the case of ideal gas when all the constituents have the same ratio of specific heats (the same degree of freedom), the diffusion temperature flux cannot be observed in the first approximation. The same occurs if the mixture is globally incompressible (div $\mathbf{v}=0$) or in the static case ($\mathbf{v}=0$).

We observe that in the static case where the Maxwellian iteration does not allow to evaluate the temperature of constituents it is possible to use the recent strategy proposed by Ruggeri and Lou, in which by considering the nonequilibrium one-dimensional steady heat conduction between two walls maintained at two different temperatures, it was proved that the measure of the average temperature in $2(n-1)$ points enable us to evaluate the temperature of constituents in all points [22].

The results of this study are supposed to be the starting point for future analysis of mixtures. The shock structure problem in multicomponent mixtures, as well as problems of combustion theory, like flame propagation and detonation waves, could be the possible fields of application of the developed theory.

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