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Identification of an average temperature and a dynamical pressure in a multitemperature mixture of fluids

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We present a classical approach to a mixture of compressible fluids when each constituent has its own temperature. The introduction of an average temperature together with the entropy principle dictates the classical Fick law for diffusion and also novel constitutive equations associated with the difference of temperatures between the components. The constitutive equations fit with results recently obtained through a Maxwellian iteration procedure in extended thermodynamics theory of multitemperature mixtures. The differences of temperatures between the constituents imply the existence of a dynamical pressure even if the fluids have a zero bulk viscosity. The nonequilibrium dynamical pressure can be measured and may be convenient in several physical situations, such as, for example, in cosmological circumstances where—as many authors assert—a dynamical pressure played a major role in the evolution of the early universe.

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I. MIXTURES IN RATIONAL THERMODYNAMICS

In the context of rational thermodynamics, the description of a homogeneous mixture of n constituents is based on the postulate that each constituent obeys the same balance laws that a single fluid does [1]. The laws express the equations of balance of masses, momenta, and energies,

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

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

$$\frac{\partial\left(\frac{1}{2}\rho_\alpha v_\alpha^2 + \rho_\alpha \varepsilon_\alpha\right)}{\partial t} + \operatorname{div}\left[\left(\frac{1}{2}\rho_\alpha v_\alpha^2 + \rho_\alpha \varepsilon_\alpha\right)\mathbf{v}_\alpha - \mathbf{t}_\alpha \mathbf{v}_\alpha + \mathbf{q}_\alpha\right] = e_\alpha \quad (\alpha = 1,2,\ldots,n). \tag{1}$$

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 of the constituent α. 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

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

We consider first only Stokesian fluids [i.e., $\operatorname{tr}(\boldsymbol{\sigma}_\alpha)=0$].

On the right-hand sides τ_α, $\mathbf{m}_\alpha$, and e_α represent the production terms related to the interactions between constituents. Due to the total conservation of mass, momentum, and energy of the mixture, the sum of production terms over all constituents must vanish,

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

For the sake of simplicity, we ignore in the following the possibility of chemical reactions ($\tau_\alpha=0$).

The mixture quantities ρ, $\mathbf{v}$, ε, $\mathbf{t}$, and $\mathbf{q}$ are defined as

$$\rho = \sum_{\alpha=1}^{n} \rho_\alpha, \quad \text{total mass density},$$

$$\mathbf{v} = \frac{1}{\rho}\sum_{\alpha=1}^{n} \rho_\alpha \mathbf{v}_\alpha, \quad \text{mixture velocity},$$

$$\varepsilon = \varepsilon_I + \frac{1}{2\rho}\sum_{\alpha=1}^{n} \rho_\alpha u_\alpha^2, \quad \text{internal energy},$$

$$\mathbf{t} = -p\mathbf{I} + \boldsymbol{\sigma}_I - \sum_{\alpha=1}^{n} (\rho_\alpha \mathbf{u}_\alpha \otimes \mathbf{u}_\alpha), \quad \text{stress tensor},$$

$$\mathbf{q} = \mathbf{q}_I + \sum_{\alpha=1}^{n} \rho_\alpha\left(\varepsilon_\alpha + \frac{p_\alpha}{\rho_\alpha} + \frac{1}{2}u_\alpha^2\right)\mathbf{u}_\alpha, \quad \text{flux of internal energy}, \tag{2}$$

where $\mathbf{u}_\alpha=\mathbf{v}_\alpha-\mathbf{v}$ is the diffusion velocity of the component α, $p=\Sigma_{\alpha=1}^{n}p_\alpha$ is the total pressure, $\varepsilon_I=(1/\rho)\Sigma_{\alpha=1}^{n}\rho_\alpha\varepsilon_\alpha$ is the total intrinsic internal energy, $\mathbf{q}_I=\Sigma_{\alpha=1}^{n}\mathbf{q}_\alpha$ is the total intrinsic heat flux, and $\boldsymbol{\sigma}_I=\Sigma_{\alpha=1}^{n}\boldsymbol{\sigma}_\alpha$ is the total intrinsic shear stress.

We obtain by summation of Eqs. (1)

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

$$\frac{\partial(\rho \mathbf{v})}{\partial t} + \operatorname{div}(\rho \mathbf{v} \otimes \mathbf{v} - \mathbf{t}) = 0,$$

$$\frac{\partial\left(\frac{1}{2}\rho v^2 + \rho\varepsilon\right)}{\partial t} + \operatorname{div}\left[\left(\frac{1}{2}\rho v^2 + \rho\varepsilon\right)\mathbf{v} - \mathbf{t}\mathbf{v} + \mathbf{q}\right] = 0, \quad (3)$$

which are the conservation laws of mass, momentum, and energy of the mixture. They are in the same form as for a single fluid.

In order to compare the balance equations of mixtures and single fluids, we write Eqs. (1) in the equivalent form

$$\frac{\partial \rho}{\partial t} + \operatorname{div}(\rho \mathbf{v}) = 0, \quad (4a)$$

$$\frac{\partial(\rho \mathbf{v})}{\partial t} + \operatorname{div}(\rho \mathbf{v} \otimes \mathbf{v} - \mathbf{t}) = 0, \quad (4b)$$

$$\frac{\partial\left(\frac{1}{2}\rho v^2 + \rho\varepsilon\right)}{\partial t} + \operatorname{div}\left[\left(\frac{1}{2}\rho v^2 + \rho\varepsilon\right)\mathbf{v} - \mathbf{t}\mathbf{v} + \mathbf{q}\right] = 0, \quad (4c)$$

$$\frac{\partial \rho_b}{\partial t} + \operatorname{div}(\rho_b \mathbf{v}_b) = 0, \quad (4d)$$

$$\frac{\partial(\rho_b \mathbf{v}_b)}{\partial t} + \operatorname{div}(\rho_b \mathbf{v}_b \otimes \mathbf{v}_b - \mathbf{t}_b) = \mathbf{m}_b, \quad (4e)$$

$$\frac{\partial\left(\frac{1}{2}\rho_b v_b^2 + \rho_b\varepsilon_b\right)}{\partial t} + \operatorname{div}\left[\left(\frac{1}{2}\rho_b v_b^2 + \rho_b\varepsilon_b\right)\mathbf{v}_b - \mathbf{t}_b\mathbf{v}_b + \mathbf{q}_b\right] = e_b \quad (b = 1, \ldots, n-1), \quad (4f)$$

where the index b runs from 0 to $n-1$. In this multitemperature (MT) model, used in particular in plasma physics [2], we have $5n$ independent field variables ρ_α, $\mathbf{v}_\alpha$, and T_α ($\alpha = 1, 2, \ldots, n$), where T_α is the temperature of constituent α. To close the system (4a)–(4f) of the field equations of the mixture process, we must write the constitutive equations for the quantities p_α, ε_α, $\mathbf{q}_\alpha$, and $\boldsymbol{\sigma}_\alpha$ ($\alpha=1,2,\ldots,n$), and $\mathbf{m}_b$ e_b ($b=1,\ldots,n-1$) in terms of the field variables ρ_α, $\mathbf{v}_\alpha$, and T_α ($\alpha=1,2,\ldots,n$).

II. COARSER THEORIES

Due to the difficulties in measuring the temperature of each component, a common practice among engineers and physicists is to consider only one temperature for the mixture. When we use a single temperature (ST), Eq. (4f) disappears and we get a unique global conservation of the total energy in the form (4c) (see, for example, [3]). In a recent paper, Ruggeri and Simić [4] discussed the mathematical difference between the ST and the MT models when the fluid components are Eulerian gases ($\mathbf{q}_\alpha = \mathbf{0}, \boldsymbol{\sigma}_\alpha = \mathbf{0}$). They proved that the differential system of the ST model is a *principal subsystem* [5] of the MT model, and for large times MT solutions converge to ST ones.

A further step of coarsening theory is the classical approach to mixtures, in which the independent field variables are the density, the mixture velocity, the individual temperature of the mixture and the concentrations of constituents. In that case system (4a)–(4f) reduces to the equations

$$\frac{d\rho}{dt} + \rho \operatorname{div} \mathbf{v} = 0, \quad (5a)$$

$$\rho \frac{d\mathbf{v}}{dt} - \operatorname{div} \ \mathbf{t} = 0, \quad (5b)$$

$$\rho \frac{d\varepsilon}{dt} - \mathbf{t} \operatorname{grad} \mathbf{v} + \operatorname{div} \mathbf{q} = 0, \quad (5c)$$

$$\rho \frac{dc_b}{dt} + \operatorname{div} \mathbf{J}_b = 0 \quad (b = 1, \ldots, n-1), \quad (5d)$$

where

$$\frac{d}{dt} = \frac{\partial}{\partial t} + \mathbf{v} \cdot \frac{\partial}{\partial \mathbf{x}}$$

represents the material derivative of the mixture motion,

$$c_\alpha = \frac{\rho_\alpha}{\rho} \quad \left(\sum_{\alpha=1}^{n} c_\alpha = 1\right) \quad (6)$$

are the components' concentrations, and

$$\mathbf{J}_\alpha = \rho_\alpha \mathbf{u}_\alpha = \rho_\alpha(\mathbf{v}_\alpha - \mathbf{v}) \quad \left(\sum_{\alpha=1}^{n} \mathbf{J}_\alpha = \mathbf{0}\right) \quad (7)$$

are the diffusion fluxes of the components.

In the classical approach the stress tensor—as in a single fluid—splits up into the pressure isotropic part and the viscosity stress tensor $\boldsymbol{\sigma}$ (for Stokesian fluids this is a deviatoric tensor)

$$\mathbf{t} = -p\mathbf{I} + \boldsymbol{\sigma}.$$

The system (5a)–(5d) determines the field variables ρ, T, $\mathbf{v}$, and c_b ($b=1,\ldots,n-1$). Consequently, we need constitutive relations for ε, $\boldsymbol{\sigma}$, $\mathbf{q}$, and $\mathbf{J}_b$ ($b=1,\ldots,n-1$).

We consider the pressure $p(\rho,T,c_b)$ and the internal energy $\varepsilon(\rho,T,c_b)$ as given by the equilibrium equations of state as they appear in the Gibbs equations for mixtures, viz.,

$$T\,dS = d\varepsilon - \frac{p}{\rho^2}d\rho - \sum_{b=1}^{n-1}(\mu_b - \mu_n)dc_b, \quad (8)$$

where $\mu_\alpha = \mu_\alpha(\rho,T,c_b)$, with $\alpha=1,\ldots,n$, denote the chemical potentials of the components at equilibrium, and S is the entropy density of the mixture. The entropy balance law is a consequence of Eq. (8) and system (5a)–(5d). By using arguments from the thermodynamics of irreversible processes (TIP) presented in [6] and [3], Chap. 5, we obtain the classical constitutive equations of mixtures

$$\boldsymbol{\sigma} = 2\nu \mathbf{D}^D, \tag{9a}$$

$$\mathbf{q} = L \ \text{grad}\left(\frac{1}{T}\right) + \sum_{b=1}^{n-1} L_b \ \text{grad}\left(\frac{\mu_b - \mu_n}{T}\right), \tag{9b}$$

$$\mathbf{J}_a = \widetilde{L}_a \ \text{grad}\left(\frac{1}{T}\right) - \sum_{b=1}^{n-1} L_{ab} \ \text{grad}\left(\frac{\mu_b - \mu_n}{T}\right) \tag{9c}$$

where $\mathbf{D}^D$ denotes the deviatoric part of the strain velocity tensor $\mathbf{D}=\frac{1}{2}[\boldsymbol{\nabla}\mathbf{v}+(\boldsymbol{\nabla}\mathbf{v})^T]$. The *phenomenological coefficients* L, L_b, $\widetilde{L}_a$, and L_{ab} $(a,b=1,\ldots,n-1)$ are the transport coefficients of heat conduction and diffusion.

Let us note that relation (9a) is the classical Navier-Stokes equation of a Newtonian (Stokesian and isotropic) fluid, while (9b) and (9c) are generalizations of the original phenomenological laws of Fourier and Fick, according to which the heat flux and the diffusion flux depend on the gradients of temperature and concentrations, respectively (but not on both). The TIP permits the temperature gradient to influence the diffusion fluxes and concentration gradients to influence the heat flux; both effects are indeed observed and they are called, respectively, the thermodiffusion and diffusion-thermal or Soret effects. Additionally, the Onsager conditions of symmetry yield the following symmetries of coefficients [7]

$$L_{ab} = L_{ba}, \quad \widetilde{L}_b = L_b \quad (a,b = 1, \ldots, n-1) \tag{10}$$

and the following inequalities must be satisfied:

$$\begin{bmatrix} L & L_b \\ \widetilde{L}_a & L_{ab} \end{bmatrix} \quad \text{is a positive definite form,}$$

$$\text{and} \quad \nu \geq 0, \tag{11}$$

so that the entropy inequality can be satisfied.

III. A CLASSICAL APPROACH TO MULTITEMPERATURE MIXTURES AND THE AVERAGE TEMPERATURE

To reveal the relation between the extended and classical models, a formal iterative scheme known as *Maxwellian iteration* is applied (see, e.g., [3]). In the case of the ST model the first iterates $\mathbf{J}_a^{(1)}$ are calculated from the right-hand sides of the balance law (4e) by using "zeroth" iterates—equilibrium values $\mathbf{J}_a^{(0)}=\mathbf{0}$ on the left-hand sides. The next step, second iterates $\mathbf{J}_a^{(2)}$ are obtained from the right-hand sides of the same equations by putting the first iterates $\mathbf{J}_a^{(1)}$ on their left-hand sides, and so on. If we apply the first Maxwellian iteration the Fick laws of diffusion flux (9c) are obtained. Roughly speaking, the Fick laws are obtained by neglecting the accelerations of the relative motions of the constituents, and the classical theory is an approximation of the ST model (see [3], Chap. 5).

In a recent paper, Ruggeri and Simić [8] considered the Maxwellian iteration of system (4a)–(4f) in the case of a binary mixture of Eulerian fluids; they obtained the Fick laws as a first-order term of the expansion of the component momentum equations. When each component has its own temperature, an additive constitutive equation comes from a limiting case of the constituent equation of energy in the form

$$\Theta = L_\theta(\gamma_1 - \gamma_2)\text{div } \mathbf{v}, \tag{12}$$

where L_θ is a positive phenomenological coefficient and

$$\Theta = T_2 - T_1.$$

Equation (12) is not obtained in classical theory. The aim of this paper is to find a variant form of classical approach to recover also equations like (12) in the general case of mixtures with n not necessarily Eulerian compressible fluids.

In the classical approach, the velocity field $\mathbf{v}$ corresponds to an average velocity with respect to the mass components. Thanks to the Fick laws, the diffusion fluxes $\mathbf{J}_\alpha=\rho_\alpha(\mathbf{v}_\alpha-\mathbf{v})$ determine the component velocities $\mathbf{v}_\alpha$. By analogy with the velocity fields a natural extension of the classical approach is to consider an average temperature T and $\Theta_\alpha=T_\alpha-T(\alpha=1,\ldots,n)$ as constitutive quantities; similarly with the diffusion velocity fluxes, we name Θ_α the *diffusion temperature fluxes*.

To define an average temperature T, Ruggeri and Simić assumed that the total intrinsic internal energy of the mixture [which coincides with the full internal energy for processes not so far from equilibrium; see (2)] is the same in the multitemperature case as in the ST model when the temperature is T [9]. Consequently, T is defined through the local implicit solution of the equation

$$\rho\varepsilon \equiv \sum_{\alpha=1}^{n} \rho_\alpha \varepsilon_\alpha(\rho_\alpha, T) = \sum_{\alpha=1}^{n} \rho_\alpha \varepsilon_\alpha(\rho_\alpha, T_\alpha). \tag{13}$$

This choice comes from the case of particular classes of solutions for perfect gases [9] and from the fact that the equation of energy governs the evolution of the common temperature T for the ST model. The consequences on the entropy of the mixture will confirm the physical grounds of Eq. (13).

Taking into account Eqs. (5a), (5d), and (13), Eq. (5c) of the energy of the mixture can be written as a differential equation for the average temperature T,

$$\rho\varepsilon_{,T}\frac{dT}{dt} = \rho^2\varepsilon_{,\rho} \text{ div } \mathbf{v} + \sum_{b=1}^{n-1} \varepsilon_{,c_b} \text{ div } \mathbf{J}_b + \mathbf{t} \text{ grad } \mathbf{v} - \text{div } \mathbf{q}, \tag{14}$$

where the comma denotes the partial derivative with respect to the subscript. As $\mathbf{J}_\alpha$ $(\alpha=1,\ldots,n)$ are associated with the difference between component and average velocities,

$$\Theta_\alpha = T_\alpha - T \quad (\alpha = 1, \ldots, n),$$

corresponding to the difference between component and average temperatures, are nonequilibrium thermodynamical variables. Near equilibrium, Eq. (13) can be expanded to the first order; then

$$\sum_{\alpha=1}^{n} \rho_\alpha c_V^{(\alpha)} \Theta_\alpha = 0 \Leftrightarrow T = \frac{\sum_{\alpha=1}^{n} \rho_\alpha c_V^{(\alpha)} T_\alpha}{\sum_{\alpha=1}^{n} \rho_\alpha c_V^{(\alpha)}}, \tag{15}$$

where

$$c_V^{(\alpha)} = \frac{\partial \varepsilon_\alpha}{\partial T_\alpha}(\rho_\alpha, T) \tag{16}$$

denotes the specific heat at constant volume for the constituent α at equilibrium. Consequently, Eq. (15) yields

$$\Theta_n = -\frac{1}{\rho_n c_V^{(n)}} \sum_{b=1}^{n-1} \rho_b c_V^{(b)} \Theta_b . \tag{17}$$

The definition of the total specific entropy S of the mixture is

$$\rho S = \sum_{\alpha=1}^{n} \rho_\alpha S_\alpha(\rho_\alpha, T_\alpha), \tag{18}$$

where $S_\alpha (\alpha=1, \ldots, n)$ are the specific entropies of the components. Let us note that the specific entropy S depends only on T and not on Θ_b $(b=1, \ldots, n-1)$. This property comes from the Gibbs relation of each constituent,

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

which implies

$$T_\alpha \frac{\partial S_\alpha}{\partial T_\alpha}(\rho_\alpha, T_\alpha) = \frac{\partial \varepsilon_\alpha}{\partial T_\alpha}(\rho_\alpha, T_\alpha). \tag{19}$$

The first-order expansion of Eq. (18) yields

$$\rho S = \sum_{\alpha=1}^{n} \left(\rho_\alpha S_\alpha(\rho_\alpha, T) + \rho_\alpha \frac{\partial S_\alpha}{\partial T_\alpha}(\rho_\alpha, T) \Theta_\alpha \right).$$

Equation (19) can be evaluated for $T_\alpha = T$; by using Eq. (15) we deduce

$$\sum_{\alpha=1}^{n} \rho_\alpha \frac{\partial S_\alpha}{\partial T_\alpha}(\rho_\alpha, T) \Theta_\alpha = 0$$

and consequently

$$\rho S = \sum_{\alpha=1}^{n} \rho_\alpha S_\alpha(\rho_\alpha, T). \tag{20}$$

The specific entropy S does not depend on Θ_b $(b=1, \ldots, n-1)$.

On the contrary, a first-order expansion of the total pressure of the mixture $p = \Sigma_{\alpha=1}^{n} p_\alpha(\rho_\alpha, T_\alpha)$ together with Eq. (17) yields

$$p = p_0 + \pi_\theta , \tag{21}$$

where

$$p_0 = \sum_{\alpha=1}^{n} p_\alpha(\rho_\alpha, T), \qquad \pi_\theta = \sum_{b=1}^{n-1} r_b \Theta_b , \tag{22}$$

and

$$r_b = \frac{1}{\rho_n c_V^{(n)}} \left(\rho_n c_V^{(n)} \frac{\partial p_b}{\partial T_b}(\rho_b, T) - \rho_b c_V^{(b)} \frac{\partial p_n}{\partial T_n}(\rho_n, T) \right) \quad (b = 1, \ldots, n-1). \tag{23}$$

Therefore, the total pressure p of the mixture is a sum of the equilibrium part p_0 depending on T and a dynamical pressure part (as a nonequilibrium term) π_θ due to the difference of temperatures between the constituents.

We emphasize that the fact that the entropy density depends only on T and not on Θ_a justifies—in the present theory—the consideration of Θ_a as constitutive quantities (undetermined quantities). This is a key point in the model. Consequently, the aim of the next section consists in determining the constitutive equations for the Θ_a by using the entropy principle and TIP arguments.

IV. ENTROPY PRINCIPLE AND CONSTITUTIVE EQUATIONS

We still assume that the internal energy $\varepsilon(\rho, T, c_b)$ and the equilibrium pressure $p_0(\rho, T, c_b)$ satisfy the Gibbs equation

$$T\, dS = d\varepsilon - \frac{p_0}{\rho^2} d\rho - \sum_{b=1}^{n-1} (\mu_b - \mu_n) dc_b . \tag{24}$$

The differences between Eq. (8) and Eq. (24) consist in the fact that in Eq. (24) T means the average temperature when each component α has its own temperature T_α and p_0 takes the place of p. At equilibrium, the component chemical potentials are

$$\mu_\alpha = \varepsilon_\alpha(\rho_\alpha, T) + \frac{p_\alpha(\rho_\alpha, T)}{\rho_\alpha} - T S_\alpha(\rho_\alpha, T).$$

As in the classical case with a single temperature, the time derivative can be eliminated between Eqs (5a), (5d), and (14). The second-order terms due to the diffusion velocities $\mathbf{u}_\alpha$ $(\alpha=1, \ldots, n)$ are neglected; because we consider a Stokesian fluid, the viscous stress tensor is deviatoric and we obtain the balance law in the form

$$\begin{aligned} \rho \frac{dS}{dt} + \operatorname{div}\left[\frac{1}{T}\left(\mathbf{q} - \sum_{b=1}^{n-1} (\mu_b - \mu_n) \mathbf{J}_b\right) \right] &= \mathbf{q} \cdot \operatorname{grad}\left(\frac{1}{T}\right) - \sum_{b=1}^{n-1} \mathbf{J}_b \cdot \operatorname{grad}\left(\frac{\mu_b - \mu_n}{T}\right) \\ &\quad + \frac{1}{T} \operatorname{tr}(\mathbf{J}_{\mathrm{mech}} \mathbf{D}), \end{aligned} \tag{25}$$

where the mechanical flux (for Stokesian fluids) is

$$\mathbf{J}_{\mathrm{mech}} = \boldsymbol{\sigma} - \pi_\theta \mathbf{I}. \tag{26}$$

Equation (25) can be interpreted as a balance of entropy, if we consider

$$\Phi = \frac{1}{T}\left(\mathbf{q} - \sum_{b=1}^{n-1} (\mu_b - \mu_n)\mathbf{J}_b\right)$$

and

$$\Sigma = \mathbf{q}\cdot \operatorname{grad}\left(\frac{1}{T}\right) - \sum_{b=1}^{n-1} \mathbf{J}_b \cdot \operatorname{grad}\left(\frac{\mu_b - \mu_n}{T}\right) + \frac{1}{T}\operatorname{tr}(\mathbf{J}_{\mathrm{mech}}\mathbf{D}) \tag{27}$$

as the entropy flux and the entropy production, respectively.

We observe that the entropy production is the sum of products of the following quantities:

thermodynamic fluxes	**thermodynamic forces**
heat flux $\mathbf{q}$	temperature gradient grad $\left(\frac{1}{T}\right)$,
diffusion fluxes $\mathbf{J}_b$	chemical potential gradients grad $\left(\frac{\mu_b - \mu_n}{T}\right)$,
mechanical flux $\mathbf{J}_{\mathrm{mech}}$	velocity gradient $\mathbf{D}$.

In accordance with the case of a single-temperature model [10,11] and [3], Chap. 5, in TIP near equilibrium, the fluxes depend linearly on the associated forces (see also for the general methodology of the TIP [6,7,12,13]): For the heat flux and the diffusion fluxes, we obtain the constitutive equations in the form of Eqs. (9b) and (9c); for Stokesian fluids, the last term of Eq. (27) corresponding to the mechanical production of entropy can be written in a separated form as

$$\frac{1}{T}\operatorname{tr}(\mathbf{J}_{\mathrm{mech}}\mathbf{D}) = \frac{1}{T}\operatorname{tr}(\boldsymbol{\sigma}\mathbf{D}^D) - \frac{1}{T}\pi_\theta \operatorname{div} \mathbf{v}.$$

We obtain the constitutive equation of the viscous stress tensor in the form of Eq. (9a) and the dynamical pressure part due to the difference of temperatures yields

$$\pi_\theta = \sum_{b=1}^{n-1} r_b \Theta_b = - L_\pi \operatorname{div} \mathbf{v}, \tag{28}$$

where L_π is a scalar coefficient of proportionality.

The production of entropy must be non-negative [14,15] and therefore the phenomenological coefficients must satisfy the inequalities (11) and

$$L_\pi \geq 0. \tag{29}$$

Taking into account that the terms r_b given by Eq. (23) depend on (ρ_b, T), from Eq. (28) we deduce that the constitutive quantities Θ_a (depending *a priori* on $\nabla \mathbf{v}$) must be proportional to div $\mathbf{v}$:

$$\Theta_a = k_a \operatorname{div} \mathbf{v} \quad (a = 1, \ldots, n-1).$$

Let $\|M_{ab}\|$ be the matrix such that $k_a = \Sigma_{b=1}^{n-1} M_{ab} r_b$, we have

$$\Theta_a = - \sum_{b=1}^{n-1} M_{ab} r_b \operatorname{div} \mathbf{v} \quad (a = 1, \ldots, n-1). \tag{30}$$

Introducing expression (30) into Eq. (28), we obtain

$$L_\pi = \sum_{a,b=1}^{n-1} M_{ab} r_a r_b \geq 0,$$

and assuming the Onsager symmetry property, $M_{ab} = M_{ba}$ $(a, b = 1, \ldots, n-1)$, we deduce that the coefficients M_{ab} are associated with a positive definite quadratic form. Finally, the results are the same as in classical theory, but in addition we get the constitutive equations (30) for the difference of temperatures.

We have considered the simple case of Stokes fluids. If the fluid is non-Stokesian, the Navier-Stokes stress tensor of viscosity is

$$\boldsymbol{\sigma} = \lambda(\operatorname{div} \mathbf{v})\mathbf{I} + 2\nu \mathbf{D}^D,$$

where λ is the bulk viscosity. The stress tensor $\mathbf{t}$ becomes

$$\mathbf{t} = -(p_0 + \pi_\theta)\mathbf{I} + \boldsymbol{\sigma} = -p\mathbf{I} + 2\nu \mathbf{D}^D,$$

with

$$p = p_0 + \pi_\theta + \pi_\sigma.$$

The nonequilibrium pressure $p - p_0$ is separated into two different parts. The first one $\pi_\sigma = -\lambda$ div $\mathbf{v}$ is related to the bulk viscosity and the second one $\pi_\theta = -L_\pi$ div $\mathbf{v}$ to the multitemperature effects between components.

For example, we consider the case of mixtures of perfect gases

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

where k and m_α are, respectively, the Boltzmann constant and the atomic mass of constituent α. From Eq. (23), we get

$$r_b = \rho_b c_V^{(b)} (\gamma_b - \gamma_n)$$

and consequently

$$\Theta_a = -\sum_{b=1}^{n-1} M_{ab}\rho_b c_V^{(b)}(\gamma_b - \gamma_n)\operatorname{div}\mathbf{v}. \tag{31}$$

The dynamical pressure is

$$\pi_\theta = -L_\pi \operatorname{div}\mathbf{v}$$

$$\text{with}\quad L_\pi = \sum_{a,b=1}^{n-1} M_{ab}\rho_a\rho_b c_V^{(a)} c_V^{(b)}(\gamma_a - \gamma_n)(\gamma_b - \gamma_n). \tag{32}$$

Let us note that Eq. (31) yields the result of Ruggeri and Simić [8] for binary mixtures:

$$\Theta = L_\theta(\gamma_1 - \gamma_2)\operatorname{div}\mathbf{v} \quad \text{with}\quad L_\theta = M_{11}\frac{\rho_1 c_V^{(1)}}{\rho_2 c_V^{(2)}}(\rho_1 c_V^{(1)} + \rho_2 c_V^{(2)}). \tag{33}$$

V. KINETIC VALUES OF THE PHENOMENOLOGICAL COEFFICIENTS

While the TIP yields only inequalities for the phenomenological coefficients, they can be determined by the fact that our approach is a limiting case of system (4a)–(4f) which is in agreement with kinetic theory. For high-temperature plasma physics [2], the phenomenological coefficients appear through the production terms $\mathbf{m}_b$ and e_b of Eq. (4a)–(4f) and have explicit expressions. Therefore, by using the Maxwellian iteration, we can evaluate coefficients L_{ab} and M_{ab}. For a binary mixture of Eulerian gases the calculus is done in [8] and [9] and we get

$$L_{11} = \tau_J \frac{\rho_1\rho_2}{\rho}T \quad \text{and}\quad L_\theta = \tau_\theta T, \tag{34}$$

where τ_J and τ_θ are, respectively, the relaxation times of the mechanical and the multitemperature diffusions,

$$\tau_J = \frac{1}{2\Gamma'_{12}}\frac{m_1+m_2}{m_1 m_2}\frac{\rho_1\rho_2}{\rho},$$

$$\tau_\theta = \frac{1}{3\Gamma'_{12}}\frac{(m_1+m_2)^2}{m_1 m_2}\frac{\rho_1\rho_2}{\rho_1 m_2(\gamma_2-1)+\rho_2 m_1(\gamma_1-1)}, \tag{35}$$

where Γ'_{12} is the number of collisions per unit of volume and time. The coefficient L_π of the dynamical pressure π_θ in Eq. (32) is directly obtained from the second part of Eq. (33) and Eqs. (34) and (35),

$$L_\pi = \frac{kT\rho_1^2\rho_2^2}{3\Gamma'_{12}m_1 m_2}\frac{(m_1+m_2)^2}{[\rho_1 m_2(\gamma_2-1)+\rho_2 m_1(\gamma_1-1)]^2}(\gamma_1-\gamma_2)^2.$$

This coefficient is null only if the two gases have the same γ_1 and γ_2 values.

The ratio of the two relaxation times is

$$\frac{\tau_\theta}{\tau_J} = \frac{2}{3}\frac{(m_1+m_2)\rho}{\rho_1 m_2(\gamma_2-1)+\rho_2 m_1(\gamma_1-1)}.$$

This ratio is always greater than 1. In fact, if we assume that $\gamma_1 \neq \gamma_2$ and denote by $\gamma_{\max} = \max(\gamma_1, \gamma_2)$, we get ($c = \rho_1/\rho$),

$$\frac{\tau_\theta}{\tau_J} > \frac{2}{3}\frac{(m_1+m_2)}{cm_2+(1-c)m_1}\frac{1}{(\gamma_{\max}-1)} > \frac{2}{3}\frac{1}{(\gamma_{\max}-1)} \geq 1$$

(the last inequality is because $\gamma_\alpha \leq 5/3$ for all ideal gases).

In contrast with the usual approach, in which we consider diffusion and neglect the difference of temperatures between constituents, the relaxation time of the multitemperature diffusion is always greater than the relaxation time of classical diffusion. From Eq. (34), we can see that if τ_θ is small enough, to obtain L_θ and L_{11} values close to unity, it is necessary to have a high temperature T. Consequently, in the high-temperature cases, the multitemperature diffusion terms cannot be neglected.

VI. CONCLUSION

In the case of fluid mixtures with different temperatures, a classical framework allows one to determine the constitutive equation (30) for the difference of temperatures in addition to the classical Navier-Stokes, Fourier, and Fick laws. The difference of the temperatures produces a dynamical pressure term, which has a physical meaning and consequently can be measured. We point out that the dynamical pressure associated with multitemperature fluid mixtures exists even if the bulk viscosity is null. For rarefied gases, it is well known that the bulk viscosity λ is null (Stokes fluids) and consequently no dynamical pressure exists in a classical mixture with one temperature; in a relativistic context, this pressure exists but remains very small [3]. Due to the nonzero dynamical pressure even for Stokes fluids, we conclude that multitemperature mixtures of fluids have great importance.

Perhaps such a model may be used to analyze the evolution of the early universe in which a dynamical pressure seems essential [16,17]. Of course, we have to take into account a relativistic framework and the chemical reactions. Nevertheless, the preliminary result—a dynamical pressure exists also in the nonrelativistic limit and without chemical reactions—shows promise and deserves attention for future work.

We focus attention on the fact that the present results are obtained thanks to an average temperature corresponding to the same internal energy as for the single-temperature model. It is important to note that the total energy conservation law yields the evolution of T, the entropy principle can be used because the entropy density S depends only on T, and the Gibbs equation is always defined by using Eq. (24). Finally, if we consider Eq. (14) for the field variables to be spatially homogeneous, T is constant, as we expect from a physical point of view (see Ref. [9]).

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