A simple thermodynamic framework for heat-conducting flows of mixtures of two interacting fluids

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Goal, co-authors and main references

- To develop a simple model for heat-conducting binary fluid mixtures described in the terms of the densities and the velocities for each fluid and the temperature field for the mixture as a whole.

J. Málek, **K. R. Rajagopal**: A thermodynamic framework for a mixture of two liquids. *Nonlinear Analysis: Real World Applications*, Vol. 9 (2008) 1649–1649.

O. Souček, V. Pruša, J. Málek, **K. R. Rajagopal**: On the natural structure of thermodynamic potentials and fluxes in the theory of chemically non-reacting binary mixtures. *Acta Mechanica*, Vol. 225 (2014) 3157–3186.

J. Málek, **O. Souček**: A simple thermodynamic framework for heat-conducting flows of mixtures of two interacting fluids (2021), prepared for submission.

- framework of the theory of interacting continua (theory of mixtures)
- simplicity: the response of the whole mixture determined from a small (minimal) set of material parameters
- simplicity: of a thermodynamic approach used in the derivation

A thermodynamic framework - single continuum

Balance equations of continuum thermomechanics

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

$$\frac{\partial (\rho \mathbf{v})}{\partial t} + \operatorname{div}(\rho \mathbf{v} \otimes \mathbf{v}) = \operatorname{div} \mathbb{T} + \rho \mathbf{f}$$

$$\frac{\partial (\rho E)}{\partial t} + \operatorname{div}(\rho E \mathbf{v}) = \operatorname{div}(\mathbb{T}\mathbf{v} - \mathbf{j}_e) + \rho \mathbf{f} \cdot \mathbf{v} \qquad E = \frac{1}{2}|\mathbf{v}|^2 + e$$

$$\frac{\partial (\rho \eta)}{\partial t} + \operatorname{div}(\rho \eta \mathbf{v}) = \operatorname{div} \mathbf{j}_\eta + \xi \quad \text{and} \quad \xi \geq 0$$

Constitutive relations

stress tensor $\mathbb{T}$, energy flux $\mathbf{j}_e$, entropy flux $\mathbf{j}_\eta$, entropy production ξ

can be determined from the knowledge of constitutive equations for

entropy	η	(e, ψ, H, G)
entropy production	ξ	

$$\psi = \widetilde{\psi}(\rho, \theta) \text{ with } \eta = -\frac{\partial \widetilde{\psi}}{\partial \theta} \text{ and } p := \rho^2 \frac{\partial \widetilde{\psi}}{\partial \rho} \qquad \psi := e - \theta\eta$$

$$\theta\xi = \mathbb{T}_\delta \cdot \mathbb{D}_\delta + (\frac{1}{3}\operatorname{tr}\mathbb{T} + p)\operatorname{div}\mathbf{v} + \mathbf{j}_\eta \cdot (-\nabla\theta) \tag{1}$$

$$\mathbb{T}_\delta = 2\nu\mathbb{D}_\delta \qquad \nu > 0$$

$$\frac{1}{3}\operatorname{tr}\mathbb{T} + p = \lambda \operatorname{div}\mathbf{v} \qquad \lambda > 0$$

$$\mathbf{j}_\eta = -\kappa\nabla\theta \qquad \kappa > 0$$

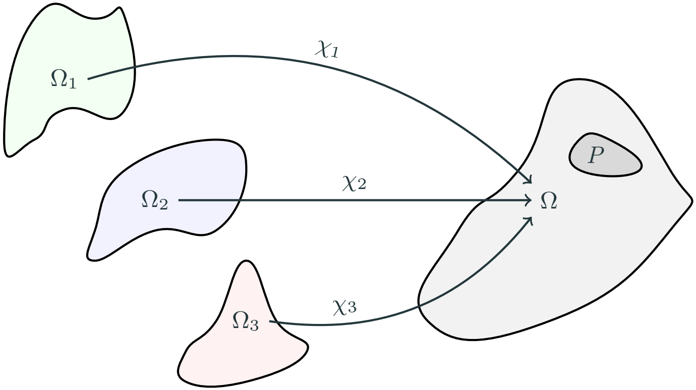
$$\theta\xi = 2\nu|\mathbb{D}_\delta|^2 + \lambda(\operatorname{div}\mathbf{v})^2 + \kappa|\nabla\theta|^2 =: \tilde{\zeta}(\mathbb{D}_\delta, \operatorname{div}\mathbf{v}, \nabla\theta)$$

Rajagopal, Srinivasa (2004): the same constitutive equations are achieved by a constrained maximization

$$\max_{(\mathbb{D}_\delta, \operatorname{div}\mathbf{v}, \nabla\theta)\in\mathcal{A}} \tilde{\zeta}(\mathbb{D}_\delta, \operatorname{div}\mathbf{v}, \nabla\theta) \quad \text{where} \quad \mathcal{A} := \{\mathbb{D}_\delta, \operatorname{div}\mathbf{v}, \nabla\theta; \tilde{\zeta} = \text{RHS}(1)\}$$

Easy to incorporate the incompressibility $\operatorname{div}\mathbf{v} = 0$

Co-existence of individual constituents



- $\mathcal{M}(P)$, $\mathcal{V}(P)$ - the total mass and the volume of P
- $\mathcal{M}_\alpha(P)$, $\mathcal{V}_\alpha(P)$ - the mass and the volume of the α-constituent in P

Theory of interacting continua - mass and volume densities

Natural requirements $\mathcal{M} \ll \mathcal{V}$, $\mathcal{M}_\alpha \ll \mathcal{V}$, $\mathcal{M}_\alpha \ll \mathcal{V}_\alpha$, $\mathcal{M}_\alpha \ll \mathcal{M}$, $\mathcal{V}_\alpha \ll \mathcal{V}$

- ρ density of the mixture as a whole
- ρ_α density of the α-constituent
- $\rho_\alpha^{\mathrm{tr}}$ true density of the α-constituent
- c_α mass fraction/concentration
- ϕ_α volume fraction

$$\mathcal{M}(P) = \int_P \rho \, d\mathcal{V} \quad \mathcal{M}_\alpha(P) = \int_P \rho_\alpha \, d\mathcal{V} \quad \mathcal{M}_\alpha(P) = \int_P \rho_\alpha^{\mathrm{tr}} \, d\mathcal{V}_\alpha$$

$$\mathcal{M}_\alpha(P) = \int_P c_\alpha \, d\mathcal{M} \quad \mathcal{V}_\alpha(P) = \int_P \phi_\alpha \, d\mathcal{V} \implies \boxed{\rho_\alpha = \rho c_\alpha} \quad \boxed{\rho_\alpha = \phi_\alpha \rho_\alpha^{\mathrm{tr}}}$$

In addition, if M_α denotes molar mass of the α-constituent, then

$$c_\alpha^{\mathsf{M}} := \frac{\rho_\alpha}{M_\alpha} \qquad c^{\mathsf{M}} := \sum_\alpha c_\alpha^{\mathsf{M}} \qquad x_\alpha := \frac{c_\alpha^{\mathsf{M}}}{c^{\mathsf{M}}}$$

- x_α molar fractions $\qquad \sum_\alpha c_\alpha = 1 \qquad \sum_\alpha x_\alpha = 1$

Mass and volume additivity constraints, whole-mixture velocities

Mass additivity constraint

$$\rho = \sum_\alpha \rho_\alpha \quad \Longrightarrow \quad 1 = \sum_\alpha c_\alpha$$

Molar mass additivity constraint

$$c^{\mathsf{M}} := \sum_\alpha c_\alpha^{\mathsf{M}} \quad \Longrightarrow \quad 1 = \sum_\alpha x_\alpha$$

Volume additivity constraint

$$\mathcal{V}(P) = \sum_\alpha \mathcal{V}_\alpha(P) \quad \Longrightarrow \quad 1 = \sum_\alpha \phi_\alpha$$

Velocities associated with the mixture as a whole

$$\mathbf{v} = \frac{1}{\rho} \sum_\alpha \rho_\alpha \mathbf{v}_\alpha = \sum_\alpha c_\alpha \mathbf{v}_\alpha$$
$$\mathbf{v}^{\mathsf{M}} = \sum_\alpha x_\alpha \mathbf{v}_\alpha$$
$$\mathbf{v}^{\phi} = \sum_\alpha \phi_\alpha \mathbf{v}_\alpha$$

Balance equations of the theory of interacting continua $\alpha = 1, \dots, N$

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

$$\frac{\partial (\rho_\alpha \mathbf{v}_\alpha)}{\partial t} + \operatorname{div}(\rho_\alpha \mathbf{v}_\alpha \otimes \mathbf{v}_\alpha) = \operatorname{div} \mathbb{T}_\alpha + \rho_\alpha \mathbf{f}_\alpha + m_\alpha \mathbf{v}_\alpha + \mathbf{I}_\alpha$$

$$\frac{\partial}{\partial t}\left(\sum_\alpha \rho_\alpha E_\alpha\right) + \operatorname{div}\left(\sum_\alpha \rho_\alpha E_\alpha \mathbf{v}_\alpha\right) = \operatorname{div}\left(\sum_\alpha \mathbb{T}_\alpha \mathbf{v}_\alpha - \mathbf{j}_e\right) + \sum_\alpha \rho_\alpha \mathbf{f}_\alpha \cdot \mathbf{v}_\alpha$$

$$\frac{\partial}{\partial t}\left(\sum_\alpha \rho_\alpha \eta_\alpha\right) + \operatorname{div}\left(\sum_\alpha \rho_\alpha \eta_\alpha \mathbf{v}_\alpha\right) = \operatorname{div} \mathbf{j}_\eta + \xi \quad \text{and} \quad \xi \geq 0$$

$$E_\alpha = \tfrac{1}{2}|\mathbf{v}_\alpha|^2 + e_\alpha$$

$$\sum_\alpha m_\alpha = 0 \qquad \sum_\alpha (m_\alpha \mathbf{v}_\alpha + \mathbf{I}_\alpha) = \mathbf{0}$$

How to determine the form of constitutive relations involving

stress tensors $\mathbb{T}_\alpha$, partial mass sources/gains m_α, interaction terms $\mathbf{I}_\alpha$

energy flux $\mathbf{j}_e$, entropy flux $\mathbf{j}_\eta$, entropy production ξ

Binary fluid mixtures - $N = 2$

Various forms of the whole-mixture velocity $\mathbf{v}^{\text{mixt}} := \omega \mathbf{v}_1 + (1-\omega)\mathbf{v}_2$

$$\mathbf{v} = c\mathbf{v}_1 + (1-c)\mathbf{v}_2 \qquad \omega = c := c_1$$

$$\mathbf{v}^{\mathsf{M}} = x\mathbf{v}_1 + (1-x)\mathbf{v}_2 \qquad \omega = x := x_1$$

$$\mathbf{v}^{\phi} = \phi\mathbf{v}_1 + (1-\phi)\mathbf{v}_2 \qquad \omega = \phi := \phi_1$$

In addition, we can include the constraint: all admissible processes associated with the whole-mixture are volume conserving

$$\operatorname{div} \mathbf{v}^{\text{mixt}} = 0$$

Material derivative associated with the mixture as the whole

$$\dot{\mathrm{z}} := \frac{\partial \mathrm{z}}{\partial t} + \mathbf{v}^{\text{mixt}} \cdot \nabla \mathrm{z}$$

Binary mixtures - constitutive assumptions

Helmholtz free energy

$$\rho\psi = \widehat{\rho\psi}(\theta, \rho_1, \rho_2) = \widehat{\rho_1\psi_1}(\theta, \rho_1, \rho_2) + \widehat{\rho_2\psi_2}(\theta, \rho_1, \rho_2)$$

$$\rho_\alpha\psi_\alpha := \rho_\alpha e_\alpha - \theta\rho_\alpha\eta_\alpha$$

$$\rho_\alpha\eta_\alpha := -\frac{\partial\widehat{\rho_\alpha\psi_\alpha}}{\partial\theta} \quad (\alpha = 1, 2)$$

$$\mu_\alpha := \frac{\partial\widehat{\rho\psi}}{\partial\rho_\alpha} \quad (\alpha = 1, 2) \qquad \mu := \mu_1 - \mu_2$$

$$p := -\rho e + \theta\rho\eta + \sum_\alpha \rho_\alpha\mu_\alpha \qquad \rho e = \rho_1 e_1 + \rho_2 e_2, \quad \rho\eta = \rho_1\eta_1 + \rho_2\eta_2$$

Entropy production

$$\begin{aligned}\theta\xi &= \widetilde{\zeta}(\mathbb{D}_\delta^{\mathrm{mixt}}, \operatorname{div}\mathbf{v}^{\mathrm{mixt}}, \nabla\theta, \mu, \mathbf{v}_1 - \mathbf{v}_2)\\ &= 2\nu|\mathbb{D}_\delta^{\mathrm{mixt}}|^2 + \lambda(\operatorname{div}\mathbf{v}^{\mathrm{mixt}})^2 + \kappa|\nabla\theta|^2 + \beta\mu^2 + \alpha|\mathbf{v}_1 - \mathbf{v}_2|^2\end{aligned}$$

$$\mathbb{D}^{\mathrm{mixt}} = \frac{1}{2}\Big((\nabla\mathbf{v}^{\mathrm{mixt}}) + (\nabla\mathbf{v}^{\mathrm{mixt}})^T\Big)$$

Application of the constrained maximization:

$$\max_{\mathbb{D}_\delta(\mathbf{v}_1),\operatorname{div}\mathbf{v}_1,\mathbb{D}_\delta(\mathbf{v}_2),\operatorname{div}\mathbf{v}_2,\nabla\theta,\mu,\mathbf{v}_1-\mathbf{v}_2\in\mathcal{A}} \tilde{\zeta}(\mathbb{D}_\delta(\mathbf{v}^{\text{mixt}}),\operatorname{div}\mathbf{v}^{\text{mixt}},\nabla\theta,\mu,\mathbf{v}_1-\mathbf{v}_2)$$

where

$$\mathcal{A} := \{\mathbb{D}_\delta(\mathbf{v}_1),\operatorname{div}\mathbf{v}_1,\mathbb{D}_\delta(\mathbf{v}_2),\operatorname{div}\mathbf{v}_2,\nabla\theta,\mu,\mathbf{v}_1-\mathbf{v}_2;\tilde{\zeta}=\text{RHS }\textbf{(???)}\}$$

To achieve **(???)**

- start with the constitutive equation for $\rho\psi$
- apply material derivative associated with $\mathbf{v}^{\text{mixt}}$
- use the balance equations governing flows of a binary mixture

(???) takes the form

$$\zeta = \left(\frac{1}{3}\operatorname{tr}\mathbb{T}_1 - \gamma E_{12}^{\text{mixt}} + \omega p\right)\operatorname{div}\mathbf{v}_1 + \left(\frac{1}{3}\operatorname{tr}\mathbb{T}_2 + \gamma E_{12}^{\text{mixt}} + (1-\omega)p\right)\operatorname{div}\mathbf{v}_2 - \mu m$$
$$+ (\mathbb{T}_1)_\delta : \mathbb{D}_\delta(\mathbf{v}_1) + (\mathbb{T}_2)_\delta : \mathbb{D}_\delta(\mathbf{v}_2) - \frac{\mathbf{j}_e + \left((1-\gamma)E_{12}^{\text{mixt}} - \boldsymbol{\mu}_{12}^{\text{mixt}}\right)(\mathbf{v}_1 - \mathbf{v}_2)}{\theta}\cdot\nabla\theta$$
$$- \left(\mathbf{I} + \frac{m}{2}(\mathbf{v}_1 - \mathbf{v}_2) + \nabla(\gamma E_{12}^{\text{mixt}}) - p\nabla\omega + \boldsymbol{\mu}_{12}^{\text{mixt}}\right)\cdot(\mathbf{v}_1 - \mathbf{v}_2)$$

where $E_{12}^{\text{mixt}} := (1-\omega)\rho_1 e_1 - \omega\rho_2 e_2$ $\quad$ $\boldsymbol{\mu}_{12}^{\text{mixt}} := (1-\omega)\rho_1\nabla\mu_1 - \omega\rho_2\nabla\mu_2$

Maximization procedure results at

$$\mathbb{T}_1 = \gamma E_{12}^{\text{mixt}}\mathbb{I} + \omega\left(-p\mathbb{I} + \lambda\operatorname{div}\mathbf{v}^{\text{mixt}}\mathbb{I} + 2\nu\mathbb{D}(\mathbf{v}^{\text{mixt}})\right)$$
$$\mathbb{T}_2 = -\gamma E_{12}^{\text{mixt}}\mathbb{I} + (1-\omega)\left(-p\mathbb{I} + \lambda\operatorname{div}\mathbf{v}^{\text{mixt}}\mathbb{I} + 2\nu\mathbb{D}(\mathbf{v}^{\text{mixt}})\right)$$
$$\mathbf{j}_e = -\kappa\nabla\theta - \left((1-\gamma)E_{12}^{\text{mixt}} - \boldsymbol{\mu}_{12}^{\text{mixt}}\right)(\mathbf{v}_1 - \mathbf{v}_2)$$
$$m = -\beta\mu$$
$$\mathbf{I} = -\nabla\omega\left(-p\mathbb{I} + 2\nu\mathbb{D}(\mathbf{v}^{\text{mixt}}) + \lambda\operatorname{div}\mathbf{v}^{\text{mixt}}\mathbb{I}\right) - \nabla(\gamma E_{12}^{\text{mixt}}) - \boldsymbol{\mu}_{12}^{\text{mixt}}$$
$$- \left(\alpha + \frac{m}{2}\right)(\mathbf{v}_1 - \mathbf{v}_2)$$

Binary mixtures - Final set of governing equations

$$\frac{\partial \rho_1}{\partial t} + \operatorname{div}(\rho_1 \mathbf{v}_1) = -\beta\mu \qquad \mu(\theta, \rho_1, \rho_2) = \mu_1 - \mu_2$$

$$\frac{\partial \rho_2}{\partial t} + \operatorname{div}(\rho_2 \mathbf{v}_2) = \beta\mu$$

$$\begin{aligned}
\frac{\partial \rho_1 \mathbf{v}_1}{\partial t} + \operatorname{div}(\rho_1 \mathbf{v}_1 \otimes \mathbf{v}_1) &= \omega\Big(-\nabla p + 2\nu \operatorname{div} \mathbb{D}(\mathbf{v}^{\mathsf{mixt}}) + \lambda \nabla \operatorname{div} \mathbf{v}^{\mathsf{mixt}}\Big) \\
&\quad + \rho_1 \mathbf{f}_1 - \boldsymbol{\mu}_{12}^{\mathsf{mixt}} - \big(\alpha + \tfrac{\beta\mu}{2}\big)(\mathbf{v}_1 - \mathbf{v}_2) - \beta\mu\mathbf{v}_1
\end{aligned}$$

$$\begin{aligned}
\frac{\partial \rho_2 \mathbf{v}_2}{\partial t} + \operatorname{div}(\rho_2 \mathbf{v}_2 \otimes \mathbf{v}_2) &= (1-\omega)\Big(-\nabla p + \operatorname{div} \mathbb{D}(\mathbf{v}^{\mathsf{mixt}}) + \lambda \nabla \operatorname{div} \mathbf{v}^{\mathsf{mixt}}\Big) \\
&\quad + \rho_2 \mathbf{f}_2 + \boldsymbol{\mu}_{12}^{\mathsf{mixt}} + \big(\alpha - \tfrac{\beta\mu}{2}\big)(\mathbf{v}_1 - \mathbf{v}_2) + \beta\mu\mathbf{v}_2
\end{aligned}$$

$$\begin{aligned}
\frac{\partial \rho e}{\partial t} + \operatorname{div}\Big((\rho e + p)\mathbf{v}^{\mathsf{mixt}}\Big) &= \operatorname{div}(\kappa \nabla \theta) - \sum_{\alpha=1}^{2} \mu_\alpha \operatorname{div}(\rho_\alpha(\mathbf{v}_\alpha - \mathbf{v}^{\mathsf{mixt}})) \\
&\quad + \lambda(\operatorname{div} \mathbf{v}^{\mathsf{mixt}})^2 + 2\nu|\mathbb{D}(\mathbf{v}^{\mathsf{mixt}})|^2 + \alpha|\mathbf{v}_1 - \mathbf{v}_2^{\mathsf{mixt}}|^2
\end{aligned}$$

$$\rho e = \widehat{\rho\psi}(\theta, \rho_1, \rho_2) - \theta \frac{\partial \widehat{\rho\psi}}{\partial \theta}(\theta, \rho_1, \rho_2)$$

Conclusions

- We presented a thermodynamic approach to develop the simplest models for binary fluid mixtures. The simplicity concerns the number of material moduli needed towards the derivation. For comparison, see the formulas for models that come out from the rational thermodynamics:

$$\mathbb{T}_1 = (-\rho_1 + \lambda_1 \operatorname{div} \mathbf{v}_1 + \lambda_2 \operatorname{div} \mathbf{v}_2)\mathbb{I} + 2\mu_1 \mathbb{D}(\mathbf{v}_1) + 2\mu_2 \mathbb{D}(\mathbf{v}_2) + \lambda_5 \mathbb{V}_{12}$$

$$\mathbb{T}_2 = (-\rho_2 + \lambda_3 \operatorname{div} \mathbf{v}_1 + \lambda_4 \operatorname{div} \mathbf{v}_2)\mathbb{I} + 2\mu_3 \mathbb{D}(\mathbf{v}_1) + 2\mu_4 \mathbb{D}(\mathbf{v}_2) - \lambda_5 \mathbb{V}_{12}$$

$$\boxed{\mu_1, \mu_2, \mu_3, \mu_4, \lambda_1, \lambda_2, \lambda_3, \lambda_4, \lambda_5} \qquad \mathbb{V}_{12} := \frac{\nabla \mathbf{v}_1 - (\nabla \mathbf{v}_1)^T}{2} - \frac{\nabla \mathbf{v}_2 - (\nabla \mathbf{v}_2)^T}{2}$$

- We removed deficiences of Málek and Rajagopal (2008).
  - different functions $\rho_\alpha \psi_\alpha$ for constituents
  - thermal effects included
  - in equillibrium the mixture of ideal gases was not covered. This brought us to incorporate various forms of the whole-mixture velocities.
- We derived the equations for non-dissipative binary fluid mixtures as well
- We also derived the models with an additional constraint $\operatorname{div} \mathbf{v}^{\text{mixt}} = 0$
- We also derived the boundary conditions for balance of linear momenta of each fluid from the boundary conditions formulated for the mixture as a whole.

Boundary condition: from mixtures to individual fluids

$$\boxed{\mathbf{v}^{\text{mixt}} \cdot \mathbf{n} = 0} \quad \text{and} \quad \boxed{(-\mathbb{T}\mathbf{n})_\tau = a\mathbf{v}_\tau^{\text{mixt}}} \qquad (a > 0)$$

Since $\mathbf{v}_1 \cdot \mathbf{n} = \mathbf{v}_2 \cdot \mathbf{n} = 0$ and

$$\mathbb{T} = \mathbb{T}_1 + \mathbb{T}_2 - \sum_{\alpha=1}^{2} \rho_\alpha (\mathbf{v} - \mathbf{v}_\alpha) \otimes (\mathbf{v} - \mathbf{v}_\alpha)$$

$$\text{where } \mathbb{T}_1 + \mathbb{T}_2 = -p\mathbb{I} + \lambda \operatorname{div} \mathbf{v}^{\text{mixt}} \mathbb{I} + 2\nu \mathbb{D}(\mathbf{v}^{\text{mixt}})$$

one gets

$$(-\mathbb{T}\mathbf{n})_\tau = \left((\mathbb{T}_1 + \mathbb{T}_2)\mathbf{n}\right)_\tau = 2\nu(\mathbb{D}(\mathbf{v}^{\text{mixt}})\mathbf{n})_\tau = \begin{cases} \frac{1}{\omega}(\mathbb{T}_1\mathbf{n})_\tau \\ \\ \frac{1}{(1-\omega)}(\mathbb{T}_2\mathbf{n})_\tau \end{cases}$$

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