

THERMODYNAMICAL ANALYSIS OF KORTEWEG FLUIDS

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NON-EQUILIBRIUM THERMODYNAMICS, CONTINUUM PHYSICS AND APPLIED PERSPECTIVES

Accademia Peloritana dei Pericolanti

Messina, June 23–24, 2022

Field equations

Let \mathcal{B} be a fluid occupying a compact and simply connected region \mathcal{C} of a Euclidean point space E^3 ; at a continuum level, its evolution is ruled by the field equations (neglecting body forces and heat sources):

$$\mathcal{E}^{(1)} \equiv \frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{v}) = 0,$$

$$\mathcal{E}^{(2)} \equiv \rho \left(\frac{\partial \mathbf{v}}{\partial t} + (\mathbf{v} \cdot \nabla) \mathbf{v} \right) - \nabla \cdot \mathbf{T} = 0,$$

$$\mathcal{E}^{(3)} \equiv \rho \left(\frac{\partial \varepsilon}{\partial t} + \mathbf{v} \cdot \nabla \varepsilon \right) - \mathbf{T} \cdot \nabla \mathbf{v} + \nabla \cdot \mathbf{q} = 0,$$

where ρ is the **mass density**, $\mathbf{v} \equiv (v_1, v_2, v_3)$ the **velocity**, ε the **internal energy per unit mass**, \mathbf{T} the symmetric **Cauchy stress tensor**, and \mathbf{q} the **heat flux**.

This system is **underdetermined** and must be closed by **constitutive equations** for \mathbf{T} and \mathbf{q} in such a way the local entropy production

$$\sigma_s = \rho \left(\frac{\partial s}{\partial t} + \mathbf{v} \cdot \nabla s \right) + \nabla \cdot \mathbf{J} \geq 0$$

along any admissible thermodynamic process, s being the **specific entropy**, and \mathbf{J} the **entropy flux**.

Remark

Also s and $J = (J_1, J_2, J_3)$ need to be considered as constitutive quantities.

The second law of thermodynamics requires the entropy inequality be satisfied for all admissible thermodynamical processes, and this requirement restricts the form of the constitutive equations, that may be **local** or **nonlocal**!

Local vs. nonlocal constitutive equations

A constitutive theory requires to fix the state space, *i.e.*, the set of variables the constitutive relations depend on. These are the basic fields, in the case of local constitutive theories, or the basic fields together with some of their gradients, in the case of nonlocal constitutive theories.

The constitutive equations have to satisfy some universal principles (invariance with respect to rigid motions, time translation, scale changes of fundamental quantities, Galilei or Lorentz transformations, etc.). Furthermore, general representation theorems for isotropic scalar, vectorial or tensorial constitutive equations have to be taken into account.

Exploitation of entropy-like inequality

The restrictions imposed by the second law of thermodynamics

$$\rho \left(\frac{\partial s}{\partial t} + \mathbf{v} \cdot \nabla s \right) + \nabla \cdot \mathbf{J} \geq 0$$

on constitutive equations are derived through the following steps:

- ① expand the derivatives;
- ② evaluate the result on the equations; this can be done in two ways:
 - eliminate, by using the balance equations, some derivatives [Coleman^a, Noll, 1963];
 - take into account the balance equations by means of some Lagrange multipliers [Liu^b, 1972];
- ③ obtain the conditions compatible with second law of thermodynamics.

^aB. D. Coleman and W. Noll, *The thermodynamics of elastic materials with heat conduction and viscosity*, Arch. Ration. Mech. Anal. **13**, 167–178, 1963.

^bI–Shih Liu, *Method of Lagrange multipliers for exploitation of the entropy principle*, Arch. Ration. Mech. Anal. **46**, 131–148, 1972.

Extended Liu procedure

Mathematical overview

If we have nonlocal constitutive laws, mathematics imposes us to use in the entropy inequality as constraints the field equations and their gradient extensions up to the order of the state space variables. In fact, the thermodynamic processes are solutions of the field equations, and, if these solutions are smooth enough, are trivially solutions of their differential consequences.

Algorithm [Cimmelli¹, 2007]

- ① Associate to each field equation and spatial gradient extension a Lagrange multiplier;
- ② Subtract from the Clausius-Duhem inequality the sum of the products of Lagrange multipliers times the corresponding equations.

Expanding derivatives, we may distinguish:

- **highest derivatives**: time derivatives of the field and state space variables, and spatial derivatives with highest order;
- **higher derivatives**: spatial derivatives whose order is not maximal but higher than that of the gradients entering the state space.

Highest and higher derivatives can be freely varied, whereas their coefficients cannot be arbitrary!

V. A. Cimmelli, *An extension of Liu procedure in weakly nonlocal thermodynamics*, J. Math. Phys. **48**, 113510, 2007.

Korteweg fluids

Korteweg², 1901

Korteweg introduced a constitutive relation for the stress tensor \mathbf{T} involving, in its elastic part, the first and second order gradients of the mass density, in order to describe the cohesive forces due to long-range interactions:

$$\mathbf{T} = (-p + \alpha_1 \Delta \rho + \alpha_2 |\nabla \rho|^2) \mathbf{I} + \alpha_3 \nabla \rho \otimes \nabla \rho + \alpha_4 \nabla \nabla \rho,$$

where p is the pressure, ρ the mass density, \mathbf{I} the identity matrix and α_i ($i = 1, \dots, 4$) are material coefficients depending on ρ .

²D. J. Korteweg, *Sur la forme qui prennent les équations du mouvement des fluides si l'on tient compte des forces capillaires par des variations de densité considérables mais continues et sur la théorie de la capillarité dans l'hypothèse d'une variation continue de la densité*, Archives Néerlandaises des sciences exactes et naturelles **6** Ser. II, 1–24, 1901.

Korteweg fluids

Dunn³, Serrin, 1985

Dunn and Serrin observed that such constitutive equations are, in general, incompatible with the restrictions placed by second law and postulated the existence of an additional rate of supply of mechanical energy (the **interstitial working**):

$$\rho \left(\frac{\partial \varepsilon}{\partial t} + \mathbf{v} \cdot \nabla \varepsilon \right) - \mathbf{T} \cdot \nabla \mathbf{v} + \nabla \cdot \mathbf{q} - \nabla \cdot \mathbf{u} = 0,$$

where \mathbf{u} is the interstitial work flux.

Another possibility is to generalize the entropy inequality as follows,

$$\rho \left(\frac{\partial s}{\partial t} + \mathbf{v} \cdot \nabla s \right) + \nabla \cdot \left(\frac{\mathbf{q}}{\theta} + \mathbf{k} \right) \geq 0,$$

with s as the specific entropy and \mathbf{k} as the difference between the total entropy flux \mathbf{J} and that postulated in rational thermodynamics.

³J. E. Dunn and J. Serrin, *On the thermomechanics of the interstitial working*, Arch. Rat. Mech. Anal. **88**, 95–133, 1985.

Korteweg fluids and extended Liu procedure: contributions

- [1] V. A. Cimmelli, A. Sellitto and V. Triani, *A new thermodynamic framework for second-grade Korteweg-type viscous fluids*, J. Math. Phys. **50**, 053101, 2009.
- [2] V. A. Cimmelli, A. Sellitto and V. Triani, *A new perspective on the form of the first and second laws in rational thermodynamics: Korteweg fluids as an example*, J. Non-Equilib. Thermodyn. **35**, 251–265, 2010.
- [3] V. A. Cimmelli, F. Oliveri and A. R. Pace, *On the thermodynamics of Korteweg fluids with heat conduction and viscosity*, J. Elast. **104**, 115–131, 2011.
- [4] M. Gorgone, F. Oliveri and P. Rogolino, *Continua with non-local constitutive laws: Exploitation of entropy inequality*, Int. J. Non-Linear Mech. **126**, 103573, 2020.
- [5] V. A. Cimmelli, M. Gorgone, F. Oliveri and A. R. Pace, *Weakly nonlocal thermodynamics of binary mixtures of Korteweg fluids with two velocities and two temperatures*, European J. Mechanics B/Fluids **83**, 58–65, 2020.
- [6] M. Gorgone and P. Rogolino, *On the characterization of constitutive equations for third-grade viscous Korteweg fluids*, Phys. Fluids **33**, 043107, 2021.
- [7] M. Gorgone, F. Oliveri and P. Rogolino, *Thermodynamical analysis and constitutive equations for a mixture of viscous Korteweg fluids*, Phys. Fluids **33**, 093102, 2021.
- [8] M. Gorgone and P. Rogolino, *A thermodynamical description of third grade fluid mixtures*, J. Non-Equilib. Thermodyn. **47**, 133–142, 2022.

Exploitation of entropy inequality for a viscous Korteweg fluid⁴

Field equations:

$$\begin{cases} \mathcal{E}^{(1)} \equiv \frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{v}) = 0, \\ \mathcal{E}^{(2)} \equiv \rho \left(\frac{\partial \mathbf{v}}{\partial t} + (\mathbf{v} \cdot \nabla) \mathbf{v} \right) - \nabla \cdot \mathbb{T} = 0, \\ \mathcal{E}^{(3)} \equiv \rho \left(\frac{\partial \varepsilon}{\partial t} + \mathbf{v} \cdot \nabla \varepsilon \right) - \mathbb{T} \cdot \nabla \mathbf{v} + \nabla \cdot \mathbf{q} = 0. \end{cases}$$

Let us assume the state space spanned by

$$\mathcal{Z} \equiv \{\rho, \varepsilon, \nabla \rho, \mathbb{L}, \nabla \varepsilon, \nabla \nabla \rho\},$$

where $\mathbb{L} = \text{sym}(\nabla \mathbf{v})$.

In order to characterize the form of the constitutive equations by the extended Liu procedure, let us introduce some Lagrange multipliers, depending on the state space variables; thus, the entropy inequality reads

$$\begin{aligned} & \rho \left(\frac{\partial s}{\partial t} + \mathbf{v} \cdot \nabla s \right) + \nabla \cdot \mathbf{J} - \lambda^{(1)} \mathcal{E}^{(1)} - \lambda^{(2)} \cdot \mathcal{E}^{(2)} - \lambda^{(3)} \mathcal{E}^{(3)} \\ & - \Lambda^{(1)} \cdot \nabla \mathcal{E}^{(1)} - \Lambda^{(2)} \cdot \nabla \mathcal{E}^{(2)} - \Lambda^{(3)} \cdot \nabla \mathcal{E}^{(3)} - \Theta^{(1)} \cdot \nabla \nabla \mathcal{E}^{(1)} \geq 0. \end{aligned}$$

⁴M. Gorgone and P. Rogolino, *On the characterization of constitutive equations for third-grade viscous Korteweg fluids*, Phys. Fluids **33**, 043107, 2021.

Exploitation of entropy inequality

By expanding derivatives with the chain rule (the long computations are done using some routines written in the Computer Algebra System Reduce⁵), the entropy inequality can be written as

$$\begin{aligned}
 & \left(\rho \frac{\partial s}{\partial \rho} - \lambda^{(1)} \right) \rho_{,t} - \left(\rho_{,k} \Lambda_{ik}^{(2)} + \rho \lambda_i^{(2)} \right) v_{i,t} + \left(\rho \frac{\partial s}{\partial \varepsilon} - \rho_{,k} \Lambda_k^{(3)} - \rho \lambda^{(3)} \right) \varepsilon_{,t} \\
 & + \left(\rho \frac{\partial s}{\partial \rho_{,k}} - \Lambda_k^{(1)} \right) \rho_{,kt} + \left(\rho \frac{\partial s}{\partial v_{i,k}} - \rho \Lambda_{ik}^{(2)} \right) v_{i,kt} + \left(\rho \frac{\partial s}{\partial \varepsilon_{,k}} - \rho \Lambda_k^{(3)} \right) \varepsilon_{,kt} \\
 & + \left(\rho \frac{\partial s}{\partial \rho_{,ik}} - \Theta_{ik}^{(1)} \right) \rho_{,ikt} + \left(\Lambda_{ik}^{(2)} \frac{\partial T_{ij}}{\partial v_{n,m}} - \Lambda_k^{(3)} \frac{\partial q_j}{\partial v_{n,m}} - \rho \Theta_{km}^{(1)} \delta_{jn} \right) v_{n,jkm} \\
 & + \left(\Lambda_{ik}^{(2)} \frac{\partial T_{ij}}{\partial \varepsilon_{,m}} - \Lambda_k^{(3)} \frac{\partial q_j}{\partial \varepsilon_{,m}} \right) \varepsilon_{,jkm} + \left(\Lambda_{ik}^{(2)} \frac{\partial T_{ij}}{\partial \rho_{,mn}} - \Lambda_k^{(3)} \frac{\partial q_j}{\partial \rho_{,mn}} \right) \rho_{,jkmn} \\
 & + f(\rho, v_i, \varepsilon, \rho_{,i}, v_{i,j}, \varepsilon_{,i}, \rho_{,ij}, v_{i,jk}, \varepsilon_{,ij}, \rho_{,ijk}) \geq 0,
 \end{aligned}$$

where the subscripts $_{,t}$ and $_{,j}$ denote partial derivatives, and the expression of the function f is omitted, because of its length.

⁵A. C. Hearn, *REDUCE user's manual, version 3.8*. (Technical report, Rand Corporation, Santa Monica, CA, USA, 1995)

Exploitation of entropy inequality

By identifying

$$X \equiv \{ \rho_{,t}, v_{i,t}, \varepsilon_{,t}, \rho_{,it}, v_{i,jt}, \varepsilon_{,it}, \rho_{,ijt}, v_{i,jkl}, \varepsilon_{,ijk}, \rho_{,ijkl} \},$$

$$Y \equiv \{ v_{i,jk}, \varepsilon_{,ij}, \rho_{,ijk} \},$$

highest derivatives,

higher derivatives,

the entropy inequality can be written in compact form as

$$A \cdot X + Y^T B Y + C \cdot Y + D \geq 0,$$

where A and C are vectors, B is a symmetric matrix, D is a scalar.

A , B , C , D depend at most on field and state space variables.

Exploitation of entropy inequality

Sufficient conditions⁶

Since in principle nothing prevents the possibility of a thermodynamical process where $D = 0$, the entropy inequality

$$A \cdot X + Y^T B Y + C \cdot Y + D \geq 0$$

is satisfied for every thermodynamical process if the following conditions hold:

- A and C are vanishing vectors;
- B is a positive semidefinite symmetric matrix;
- $D \geq 0$.

V. A. Cimmelli, F. Oliveri, and V. Triani, *Exploitation of the entropy principle: Proof of Liu theorem if the gradients of the governing equations are considered as constraints*, J. Math. Phys. **52**, 023511, 2011.

Remark

From these conditions, we are able to determine the Lagrange multipliers but the remaining derived set of thermodynamical restrictions on the specific entropy, Cauchy stress tensor and heat flux are still too much general for being useful in concrete applications; therefore, a further simplification is necessary.

Exploitation of entropy inequality

Lagrange multipliers

From $A = 0$:

$$\begin{aligned}\lambda^{(1)} &= \rho \frac{\partial s}{\partial \rho}, & \lambda_i^{(2)} &= -\frac{\rho_{,k}}{\rho} \frac{\partial s}{\partial v_{i,k}}, & \lambda^{(3)} &= \frac{\partial s}{\partial \varepsilon} - \frac{\rho_{,k}}{\rho} \frac{\partial s}{\partial \varepsilon_{,k}}, \\ \Lambda_k^{(1)} &= \rho \frac{\partial s}{\partial \rho_{,k}}, & \Lambda_{ik}^{(2)} &= \frac{\partial s}{\partial v_{i,k}}, & \Lambda_k^{(3)} &= \frac{\partial s}{\partial \varepsilon_{,k}}, & \Theta_{ik}^{(1)} &= \rho \frac{\partial s}{\partial \rho_{,ik}}.\end{aligned}$$

Other thermodynamic restrictions from highest derivatives

$$\begin{aligned}\left\langle \frac{\partial s}{\partial v_{i,k}} \frac{\partial T_{ij}}{\partial v_{n,m}} \right\rangle_{(jkm)} &= \left\langle \frac{\partial s}{\partial \varepsilon_{,k}} \frac{\partial q_j}{\partial v_{n,m}} + \rho^2 \frac{\partial s}{\partial \rho_{,km}} \delta_{jn} \right\rangle_{(jkm)}, \\ \left\langle \frac{\partial s}{\partial v_{i,k}} \frac{\partial T_{ij}}{\partial \varepsilon_{,m}} \right\rangle_{(jkm)} &= \left\langle \frac{\partial s}{\partial \varepsilon_{,k}} \frac{\partial q_j}{\partial \varepsilon_{,m}} \right\rangle_{(jkm)}, \\ \left\langle \frac{\partial s}{\partial v_{i,k}} \frac{\partial T_{ij}}{\partial \rho_{,mn}} \right\rangle_{(jkmn)} &= \left\langle \frac{\partial s}{\partial \varepsilon_{,k}} \frac{\partial q_j}{\partial \rho_{,mn}} \right\rangle_{(jkmn)},\end{aligned}$$

where $\langle \mathcal{F} \rangle_{(i_1 \dots i_r)}$ denotes the symmetric part of the tensor function \mathcal{F} with respect to the indices $i_1 \dots i_r$.

Exploitation of entropy inequality

Constitutive equations for viscous Korteweg fluids: assumptions

$$\mathbf{T} = \left(-p + \alpha_1 \Delta \rho + \alpha_2 |\nabla \rho|^2 \right) \mathbf{I} + \alpha_3 \nabla \rho \otimes \nabla \rho + \alpha_4 \nabla \nabla \rho + \alpha_5 (\nabla \cdot \mathbf{v}) \mathbf{I} + \alpha_6 \mathbf{L},$$

$$\mathbf{q} = \mathbf{q}^{(1)} \nabla \varepsilon + \mathbf{q}^{(2)} \nabla \rho,$$

$$s = s_0 + s_1 |\nabla \rho|^2 + s_2 \nabla \rho \cdot \nabla \varepsilon + s_3 |\nabla \varepsilon|^2 + s_4 \nabla \cdot \mathbf{v} + s_5 \Delta \rho,$$

where p , α_i ($i = 1, \dots, 6$), $\mathbf{q}^{(j)}$ ($j = 1, 2$) and s_k ($k = 0, \dots, 5$) depend on (ρ, ε) .

Exploitation of entropy inequality

Constitutive equations for viscous Korteweg fluids: assumptions

$$\mathbf{T} = \left(-p + \alpha_1 \Delta \rho + \alpha_2 |\nabla \rho|^2 \right) \mathbf{I} + \alpha_3 \nabla \rho \otimes \nabla \rho + \alpha_4 \nabla \nabla \rho + \alpha_5 (\nabla \cdot \mathbf{v}) \mathbf{I} + \alpha_6 \mathbf{L},$$

$$\mathbf{q} = \mathbf{q}^{(1)} \nabla \varepsilon + \mathbf{q}^{(2)} \nabla \rho,$$

$$s = s_0 + s_1 |\nabla \rho|^2 + s_2 \nabla \rho \cdot \nabla \varepsilon + s_3 |\nabla \varepsilon|^2 + s_4 \nabla \cdot \mathbf{v} + s_5 \Delta \rho,$$

where p , α_i ($i = 1, \dots, 6$), $\mathbf{q}^{(j)}$ ($j = 1, 2$) and s_k ($k = 0, \dots, 5$) depend on (ρ, ε) .

Constitutive equations for viscous Korteweg fluids: results

$$p = -\rho^2 \frac{\partial s_0}{\partial \rho} \left(\frac{\partial s_0}{\partial \varepsilon} \right)^{-1}, \quad \alpha_1 = -2\rho^2 s_1 \left(\frac{\partial s_0}{\partial \varepsilon} \right)^{-1},$$

$$\alpha_2 = -\rho \left(\frac{\partial s_0}{\partial \varepsilon} \right)^{-1} \left(\rho \frac{\partial s_1}{\partial \rho} + 2s_1 \right), \quad \alpha_3 = 2\rho s_1 \left(\frac{\partial s_0}{\partial \varepsilon} \right)^{-1}, \quad \alpha_4 = 0,$$

$$s = s_0(\rho, \varepsilon) + s_1(\rho) |\nabla \rho|^2, \quad s_1(\rho) \leq 0,$$

$$\mathbf{J} = \frac{\mathbf{q}}{\theta} + 2\rho^2 s_1 (\nabla \cdot \mathbf{v}) \nabla \rho,$$

where the absolute temperature θ is defined by

$$\frac{1}{\theta} = \frac{\partial s_0(\rho, \varepsilon)}{\partial \varepsilon}.$$

Exploitation of entropy inequality

Reduced entropy inequality

The residual entropy inequality turns out to be a homogeneous quadratic polynomial in some gradients entering the state space, whose coefficients depend at most on the field variables:

$$(\alpha_5(\nabla \cdot \mathbf{v})^2 + \alpha_6 \mathbf{L} \cdot \mathbf{L}) \frac{\partial s_0}{\partial \varepsilon} + \mathbf{q} \cdot \nabla \left(\frac{\partial s_0}{\partial \varepsilon} \right) \geq 0.$$

Restrictions from the reduced entropy inequality

$$\begin{aligned} q^{(1)} \frac{\partial^2 s_0}{\partial \rho \partial \varepsilon} - q^{(2)} \frac{\partial^2 s_0}{\partial \varepsilon^2} &= 0, \\ q^{(1)} &\leq 0, & q^{(2)} &\geq 0, \\ \alpha_5 &\geq 0, & \alpha_6 &\geq 0. \end{aligned}$$

Phase boundaries at the equilibrium

Equilibrium condition

The search for equilibrium configurations ($\theta = \text{const}$ and $\mathbf{v} = 0$) of a Korteweg fluid requires to solve the condition

$$\nabla \cdot \left((-p + \alpha_1 \Delta \rho + \alpha_2 |\nabla \rho|^2) \mathbf{I} + \alpha_3 \nabla \rho \otimes \nabla \rho + \alpha_4 \nabla \nabla \rho \right) = 0,$$

where p and α_i ($i = 1, \dots, 4$) depend only on ρ .

This system has three independent components while liquid-vapor phase equilibria are determined by just one physical variable, namely the mass density, *i.e.*, it is **overdetermined!**

Phase boundaries at the equilibrium

Equilibrium condition

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$$\nabla \cdot \left((-p + \alpha_1 \Delta \rho + \alpha_2 |\nabla \rho|^2) \mathbf{I} + \alpha_3 \nabla \rho \otimes \nabla \rho + \alpha_4 \nabla \nabla \rho \right) = 0,$$

where p and α_i ($i = 1, \dots, 4$) depend only on ρ .

This system has three independent components while liquid-vapor phase equilibria are determined by just one physical variable, namely the mass density, *i.e.*, it is **overdetermined!**

Remark [Serrin⁷, 1983]

Serrin established that the coefficients entering the Cauchy stress tensor have to satisfy the condition

$$(\alpha_2 + \alpha_3) \left(\frac{\partial \alpha_4}{\partial \rho} - \alpha_3 \right) + \frac{1}{2} \left(\left(\frac{\partial \alpha_4}{\partial \rho} - \alpha_3 \right)^2 - (\alpha_1 + \alpha_4) \left(\frac{\partial^2 \alpha_4}{\partial \rho^2} - \frac{\partial \alpha_3}{\partial \rho} \right) \right) = 0,$$

in order to avoid that any solution is described only by level surfaces with constant mean and Gaussian curvature, which are either concentric spheres, or concentric circular cylinders, or parallel planes.

J. Serrin, *The form of interfacial surfaces in Korteweg's theory of phase equilibria*, Quart. Appl. Math. **41**, 357–364, 1983.

Phase boundaries at the equilibrium – Results

Constraints from equilibrium condition

Serrin condition for a Korteweg fluid leads to

$$s_0(\rho, \varepsilon) = s_{01}(\rho) + s_{02}(\varepsilon).$$

Thus, from the thermodynamical restrictions, it is $\varepsilon = \varepsilon(\theta)$, and the heat flux reduces to

$$\mathbf{q} = q^{(1)} \frac{d\varepsilon}{d\theta} \nabla \theta,$$

i.e., the classical Fourier law of heat conduction.

Open problem

Along with this condition, the form of the phase boundaries is not restricted to only special geometrical configurations.

Work is in progress (with F. Oliveri, A. Ricciardello & P. Rogolino) to numerically integrate the equilibrium conditions and determine the level surfaces of phase boundaries!

The extended Liu procedure allows:

- the exploitation of entropy inequality neither modifying the energy balance with the inclusion of extra-terms (like the interstitial working), nor *a priori* including an entropy extra-flux;
- the Cauchy stress tensor to depend on the first and second order gradients of the mass density, so rendering Korteweg fluids compatible with second law of thermodynamics;
- to determine an explicit expression for the material functions involved in the Cauchy stress tensor and heat flux by expanding the specific entropy around a homogeneous equilibrium;
- to recover the form of the entropy flux algorithmically, which includes the contribution of the classical term $\frac{q}{\theta}$ and an entropy extra-flux;
- the constitutive quantities to be also compatible with a constraint arising from mechanical equilibrium where the form of the phase boundaries is not restricted to only very special configurations.

A non-reacting binary mixture of third grade fluids⁸

Governing equations

$$\begin{cases} \mathcal{E}^{(1)} \equiv \frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{v}) = 0, \\ \mathcal{E}^{(2)} \equiv \rho \left(\frac{\partial c}{\partial t} + \mathbf{v} \cdot \nabla c \right) + \nabla \cdot \mathbf{J}^{(m)} = 0, \\ \mathcal{E}^{(3)} \equiv \rho \left(\frac{\partial \mathbf{v}}{\partial t} + (\mathbf{v} \cdot \nabla) \mathbf{v} \right) - \nabla \cdot \mathbf{T} = 0, \\ \mathcal{E}^{(4)} \equiv \rho \left(\frac{\partial \varepsilon}{\partial t} + \mathbf{v} \cdot \nabla \varepsilon \right) - \mathbf{T} \cdot \nabla \mathbf{v} + \nabla \cdot \mathbf{q} = 0, \end{cases}$$

where ρ is the **mass density** of the mixture, c the **concentration** of one constituent, $\mathbf{v} \equiv (v_1, v_2, v_3)$ the **velocity** of the mixture, ε the **internal energy per unit mass**, $\mathbf{J}^{(m)}$ the **diffusional mass flux**, \mathbf{T} the symmetric **Cauchy stress tensor**, and \mathbf{q} the **heat flux**.

The mass density of the whole mixture and the concentration of one constituent are given by

$$\rho = \rho^{(1)} + \rho^{(2)}, \quad c = \frac{\rho^{(1)}}{\rho}.$$

⁸M. Gorgone and P. Rogolino, *A thermodynamical description of third grade fluid mixtures*, J. Non-Equilib. Thermodyn. **47**, 133–142, 2022.

Extendend Liu procedure

Let us assume the state space spanned by

$$\mathcal{Z} \equiv \{\rho, c, \varepsilon, \nabla \rho, \nabla c, L, \nabla \varepsilon, \nabla \nabla \rho, \nabla \nabla c\},$$

where $L = \text{sym}(\nabla v)$.

In order to exploit the second law of thermodynamics by means of the extended Liu procedure, let us introduce some Lagrange multipliers; in components, the entropy inequality reads

$$\begin{aligned} & \rho (s_{,t} + v_j s_{,j}) + J_{j,j}^{(s)} - \left(\lambda^{(1)} + \Lambda_i^{(1)} \frac{\partial}{\partial x_i} + \Theta_{ik}^{(1)} \frac{\partial^2}{\partial x_i \partial x_k} \right) (\rho_{,t} + \rho_{,j} v_j + \rho v_{j,j}) \\ & - \left(\lambda^{(2)} + \Lambda_i^{(2)} \frac{\partial}{\partial x_i} + \Theta_{ik}^{(2)} \frac{\partial^2}{\partial x_i \partial x_k} \right) (\rho (c_{,t} + v_j c_{,j}) + J_{j,j}^{(m)}) \\ & - \left(\lambda_i^{(3)} + \Lambda_{ik}^{(3)} \frac{\partial}{\partial x_k} \right) (\rho (v_{i,t} + v_j v_{i,j}) - T_{ij,j}) \\ & - \left(\lambda^{(4)} + \Lambda_k^{(4)} \frac{\partial}{\partial x_k} \right) (\rho (\varepsilon_{,t} + v_j \varepsilon_{,j}) - T_{ij} v_{i,j} + q_{j,j}) \geq 0, \end{aligned}$$

where s is the **specific entropy**, and $J^{(s)}$ the **entropy flux**.

Exploitation of entropy inequality

By expanding derivatives with the chain rule, we identify

$$X \equiv \{\rho, t, c, t, v_i, t, \varepsilon, t, \rho, it, c, it, v_i, kt, \varepsilon, kt, \rho, ikt, c, ikt, v_i, jklm, \varepsilon, ijkl, \rho, ijklm, c, ijklm\},$$

highest derivatives,

$$Y \equiv \{\rho, jkl, c, jkl, v_i, jk, \varepsilon, jk, \rho, ijkl, c, ijkl, v_i, jkl, \varepsilon, jk\},$$

higher derivatives,

and the entropy inequality can be written as

$$A_p X_p + B_{qrs}^{(3)} Y_q Y_r Y_s + B_{qr}^{(2)} Y_q Y_r + B_q^{(1)} Y_q + C \geq 0, \quad (*)$$

where A_p , $B_q^{(1)}$, $B_{qr}^{(2)}$, $B_{qrs}^{(3)}$ and C depend at most on the field and state variables.

Exploitation of entropy inequality

By expanding derivatives with the chain rule, we identify

$$X \equiv \{ \rho_{,t}, c_{,t}, v_{i,t}, \varepsilon_{,t}, \rho_{,it}, c_{,it}, v_{i,kt}, \varepsilon_{,kt}, \rho_{,ikt}, c_{,ikt}, v_{i,jklm}, \varepsilon_{,ijkl}, \rho_{,ijklm}, c_{,ijklm} \},$$

highest derivatives,

$$Y \equiv \{ \rho_{,jkl}, c_{,jkl}, v_{i,jk}, \varepsilon_{,jk}, \rho_{,ijkl}, c_{,ijkl}, v_{i,jkl}, \varepsilon_{,ijk} \},$$

higher derivatives,

and the entropy inequality can be written as

$$A_p X_p + B_{qrs}^{(3)} Y_q Y_r Y_s + B_{qr}^{(2)} Y_q Y_r + B_q^{(1)} Y_q + C \geq 0, \quad (*)$$

where A_p , $B_q^{(1)}$, $B_{qr}^{(2)}$, $B_{qrs}^{(3)}$ and C depend at most on the field and state variables.

Sufficient conditions

Since in principle nothing prevents the possibility of a thermodynamical process where $C = 0$, the entropy inequality (*) is satisfied for every thermodynamical process if the following conditions hold:

- $A_p = 0$, $B_q^{(1)} = 0$, $B_{qrs}^{(3)} = 0$;
- $B^{(2)}$ are the entries of a positive semidefinite symmetric matrix;
- $C \geq 0$.

Exploitation of entropy inequality

Constitutive equations: assumptions

$$\begin{aligned} \mathbb{T} = & (\tau_0 + \tau_1 |\nabla \rho|^2 + \tau_2 \nabla \rho \cdot \nabla c + \tau_3 |\nabla c|^2 + \tau_4 \Delta \rho + \tau_5 \Delta c + \tau_6 \nabla \cdot \mathbf{v}) \mathbb{I} \\ & + \tau_7 \nabla \rho \otimes \nabla \rho + \tau_8 \text{sym}(\nabla \rho \otimes \nabla c) + \tau_9 \nabla c \otimes \nabla c + \tau_{10} \nabla \nabla \rho + \tau_{11} \nabla \nabla c + \tau_{12} \mathbb{L}, \end{aligned}$$

$$\mathbf{J}^{(m)} = J_\rho \nabla \rho + J_c \nabla c,$$

$$\mathbf{q} = q \nabla \varepsilon,$$

$$s = \hat{s}_0 + \hat{s}_1 |\nabla \rho|^2 + \hat{s}_2 \nabla \rho \cdot \nabla c + \hat{s}_3 |\nabla c|^2,$$

where τ_k ($k = 0, \dots, 12$), J_ρ , J_c , q , and \hat{s}_i ($i = 0, \dots, 3$) depend at most on (ρ, c, ε) .

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Constitutive equations: results

$$J_\rho = \kappa_1 c + \kappa_2, \quad J_c = -\kappa_1 \rho + \kappa_3,$$

$$\mathbf{q} = q \frac{d\varepsilon}{d\theta} \nabla \theta,$$

$$\hat{s}_0 = s_{01}(\varepsilon) + J_c s_{02} \left(\frac{J_\rho}{J_c} \right) + s_{03}(\rho), \quad \hat{s}_1 = \frac{J_\rho^2 - \kappa_2^2}{J_c^2} \hat{s}_3 + \frac{\phi'(\rho)}{\rho}, \quad \hat{s}_2 = 2 \frac{J_\rho}{J_c} \hat{s}_3, \quad \hat{s}_3 = \frac{s_3}{\rho},$$

$$J^{(s)} = \frac{q}{\theta} + \frac{\partial \hat{s}_0}{\partial c} J^{(m)} + (\hat{s}_2 (J_\rho \Delta \rho + J_c \Delta c) + 2\rho^2 \hat{s}_1 \nabla \cdot \mathbf{v}) \nabla \rho + (2\hat{s}_3 (J_\rho \Delta \rho + J_c \Delta c) + \rho^2 \hat{s}_2 \nabla \cdot \mathbf{v}) \nabla c,$$

with

$$\frac{\kappa_2^2 s_3}{(\kappa_3 - \kappa_1 \rho)^2} - \phi' \geq 0, \quad s_3 \leq 0,$$

κ_i ($i = 1, 2, 3$) and s_3 constant, and the absolute temperature θ of the mixture defined by

$$\frac{1}{\theta} = \frac{\partial \hat{s}_0}{\partial \varepsilon} = \frac{ds_{01}}{d\varepsilon}.$$

Coefficients entering the Cauchy stress tensor

$$\tau_0 = \rho^2 \frac{\partial \hat{s}_0}{\partial \rho} \left(\frac{\partial \hat{s}_0}{\partial \varepsilon} \right)^{-1} = \rho^2 \theta \left(-\kappa_1 \left(s_{02} - \frac{J_\rho}{J_c} s'_{02} \right) + s'_{03} \right),$$

$$\tau_1 = -\frac{\partial (\rho^2 \hat{s}_1)}{\partial \rho} \left(\frac{\partial \hat{s}_0}{\partial \varepsilon} \right)^{-1} = -\theta \left(\frac{(J_\rho^2 - \kappa_2^2)(J_c + 2\kappa_1 \rho)}{J_c^3} s_3 + \frac{d(\rho \phi')}{d\rho} \right),$$

$$\tau_2 = -\left(\frac{\partial (\rho^2 \hat{s}_2)}{\partial \rho} + \rho^2 \frac{\partial \hat{s}_1}{\partial c} \right) \left(\frac{\partial \hat{s}_0}{\partial \varepsilon} \right)^{-1} = -2\theta \frac{J_\rho}{J_c^2} (J_c + 2\kappa_1 \rho) s_3,$$

$$\tau_3 = -\rho \left(\rho \frac{\partial \hat{s}_2}{\partial c} + \hat{s}_3 \right) \left(\frac{\partial \hat{s}_0}{\partial \varepsilon} \right)^{-1} = -\theta \frac{J_c + 2\kappa_1 \rho}{J_c} s_3,$$

$$\tau_4 = -2\rho^2 \hat{s}_1 \left(\frac{\partial \hat{s}_0}{\partial \varepsilon} \right)^{-1} = -2\rho \theta \left(\frac{J_\rho^2 - \kappa_2^2}{J_c^2} s_3 + \phi' \right),$$

$$\tau_5 = -\rho^2 \hat{s}_2 \left(\frac{\partial \hat{s}_0}{\partial \varepsilon} \right)^{-1} = -2\rho \theta \frac{J_\rho}{J_c} s_3, \quad \tau_7 = 2\rho \hat{s}_1 \left(\frac{\partial \hat{s}_0}{\partial \varepsilon} \right)^{-1} = 2\theta \left(\frac{J_\rho^2 - \kappa_2^2}{J_c^2} s_3 + \phi' \right),$$

$$\tau_8 = 2\rho \hat{s}_2 \left(\frac{\partial \hat{s}_0}{\partial \varepsilon} \right)^{-1} = 4\theta \frac{J_\rho}{J_c} s_3, \quad \tau_9 = 2\rho \hat{s}_3 \left(\frac{\partial \hat{s}_0}{\partial \varepsilon} \right)^{-1} = 2\theta s_3, \quad \tau_{10} = \tau_{11} = 0.$$

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Reduced entropy inequality

$$\mathbf{q} \cdot \nabla \left(\frac{\partial \hat{s}_0}{\partial \varepsilon} \right) + (\tau_6 (\nabla \cdot \mathbf{v})^2 + \tau_{12} \mathbf{L} \cdot \mathbf{L}) \frac{\partial \hat{s}_0}{\partial \varepsilon} + 2\hat{s}_3 \frac{(J_\rho \Delta \rho + J_c \Delta c)^2}{J_c} \\ + J_\rho \frac{\partial^2 \hat{s}_0}{\partial \rho \partial c} |\nabla \rho|^2 + 2J_\rho \frac{\partial^2 \hat{s}_0}{\partial c^2} \nabla \rho \cdot \nabla c + J_c \frac{\partial^2 \hat{s}_0}{\partial c^2} |\nabla c|^2 \geq 0.$$

Restrictions from the reduced entropy inequality

$$q \leq 0, \quad J_c \leq 0, \quad s_{02}'' \geq 0, \quad \tau_6 \geq 0, \quad \tau_{12} \geq 0.$$

Open problems

Phase boundaries at equilibrium

The search for equilibrium configurations of a non-reacting binary mixture that behaves like a Korteweg fluid requires to solve the condition:

$$\begin{aligned} \nabla \cdot \left((\tau_0 + \tau_1 |\nabla \rho|^2 + \tau_2 \nabla \rho \cdot \nabla c + \tau_3 |\nabla c|^2 + \tau_4 \Delta \rho + \tau_5 \Delta c) \mathbf{I} \right. \\ \left. + \tau_7 \nabla \rho \otimes \nabla \rho + \tau_8 \text{sym} (\nabla \rho \otimes \nabla c) + \tau_9 \nabla c \otimes \nabla c + \tau_{10} \nabla \nabla \rho + \tau_{11} \nabla \nabla c \right) = 0, \end{aligned}$$

where $\tau_k \equiv \tau_k(\rho, c)$.

Future perspectives

- The theoretical results contain some degrees of freedom and may serve as a basis for experimental and/or numerical investigations.
- Investigation of diffusive binary mixtures of Korteweg-type fluids with one temperature.

The End

