Exploitation of the entropy principle for third grade Korteweg fluids*

Matteo Gorgone
(joint work with P. Rogolino)

University of Messina, Department MIFT
email: mgorgone@unime.it

16th Joint European Thermodynamics Conference

Prague, June 14–18, 2021

*M. Gorgone and P. Rogolino, Phys. Fluids **33**, 043107 (2021).

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 governing equations (neglecting body forces and heat sources):

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

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

The system

$$\begin{cases} \dfrac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathrm{v}) = 0, \\ \rho \left(\dfrac{\partial \mathrm{v}}{\partial t} + (\mathrm{v} \cdot \nabla)\mathrm{v} \right) - \nabla \cdot \mathrm{T} = 0, \\ \rho \left(\dfrac{\partial \varepsilon}{\partial t} + \mathrm{v} \cdot \nabla \varepsilon \right) - \mathrm{T} \cdot \nabla \mathrm{v} + \nabla \cdot \mathrm{q} = 0, \end{cases}$$

is underdetermined and must be closed by constitutive equations for T and q in such a way the local entropy production

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

along any admissible thermodynamic process, s being the specific entropy, and J the entropy flux.

Second law of thermodynamics

Also s and $\mathrm{J} = (J_1, J_2, J_3)$ need to be considered as constitutive quantities.
The second law of thermodynamics restricts the form of the constitutive equations!
The restrictions placed by the entropy principle on the constitutive functions can be determined by

- Coleman–Noll procedure [Coleman, Noll, 1963];
- Liu procedure [Liu, 1972].

Remark

The constitutive relations 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.).

General representation theorems for isotropic scalar, vectorial or tensorial constitutive equations have to be taken into account.

Exploitation of entropy–like inequality

The constraints imposed by the second law of thermodynamics

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

on constitutive equations are derived though 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–Noll procedure);
    - take into account the balance equations by means of some Lagrange multipliers (Liu procedure);
3. obtain the conditions compatible with second law of thermodynamics.

Extended Liu procedure

Mathematical overview

For nonlocal theory, 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 [Rogolino, Cimmelli, 2019].

Algorithm [Cimmelli, 2007; Cimmelli, Sellitto, Triani, 2010; Cimmelli, Oliveri, Triani, 2011]

1. Associate to each field equation and spatial gradient extension a Lagrange multiplier;
2. Subtract from the Clausius-Duhem inequality a linear combination of the field equations and of the gradient extensions of the latter up to the order of the gradients entering the state space.

Extended Liu procedure

Highest and Higher derivatives

By expanding derivatives, as a result one obtains a very long expression that can be written as a polynomial in some derivatives of field variables with coefficients depending on field and state space variables.
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.

Remark

Highest and higher derivatives can be freely varied!
The terms involving highest derivatives provide us the Lagrange multipliers and some constraints on the constitutive equations.
The terms involving higher derivatives provide us further restrictions on the constitutive equations.

Korteweg fluids

Korteweg, 1901

Korteweg introduced a constitutive relation for the stress tensor 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 [Heida, Málek, 2010]:

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

wher p is the pressure, ρ the mass density, I the identity matrix and α_i $(i = 1, \ldots, 4)$ are material coefficients depending on ρ.

Dunn, 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):

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

where u is the interstitial work flux.

Another possibility is to generalize the entropy inequality as follows,

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

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

Korteweg fluids and extended Liu technique

Contributions

Special models of Korteweg fluids (second and third grade) have been considered within the context of the extended Liu procedure [Cimmelli, Sellitto, Triani, 2009; Cimmelli, Sellitto, Triani, 2010; Cimmelli, Oliveri, Pace, 2011; Gorgone, Oliveri, Rogolino, 2020; Cimmelli, Gorgone, Oliveri, Pace, 2020; Gorgone, Rogolino, 2021].

Important

The extended Liu procedure neither require the modification of the energy balance, that is taken in the classical form, nor an *a priori* introduction of an entropy extra-flux.

In the sequel...

An entropy extra-flux naturally will arise as a by-product of the mathematical exploitation of entropy principle with the extended Liu procedure!

Exploitation of entropy inequality for a viscous third grade Korteweg fluid

Let us assume the state space spanned by

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

where $\mathsf{L} = \mathrm{sym}\,(\nabla \mathsf{v})$.

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

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

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 Reduce), the entropy inequality can be written as

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

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

Exploitation of entropy inequality

By identifying the *highest* and *higher* derivatives,

$$X \equiv \{\rho_{,t}, v_{i,t}, \varepsilon_{,t}, \rho_{,it}, v_{i,jt}, \varepsilon_{,it}, \rho_{,ijt}, , v_{i,jk\ell}, \varepsilon_{,ijk}, \rho_{,ijk\ell}\},$$
$$Y \equiv \{v_{i,jk}, \varepsilon_{,ij}, \rho_{,ijk}\},$$

the entropy inequality can be written in compact form as

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

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 conditions

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

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

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

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

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 – Assumptions

Constitutive equations for third grade viscous Korteweg fluids

Let us assume the following constitutive equations for Cauchy stress tensor, heat flux and specific entropy:

$$
\begin{aligned}
\mathrm{T} &= \left(-p + \alpha_1 \Delta\rho + \alpha_2 |\nabla\rho|^2\right)\mathrm{I} + \alpha_3 \nabla\rho \otimes \nabla\rho + \alpha_4 \nabla\nabla\rho \\
&\quad + \alpha_5 (\nabla \cdot \mathrm{v})\mathrm{I} + \alpha_6 \mathrm{L}, \\
\mathrm{q} &= q^{(1)} \nabla\varepsilon + q^{(2)} \nabla\rho, \\
s &= s_0 + s_1 |\nabla\rho|^2 + s_2 \nabla\rho \cdot \nabla\varepsilon + s_3 |\nabla\varepsilon|^2 + s_4 \nabla \cdot \mathrm{v} + s_5 \Delta\rho,
\end{aligned}
$$

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

Remark

- The specific entropy s must satisfy the principle of maximum entropy at the equilibrium;
- We are not postulating a specific form for the entropy flux J.

Exploitation of entropy inequality – Results

Characterization of constitutive equations

By using some routines written in the CAS Reduce, we obtain:

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

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

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

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

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

where the absolute temperature θ is defined by

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

Exploitation of entropy inequality – Results

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:

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

Restrictions from the reduced entropy inequality

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

Phase boundaries at the equilibrium

Equilibrium condition

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

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

where the pressure p and the material functions α_i ($i = 1, \dots, 4$) now 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

Remark [Serrin, 1983]

Serrin established that, unless rather special conditions are satisfied, the only geometric phase boundaries which are consistent with this system are either spherical, cylindrical, or planar.
Using a general theorem proved in [Pucci, 1983], Serrin was able to prove that the coefficients entering the Cauchy stress tensor have to satisfy the following condition:

$$\mathcal{A} \equiv bc + \frac{1}{2}\left(c^2 - a\frac{\partial c}{\partial \rho}\right) = 0,$$

where

$$a = \alpha_1 + \alpha_4, \qquad b = \alpha_2 + \alpha_3, \qquad c = \frac{\partial \alpha_4}{\partial \rho} - \alpha_3.$$

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

Phase boundaries at the equilibrium – Results

Constraints from equilibrium condition

The equilibrium 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

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

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

Conclusions

For a third grade viscous Korteweg fluids, 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 $\frac{\mathbf{q}}{\theta}$ 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.

References

Current work (joint with F. Oliveri and P. Rogolino)

Thermodynamical analysis and constitutive equations for a mixture of viscous Korteweg fluids.

- B. D. Coleman and W. Noll, "The thermodynamics of elastic materials with heat conduction and viscosity", Arch. Ration. Mech. Anal. **13**, 167–178 (1963).
- I–Shih Liu, "Method of Lagrange multipliers for exploitation of the entropy principle", Arch. Ration. Mech. Anal. **46**, 131–148 (1972).
- V. A. Cimmelli, "An extension of Liu procedure in weakly nonlocal thermodynamics", J. Math. Phys. **48**, 113510 (2007).
- V. A. Cimmelli, A. Sellitto and V. Triani, "A generalized Coleman–Noll procedure for the exploitation of the entropy principle", Proc. R. Soc. A **466**, 911–925 (2010).
- 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**, 023511-1-15 (2011).
- P. Rogolino and V. A. Cimmelli, "Differential consequences of balance laws in extended irreversible thermodynamics of rigid heat conductors", Proc. R. Soc. A **16**, 20180482-1-19 (2019).

References

- D. J. Korteweg, "Sur la forme qui prennent les équations du mouvement des fluids 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).
- M. Heida and J. Málek, "On Korteweg–type compressible fluid-like materials", Int. J. Eng. Sci. **48**, 1313–1324 (2010).
- J. E. Dunn and J. Serrin, "On the thermomechanics of the interstitial working", Arch. Rat. Mech. Anal. **88**, 95–133 (1985).
- 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).
- 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).
- 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).
- 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).

References

- 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).
- M. Gorgone and P. Rogolino, "On the characterization of constitutive equations for third–grade viscous Korteweg fluids", Phys. Fluids **33**, 043107 (2021).
- A. C. Hearn, *REDUCE user's manual, version 3.8.* (Technical report, Rand Corporation, Santa Monica, CA, USA, 1995).
- A. Morro, "Entropy flux and Korteweg–type constitutive equations", Riv. Mat. Univ. Parma **5**, 81–91 (2006).
- J. Serrin, "The form of interfacial surfaces in Korteweg's theory of phase equilibria", Quart. Appl. Math. **41**, 357–364 (1983).
- P. Pucci, "An overdetermined system", Quart. Appl. Math. **41**, 365–367 (1983).