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Entropy flux and Korteweg-type constitutive equations (**)

1 - Introduction

The modelling of phase transitions through a phase field is based on the dependence of the constitutive functions on the gradient of the phase, the phase being often identified with the concentration of a constituent. Such a dependence is shown to be compatible with thermodynamics provided we cast it in an improved model of continuum such as that with microforces [**1**], [**2**], [**3**] or that with a more general balance of energy [**4**] or that with an extra entropy flux [**5**], [**6**], [**7**]. The modelling of constitutive properties through gradients of the phase of suitable order indicates that similar topics might arise for Korteweg-type materials and then that a new inspection of such materials might provide new insights and new results.

So as to model capillarity and replace a jump condition at a surface, Korteweg proposed smooth constitutive equations for stresses arising in response to temperature and (mass) density gradients. Next he dropped the dependence on the temperature gradients and arrived at a representation of the stress, for isotropic fluids, as a linear function in the first- and second-order density gradients. Also, Korteweg suggested that the same constitutive equation, with the density replaced by the concentration of one of the constituents of

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a mixture, should describe slow diffusion processes. This view emphasizes the connection of the Korteweg-type models with the phase field.

Constitutive equations in which density gradients genuinely enter require that the thermodynamic scheme be appropriately modified. Dunn and Serrin [8] preserve the equation of motion and the entropy inequality in the standard forms but modify the energy balance by allowing for an interstitial energy flux. Though the general form of the second law, with an unknown entropy flux, is classical (see [9]), the application to materials with internal variables [5] is of interest and opens new questions. It seems that a deeper investigation may provide more operative conclusions.

The purpose of this paper is to show that constitutive equations with density gradients may be framed within a thermodynamic scheme in which the entropy flux is different from the heat flux over the absolute temperature. Indeed, we first determine thermodynamic restrictions as necessary conditions on the constitutive functions. Next we set up a scheme which satisfies the necessary conditions, proves sufficient - in that satisfies the second law - and gives the constitutive equations in terms of the chosen free energy.

2 - Preliminaries and thermodynamic scheme

Let $\mathcal{B}$ be a body occupying a time-dependent region $\Omega \subset \mathbb{R}^3$. The notation $\boldsymbol{x} \in \Omega$ denotes the position vector, in Ω, relative to a chosen origin. Throughout we consider time-dependent fields on $\Omega \times \mathbb{R}$. The symbol ρ denotes the mass density, $\boldsymbol{v}$ the velocity, $\boldsymbol{T}$ the Cauchy stress tensor, $\boldsymbol{b}$ the body force (per unit mass), e the internal energy density, $\boldsymbol{q}$ the heat flux vector, $\boldsymbol{L}$ the velocity gradient, $\boldsymbol{D}$ the symmetric part of $\boldsymbol{L}$, r the heat supply, θ the absolute temperature, η the entropy density and ψ the free energy density. Also, ∇ is the gradient operator, ∂_t the partial time derivative. The superposed dot denotes the total time derivative so that for any function $g(\boldsymbol{x}, t)$, where $\boldsymbol{x} \in \Omega$ and $t \in \mathbb{R}$, we have

$$\dot{g} = \partial_t + \boldsymbol{v} \cdot \nabla g$$

where $\cdot$ denotes the inner product. In addition, $\nabla \cdot$ denotes the divergence and Δ the Laplacian.

The balance equations for mass, momentum and energy are taken in the classical form of continuum mechanics, namely

$$\dot{\rho} + \rho \nabla \cdot \boldsymbol{v} = 0, \tag{2.1}$$

$$\rho\dot{\boldsymbol{v}} = \nabla \cdot \boldsymbol{T} + \rho \boldsymbol{b}, \tag{2.2}$$

$$\rho\dot{e} = \boldsymbol{T} \cdot \boldsymbol{D} - \nabla \cdot \boldsymbol{q} + \rho r. \tag{2.3}$$

The Cauchy stress tensor $\boldsymbol{T}$ is symmetric, $\boldsymbol{T} = \boldsymbol{T}^T$.

The second law of thermodynamics, or entropy principle, is considered in differential form. We regard $\boldsymbol{\Phi}$ as the entropy flux and state the second law as follows.

Second law of thermodynamics. *The inequality*

$$\rho\dot{\eta} \geq -\nabla \cdot \boldsymbol{\Phi} + \frac{\rho r}{\theta}$$

must hold, at each point $\boldsymbol{x} \in \Omega$ *and time* $t \in \mathbb{R}$, *for all fields* $\Lambda = (\rho, \boldsymbol{v}, \boldsymbol{T}, e, \boldsymbol{q}, \theta, \boldsymbol{\Phi}, \boldsymbol{b}, r)$, *on* $\Omega \times \mathbb{R}$, *compatible with the balance equations.*

In simple models $\boldsymbol{\Phi}$ is shown, or is taken, to be $\boldsymbol{q}/\theta$. It is then convenient to write

$$\boldsymbol{\Phi} = \frac{\boldsymbol{q}}{\theta} + \boldsymbol{k}$$

and hence the entropy inequality becomes

$$\rho\dot{\eta} = -\nabla \cdot \left(\frac{\boldsymbol{q}}{\theta} + \boldsymbol{k}\right) + \frac{\rho r}{\theta}. \tag{2.4}$$

The vector field $\boldsymbol{k}$, which is called the extra entropy flux, is unknown and has to be determined so that the second law holds. There is an intrinsic non-uniqueness of $\boldsymbol{k}$ in that a divergence-free term may be added to $\boldsymbol{k}$ without affecting the inequality (2.4). It is usual to require that

$$\boldsymbol{k} \cdot \boldsymbol{n} = 0 \qquad \text{at} \quad \partial\Omega,$$

$\boldsymbol{n}$ being the unit normal, so that the entropy inequality for the whole region Ω is free from $\boldsymbol{k}$.

Letting $\psi = e - \theta\eta$ and replacing $-\nabla \cdot \boldsymbol{q} + \rho r$ through the energy equation (2.3) we can write (2.4) as

$$-\rho(\dot{\psi} + \eta\dot{\theta}) + \boldsymbol{T} \cdot \boldsymbol{D} - \frac{1}{\theta}\boldsymbol{q} \cdot \nabla\theta + \theta\nabla \cdot \boldsymbol{k} \geq 0. \tag{2.5}$$

2.1 - *Constitutive equations*

Motivated by the interest in Korteweg-type materials we express the constitutive properties by choosing

$$\Gamma = (\rho, \theta, \nabla\rho, \nabla\theta, \nabla\nabla\rho, \nabla\nabla\theta, \boldsymbol{D})$$

as the set of independent variables. So, e.g.,

$$\psi = \psi(\rho, \theta, \nabla\rho, \nabla\theta, \nabla\nabla\rho, \nabla\nabla\theta, \boldsymbol{D})$$

and the like for $\boldsymbol{T}, e, \boldsymbol{q}, \boldsymbol{k}$. The occurrence of the gradients $\nabla\rho, \nabla\theta, \nabla\nabla\rho, \nabla\nabla\theta$ and the form (2.5) of the entropy inequality requires that we know the relation between $\dot{\overline{\nabla g}}, \dot{\overline{\nabla\nabla g}}$ and $\nabla\dot{g}, \nabla\nabla\dot{g}$ for any function g on $\Omega \times \mathbb{R}$. The result is known (see [**10**]) for $\dot{\overline{\nabla g}}$ and $\nabla\dot{g}$, namely

$$\dot{\overline{\nabla g}} = \nabla\dot{g} - \boldsymbol{L}^T\nabla g. \tag{2.6}$$

We now determine the relation for $\dot{\overline{\nabla\nabla g}}$ and $\nabla\nabla\dot{g}$.

Lemma 1. *For any C^3 function $g(\boldsymbol{x}, t)$ the derivatives $\dot{\overline{\nabla\nabla g}}$ and $\nabla\nabla\dot{g}$ are related by*

$$\dot{\overline{\nabla\nabla g}} = \nabla\nabla\dot{g} - (\nabla\nabla\boldsymbol{v})\nabla g - 2\mathrm{sym}[(\nabla\nabla g)\boldsymbol{L}]. \tag{2.7}$$

Proof. By definition

$$\dot{\overline{\nabla\nabla g}} = \partial_t\nabla\nabla g + (\boldsymbol{v}\cdot\nabla)\nabla\nabla g.$$

By interchanging the order of differentiation we have

$$\partial_t\nabla\nabla g = \nabla\nabla\partial_t g$$

and, in component form,

$$(\boldsymbol{v}\cdot\nabla)\nabla\nabla g\Big|_{,jk} = v_p g_{,pjk} = (v_p g_{,p})_{,jk} - (g_{,p}v_{p,k})_{,j} - v_{p,j}g_{,pk}$$

$$= (\boldsymbol{v}\cdot\nabla g)_{,jk} - g_{,pj}v_{p,k} - g_{,p}v_{p,kj} - g_{,pk}v_{p,j}.$$

Since

$$\nabla\nabla\partial_t g + \nabla\nabla(\boldsymbol{v}\cdot g) = \nabla\nabla\dot{g}$$

we obtain (2.7) where

$$2\mathrm{sym}[(\nabla\nabla g)\boldsymbol{L}]\Big|_{jk} = g_{,pj}v_{p,k} + g_{,pk}v_{p,j}.$$

□

3 - Thermodynamic restrictions

To exploit the second law of thermodynamics we first evaluate $\dot{\psi}$ and $\nabla\cdot\boldsymbol{k}$ by the chain rule and substitute in (2.5) to obtain

$$
\begin{aligned}
&-\rho\psi_\rho\dot\rho-\rho(\psi_\theta+\eta)\dot\theta-\rho\psi_{\nabla\rho}\cdot(\nabla\dot\rho-\boldsymbol{L}^T\nabla\rho)-\rho\psi_{\nabla\theta}\cdot(\nabla\dot\theta-\boldsymbol{L}^T\nabla\theta)\\
&-\rho\psi_{\nabla\nabla\rho}(\nabla\nabla\dot\rho-(\nabla\nabla\boldsymbol{v})\nabla\rho-2\mathrm{sym}[(\nabla\nabla\rho)\boldsymbol{L}]\\
&-\rho\psi_{\nabla\nabla\theta}(\nabla\nabla\dot\theta-(\nabla\nabla\boldsymbol{v})\nabla\theta-2\mathrm{sym}[(\nabla\nabla\theta)\boldsymbol{L}]\\
&-\rho\psi_{\boldsymbol{D}}\cdot\dot{\boldsymbol{D}}-\rho\psi_{\nabla\nabla\boldsymbol{v}}\cdot\overline{\nabla\nabla\boldsymbol{v}}^{\cdot}+\boldsymbol{T}\cdot\boldsymbol{D}-\frac{1}{\theta}\boldsymbol{q}\cdot\nabla\theta\\
&+\theta(\boldsymbol{k}_\rho\cdot\nabla\rho+\boldsymbol{k}_\theta\cdot\nabla\theta+\boldsymbol{k}_{\nabla\rho}\cdot\nabla\nabla\rho+\boldsymbol{k}_{\nabla\theta}\cdot\nabla\nabla\theta\\
&+\boldsymbol{k}_{\nabla\nabla\rho}\cdot\nabla\nabla\nabla\rho+\boldsymbol{k}_{\nabla\nabla\theta}\cdot\nabla\nabla\nabla\theta+\boldsymbol{k}_{\boldsymbol{D}}\cdot\nabla\boldsymbol{D})\geq 0.
\end{aligned}
$$

The arbitrariness and linearity of $\dot\theta, \nabla\dot\theta, \nabla\nabla\dot\theta$ imply that the inequality holds only if

$$\eta=-\psi_\theta,\qquad \psi_{\nabla\theta}=0,\qquad \psi_{\nabla\nabla\theta}=0. \tag{3.1}$$

As a consequence the inequality reduces to

$$
\begin{aligned}
&-\rho\psi_\rho\dot\rho-\rho\psi_{\nabla\rho}\cdot(\nabla\dot\rho-\boldsymbol{L}^T\nabla\rho)-\rho\psi_{\nabla\nabla\rho}(\nabla\nabla\dot\rho-(\nabla\nabla\boldsymbol{v})\nabla\rho-2\mathrm{sym}[(\nabla\nabla\rho)\boldsymbol{L}]\\
&-\rho\psi_{\boldsymbol{D}}\cdot\dot{\boldsymbol{D}}+\boldsymbol{T}\cdot\boldsymbol{D}-\frac{1}{\theta}\boldsymbol{q}\cdot\nabla\theta+\theta(\boldsymbol{k}_\rho\cdot\nabla\rho+\boldsymbol{k}_\rho\cdot\nabla\theta\\
&+\boldsymbol{k}_{\nabla\rho}\cdot\nabla\nabla\rho+\boldsymbol{k}_{\nabla\theta}\cdot\nabla\nabla\theta+\boldsymbol{k}_{\nabla\nabla\rho}\cdot\nabla\nabla\nabla\rho+\boldsymbol{k}_{\nabla\nabla\theta}\cdot\nabla\nabla\nabla\theta+\boldsymbol{k}_{\boldsymbol{D}}\cdot\nabla\boldsymbol{D})\geq 0.
\end{aligned}
$$

We now observe that the quantities $\dot{\boldsymbol{D}}$ and $\nabla\nabla\nabla\rho, \nabla\nabla\nabla\theta$ are arbitrary and occur linearly. Hence the inequality holds only if

$$\psi_{\boldsymbol{D}}=0, \tag{3.2}$$

$$\boldsymbol{k}_{\nabla\nabla\rho}=0,\qquad \boldsymbol{k}_{\nabla\nabla\theta}=0. \tag{3.3}$$

Now replace $\dot\rho$ with $-\rho\nabla\cdot\boldsymbol{v}$ to obtain

$$
\begin{aligned}
&\rho^2\psi_\rho\nabla\cdot\boldsymbol{v}+\rho\psi_{\nabla\rho}(\nabla\rho\nabla\cdot\boldsymbol{v}+\rho\nabla(\nabla\cdot\boldsymbol{v})+\boldsymbol{L}^T\nabla\rho)\\
&+\rho\psi_{\nabla\nabla\rho}\cdot(\nabla\nabla\rho\,\nabla\cdot\boldsymbol{v}+2\nabla\rho\,\nabla(\nabla\cdot\boldsymbol{v})+\rho\nabla\nabla(\nabla\cdot\boldsymbol{v})+(\nabla\nabla\boldsymbol{v})\nabla\rho+2\mathrm{sym}(\nabla\nabla\rho)\boldsymbol{L})\\
&+\boldsymbol{T}\cdot\boldsymbol{D}-\frac{1}{\theta}\boldsymbol{q}\cdot\nabla\theta+\theta(\boldsymbol{k}_\rho\cdot\nabla\rho+\boldsymbol{k}_\rho\cdot\nabla\theta+\boldsymbol{k}_{\nabla\rho}\cdot\nabla\nabla\rho+\boldsymbol{k}_{\nabla\theta}\cdot\nabla\nabla\theta+\boldsymbol{k}_{\boldsymbol{D}}\cdot\nabla\boldsymbol{D})\geq 0.
\end{aligned}
$$

The arbitrariness and linearity of $\nabla\nabla(\nabla\cdot\boldsymbol{v})$ imply that

$$\psi_{\nabla\nabla\rho}=0. \tag{3.4}$$

Letting $\overset{\circ}{\boldsymbol{D}}$ be the traceless part of $\boldsymbol{D}$,

$$\overset{\circ}{\boldsymbol{D}}=\boldsymbol{D}-\frac{1}{3}(\mathrm{tr}\,\boldsymbol{D})\boldsymbol{1},$$

we can decompose $\boldsymbol{D}$ in the form

$$\boldsymbol{D} = \frac{1}{3}(\nabla \cdot \boldsymbol{v})\mathbf{1} + \overset{\circ}{\boldsymbol{D}}.$$

Hence the arbitrariness and linearity of $\nabla(\nabla \cdot \boldsymbol{v})$ and $\overset{\circ}{\boldsymbol{D}}$ imply that

$$\rho^2 \psi_{\nabla\rho} + \theta \boldsymbol{k}_{\nabla\cdot\boldsymbol{v}} = 0 \tag{3.5}$$

and $\boldsymbol{k}$ is independent of $\overset{\circ}{\boldsymbol{D}}$. Hence we are left with the inequality

$$\check{\boldsymbol{T}} \cdot \boldsymbol{L} - \frac{1}{\theta}\boldsymbol{q} \cdot \nabla\theta + \theta(\boldsymbol{k}_\rho \cdot \nabla\rho + \boldsymbol{k}_\theta \cdot \nabla\theta + \boldsymbol{k}_{\nabla\rho} \cdot \nabla\nabla\rho + \boldsymbol{k}_{\nabla\theta} \cdot \nabla\nabla\theta) \geq 0$$

where

$$\check{\boldsymbol{T}} := \boldsymbol{T} + \rho^2 \psi_\rho \mathbf{1} + \rho\nabla\rho \cdot \psi_{\nabla\rho}\mathbf{1} + \rho\nabla\rho \otimes \psi_{\nabla\rho},$$

is the stress tensor deprived of the free-energy contribution $-(\rho^2\psi_\rho\mathbf{1} + \rho\nabla\rho \cdot \psi_{\nabla\rho}\mathbf{1} + \rho\nabla\rho \otimes \psi_{\nabla\rho})$. Denote by $\boldsymbol{W}$ the skew part of $\boldsymbol{L}$ so that $\boldsymbol{L} = \boldsymbol{D} + \boldsymbol{W}$. Hence the inequality becomes

$$\check{\boldsymbol{T}} \cdot \boldsymbol{D} + \check{\boldsymbol{T}} \cdot \boldsymbol{W} - \frac{1}{\theta}\boldsymbol{q} \cdot \nabla\theta + \theta(\boldsymbol{k}_\rho \cdot \nabla\rho + \boldsymbol{k}_\theta \cdot \nabla\theta + \boldsymbol{k}_{\nabla\rho} \cdot \nabla\nabla\rho + \boldsymbol{k}_{\nabla\theta} \cdot \nabla\nabla\theta) \geq 0.$$

The arbitrariness of $\boldsymbol{W}$ requires that $\check{\boldsymbol{T}} \cdot \boldsymbol{W} = 0$ which means that $\check{\boldsymbol{T}}$ is symmetric. The symmetry of $\boldsymbol{T}$ and $\check{\boldsymbol{T}}$ requires that

$$\mathrm{skw}\,\nabla\rho \otimes \psi_{\nabla\rho} = 0. \tag{3.6}$$

As a consequence, the constitutive functions $\psi, \eta, \boldsymbol{T}, \boldsymbol{q}, \boldsymbol{k}$ are compatible with the second law of thermodynamics if and only if (3.1)-(3.6) and

$$\check{\boldsymbol{T}} \cdot \boldsymbol{D} - \frac{1}{\theta}\boldsymbol{q} \cdot \nabla\theta + \theta(\boldsymbol{k}_\rho \cdot \nabla\rho + \boldsymbol{k}_\theta \cdot \nabla\theta + \boldsymbol{k}_{\nabla\rho} \cdot \nabla\nabla\rho + \boldsymbol{k}_{\nabla\theta} \cdot \nabla\nabla\theta) \geq 0. \tag{3.7}$$

hold.

The functions $\check{\boldsymbol{T}}, \boldsymbol{q}, \boldsymbol{k}$ are required to satisfy the reduced dissipation inequality (3.7). The extra entropy flux $\boldsymbol{k}$ has to depend on $\nabla \cdot \boldsymbol{v}$ otherwise, by (3.5), ψ is independent of $\nabla\rho$ and the essential feature of the Korteweg-type materials is lost.

An interesting constitutive model follows by letting

$$\psi(\rho, \theta, \nabla\rho) = \hat{\psi}(\rho, \theta) + \alpha\, \frac{\theta}{2\rho^2}|\nabla\rho|^2.$$

Hence

$$\boldsymbol{k} = -\,\alpha\,(\nabla \cdot \boldsymbol{v})\,\nabla\rho$$

and

$$\boldsymbol{k}_{\nabla\rho} \cdot \nabla\nabla\rho = -\alpha(\nabla \cdot \boldsymbol{v})\Delta\rho.$$

This implies that

$$\boldsymbol{T} = -\rho^2\psi_\rho \mathbf{1} + \alpha\,\frac{\theta}{\rho}|\nabla\rho|^2\mathbf{1} + \alpha\frac{\theta}{\rho}\nabla\rho\otimes\nabla\rho + \alpha\Delta\rho\mathbf{1} + \tilde{\boldsymbol{T}}$$

where $\tilde{\boldsymbol{T}}$ is subject to

$$\tilde{\boldsymbol{T}} \cdot \boldsymbol{L} - \frac{1}{\theta}\boldsymbol{q} \cdot \nabla\theta \geq 0.$$

4 - A model compatible with thermodynamics

The difficulty of finding constitutive equations $\check{\boldsymbol{T}}, \boldsymbol{q}, \boldsymbol{k}$ satisfying (3.7) suggests that we look for a different approach to the restrictions placed by the second law. Upon an appropriate assumption on the function $\boldsymbol{k}$ we establish a model which is compatible with the second law inequality (sufficient conditions) and meanwhile satisfies the necessary conditions.

Preliminarily we observe that, for any vector functions $\boldsymbol{h}, \boldsymbol{k}$ and scalar function g we have

$$-\boldsymbol{h} \cdot \nabla g + \theta\nabla \cdot \boldsymbol{k} = \nabla(-g\boldsymbol{h} + \theta\boldsymbol{k}) + g\nabla \cdot \boldsymbol{h} - \boldsymbol{k} \cdot \nabla\theta.$$

Hence, because

$$g\nabla \cdot \boldsymbol{h} - \frac{1}{\theta}\boldsymbol{h}\, g\,\nabla\theta = \theta g\nabla \cdot \Big(\frac{1}{\theta}\boldsymbol{h}\Big),$$

we obtain the obvious proof of the following

Lemma 2. *If* $\theta\boldsymbol{k} = g\boldsymbol{h}$ *then*

$$-\boldsymbol{h} \cdot \nabla g + \theta\nabla \cdot \boldsymbol{k} = \theta g\nabla \cdot \Big(\frac{1}{\theta}\boldsymbol{h}\Big). \tag{4.1}$$

Again we let the necessary conditions (3.1), (3.2) and (3.4) hold. Hence the entropy inequality becomes

$$-\rho\psi_\rho\dot{\rho} - \rho\psi_{\nabla\rho} \cdot (\nabla\dot{\rho} - \boldsymbol{L}^T\nabla\rho) + \boldsymbol{T} \cdot \boldsymbol{D} - \frac{1}{\theta}\,\boldsymbol{q} \cdot \nabla\theta + \theta\nabla \cdot \boldsymbol{k} \geq 0. \tag{4.2}$$

This suggests that we let

$$\theta\boldsymbol{k} = \rho\psi_{\nabla\rho}\dot{\rho} \tag{4.3}$$

and apply Lemma 2, with the identifications $\boldsymbol{h} = \rho\psi_{\nabla\rho}, g = \dot{\rho}$. Upon replacing $\dot{\rho}$ with $-\rho\mathbf{1}\cdot\boldsymbol{L}$ we obtain from (4.2)

$$[\rho^2\psi_\rho\mathbf{1} - \rho\theta\nabla\cdot\Big(\frac{\rho}{\theta}\,\psi_{\nabla\rho}\Big)\mathbf{1} + \rho\nabla\rho\otimes\psi_{\nabla\rho} + \boldsymbol{T}]\cdot\boldsymbol{L} - \frac{1}{\theta}\,\boldsymbol{q}\cdot\nabla\theta \geq 0.$$

As a consequence,

$$\boldsymbol{T} = -\rho^2\psi_\rho\mathbf{1} + \rho\theta\nabla\cdot\Big(\frac{\rho}{\theta}\,\psi_{\nabla\rho}\Big)\mathbf{1} - \rho\nabla\rho\otimes\psi_{\nabla\rho} + \boldsymbol{\mathcal{T}} \tag{4.4}$$

where $\boldsymbol{\mathcal{T}}$ is subject to

$$\boldsymbol{\mathcal{T}}\cdot\boldsymbol{L} - \frac{1}{\theta}\boldsymbol{q}\cdot\nabla\theta \geq 0. \tag{4.5}$$

Again, upon the decomposition

$$\boldsymbol{L} = \boldsymbol{D} + \boldsymbol{W}$$

and the arbitrariness and linearity of $\boldsymbol{W}$ we obtain from (4.5) that

$$\boldsymbol{\mathcal{T}}\cdot\boldsymbol{W} = 0$$

whence it follows that $\boldsymbol{\mathcal{T}}$ is symmetric. This in turn implies the symmetry of $\nabla\rho\otimes\psi_{\nabla\rho}$, namely

$$\operatorname{skw}\nabla\rho\otimes\psi_{\nabla\rho} = 0. \tag{4.6}$$

Hence (4.5) becomes

$$\boldsymbol{\mathcal{T}}\cdot\boldsymbol{D} - \frac{1}{\theta}\boldsymbol{q}\cdot\nabla\theta \geq 0. \tag{4.7}$$

In conclusion, the constitutive functions $\psi, \eta, \boldsymbol{T}, \boldsymbol{q}, \boldsymbol{k}$, of $\varGamma$, satisfying the restrictions (3.1), (3.2), (3.4) and (4.3), (4.4), (4.6), (4.7) are sufficient for the validity of the second law in the form (2.4).

Compatibility with thermodynamics holds if, in addition to the other restrictions just listed, the stress tensor is given by (4.4). This means that, owing to the divergence $\nabla\cdot(\rho\psi_{\nabla\rho}/\theta)$, a contribution

$$\frac{\rho^2}{\theta}\psi_{\nabla\rho}\cdot\nabla\theta\,\mathbf{1}$$

occurs in the stress tensor. This is remarkable in that it provides a stress term originated by the temperature gradient. Qualitatively, though, this effect is not characteristic of the occurrence of the $1/\theta$ dependence in the divergence term. Since ψ depends also on θ, even $\nabla\cdot(\rho\psi_{\nabla\rho})\mathbf{1}$ produces a stress contribution proportional to $\nabla\theta$.

Remark. Assumption (4.5) satisfies the necessary condition (3.5) as it follows by replacing $\dot\rho$ with $-\nabla\cdot\boldsymbol{v}$. Also, (3.3) holds trivially in that ψ is independent of $\nabla\nabla\theta$ and $\nabla\nabla\rho$.

5 - Comments on Korteweg's constitutive equation

Korteweg's constitutive equation **[11]**

$$\boldsymbol{T}+p\mathbf{1}=\lambda(\mathrm{tr}\,\boldsymbol{D})\mathbf{1}+2\mu\boldsymbol{D}-\alpha|\nabla\rho|^2\mathbf{1}-\beta\nabla\rho\otimes\nabla\rho+\gamma(\Delta\rho)\mathbf{1}+\delta\nabla\nabla\rho \tag{5.1}$$

amounts to letting

$$\mathcal{T}=\lambda(\mathrm{tr}\,\boldsymbol{D})\mathbf{1}+2\mu\boldsymbol{D}$$

and

$$p=\rho^2\psi_\rho.$$

By (4.6), for isotropic materials it follows that (see **[1]**)

$$\psi_{\nabla\rho}=\omega(\rho,\theta,|\nabla\rho|^2)\nabla\rho. \tag{5.2}$$

Hence we have

$$\psi=\hat\psi(\rho,\theta)+\Psi(\rho,\theta,|\nabla\rho|^2)$$

where $\Psi_{|\nabla\rho|^2}=\omega/2$. As a consequence,

$$p=\rho^2(\hat\psi_\rho+\Psi_\rho)$$

is a function of ρ,θ and $|\nabla\rho|^2$. Substitution of (5.2) gives

$$\rho\theta\nabla\cdot\Big(\frac{\rho}{\theta}\psi_{\nabla\rho}\Big)\mathbf{1}-\rho\nabla\rho\otimes\psi_{\nabla\rho}=\xi\mathbf{1}-\rho\omega\nabla\rho\otimes\nabla\rho$$

where

$$\xi=\rho^2\Big[\Big(\omega_\rho+\frac{\omega}{\rho}+2\omega_{|\nabla\rho|^2}|\nabla\rho|^2\Big)|\nabla\rho|^2-\Big(\omega_\theta-\frac{\omega}{\theta}\Big)\nabla\rho\cdot\nabla\theta+\omega\Delta\rho\Big].$$

Accordingly, two qualitative features distinguish Korteweg's equation (5.1) from

$$\boldsymbol{T}=-\rho^2\psi_\rho\mathbf{1}+\xi\mathbf{1}-\rho\omega\nabla\rho\otimes\nabla\rho+\mathcal{T}. \tag{5.3}$$

First, the dependence on $\nabla\theta$ is not involved in (5.1) whereas $\nabla\theta$ occurs in (5.3) as $\nabla\theta\cdot\nabla\rho$ through ξ. The $\nabla\theta\cdot\nabla\rho$ term occurs both because of the dependence of ω on θ (through ω_θ) and as a consequence of $\boldsymbol{k}\cdot\nabla\theta$ and use of Lemma 2. Secondly, in (5.3) the dependence on $\nabla\nabla\rho$ is only through $\Delta\rho$, as though $\delta=0$ in (5.1). This happens because ψ is independent of $\nabla\nabla\rho$ and hence second-order derivatives arise only as a consequence of $\nabla \cdot \psi_{\nabla\rho}$. The dissipative stress $\mathcal{T}$ may be linear in $\nabla\nabla\rho$ provided (4.7) holds. For instance, functions of the form

$$\mathcal{T} = \frac{\upsilon}{\theta}|\nabla\theta|^2\nabla\nabla\rho + ..., \qquad \boldsymbol{q} = \upsilon(\nabla\nabla\rho \cdot \boldsymbol{D})\nabla\theta + ...$$

are compatible with (4.7). However they do not seem to be motivated on the physical ground.

6 - Conclusions

The model provided in § 4 gives a class of constitutive equations, characterized by (4.6) and (4.7) which are based on (4.5) about the extra entropy flux $\boldsymbol{k}$. The reduced dissipation inequality (4.7) involves the dissipative stress $\mathcal{T}$ and the heat flux $\boldsymbol{q}$ as in the classical theory of heat-conducting and dissipative fluids. The function $\boldsymbol{k}$ is fully determined by (4.5), is compatible with the thermodynamic restrictions (3.3) and (3.5), and eventually no longer appears in the entropy inequality as $\boldsymbol{k} \cdot \nabla\theta$. Owing to the analogy with the phase-field model, these results are likely to be useful in the modelling of phase transitions.

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Abstract

Korteweg-type constitutive equations describe smooth properties of capillarity through the dependence on higher-order density (or deformation) gradients. Such constitutive equations are compatible with thermodynamics provided the scheme is appropriately modified. The purpose of the paper is to show that constitutive equations with density gradients may be framed within a thermodynamic scheme in which the entropy flux is different from the heat flux over the absolute temperature. This is shown in two steps. First, thermodynamic restrictions on the constitutive functions are derived as necessary conditions placed by the second law inequality. Next a scheme is set up which satisfies the necessary conditions, proves sufficient - in that satisfies the second law - and gives the constitutive equations in terms of the chosen free energy. The immediate connection with Korteweg's equation is established.

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