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Conducting viscous bodies with phase transitions: Deriving Gurtin's postulate from the second law structure invariance

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ABSTRACT

We prove that the basic structures of phase-field models for phase-transitions in non-isothermal setting can be derived all together from a unique principle requiring structure invariance of the second law of thermodynamics, written as a Clausius-Duhem inequality, under orientation-preserving diffeomorphism-based changes of observer and standard regularity conditions. We thus prove that the independent scalar balance of actions driving phase transitions does not require to be postulated, as it was in Gurtin's 1996 proposal, rather it is a natural consequence of the invariance requirement adopted and maintains independence from constitutive choices. The approach discussed here is also a model-building framework for the dynamics of complex bodies and allows one to show that the microstructural behavior can be responsible of effects leading to wave-type heat propagation. The results indicate another role for the second law of thermodynamics, in addition to being a source of constitutive restrictions and compatibility or stability conditions.

1. Introduction

The introduction of fields as peculiar descriptors of phase transitions has been raised at the status of paradigm in Landau's work [1], in which phase fields enter the description of states and their evolution laws have variational origin: the time derivative of these field is determined by the variational derivative of a free energy (see also [2–4]). Transport of matter during the transition has been then considered by Cahn and Hilliard [5,6], who also followed a variational view. The derived evolution law, commonly known as the Cahn-Hilliard equation converges to the Hale-Shaw model in a suitable sense [7]. Its structure and physical significance stimulated interest for mathematical analyses with consequent significant results. They deal with solution estimates [8], stability conditions [9], existence of weak solutions even for variants of the Cahn-Hilliard equation [10–13], stochastic perturbations [14], and statistical mechanics based non-local extensions [15,16]. Miranville's book describes the scenario of pertinent analyses [17].

Balance equations, however, are independent in structure from constitutive prescriptions, as repeatedly pointed out by Truesdell's school [18–20]. Constitutive restrictions emerge then from the second law once the list of state variables has been chosen [21,22]. On this cultural ground, in 1996 Gurtin [23] derived the Cahn-Hilliard equation in a not necessarily variational setting by postulating a scalar balance of microstructural actions driving the phase transition, which he called a *microforce balance*; precisely, he considered first an integral balance of the type

$$\int_{\mathfrak{b}}(\beta - z)\,\mathrm{d}x + \int_{\partial\mathfrak{b}} \mathfrak{h}\cdot n\,\mathrm{d}\mathcal{H}^2(x) = 0 \tag{1}$$

and presumed it holds for any body part $\mathfrak{b}$ (the interposed dot means scalar product). In the previous equation, β is a scalar external bulk action, while z is an internal one, and $\mathfrak{h}$ a vector contact action. Under appropriate (obvious) regularity, the arbitrariness of $\mathfrak{b}$ implies the pointwise *scalar* balance

$$\beta - z + \mathrm{div}\,\mathfrak{h} = 0\,. \tag{2}$$

Gurtin [23] exploited the postulated balance in its pointwise scalar form (2). His approach justified various extensions of the Cahn-Hilliard equation including dissipative terms [24–28]. Constitutive structures enter, indeed, at a later stage and are restricted by the second law of thermodynamics.

Indeed, independent scalar balances of interactions associated with material changes at a certain spatial scale were already postulated by Nunziato and Cowin in the case of scalar (or pseudo-scalar) fields [29] (see also [30]). Above all, Capriz considered balances of interactions associated with manifold-valued phase fields [31,32], a choice that unified available models of the influence of microstructural events on the overall macroscopic material behavior. These models postulated balance equations in strong or weak form, the latter also called the *principle of virtual power*, or *virtual work* (see [33] for a postulate of the weak form of the balance equations for interactions associated with phase fields). However, if we would accept such a principle, we would have the need to presume a priori an explicit expression for the internal power, besides the one of external actions; that means we

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should assume as granted a priori the existence of a microstructural self-action (which is not present in the external power, while it appears only in the internal one) and the representation of microstructural contact actions in terms of microstress (in the case of Eq. (2), self-actions and contact actions associated with the phase transition are represented—we repeat—by z and $\mathfrak{h}$, respectively). Such assumptions are not necessary when we start only from the external power and, for non-scalar (and non-pseudo-scalar) phase fields, we impose the invariance of such a power under rigid-body type changes of observer [34,35]. This approach allows one to *derive* the representation of microstructural contact actions in terms of microstress and the need of a microstructural self-action [36,37]. However, it fails for scalar (or pseudo-scalar) phase fields because a rotating observer does not perceive changes of $\mathbb{R}$-valued fields.

To overcome the difficulty we follow a new path based on a requirement of structure invariance of the second law written in a Clausius-Duhem form, and generalize a view proposed first in [38] and refined in [39,40].

From the invariance in structure of the second law of thermodynamics and without specifying the list of state variables we *derive* the so-called "microforce balance" [23] only postulated by Gurtin in [23] (see also [41,42]). Along the way we also obtain the representation of contact microscopic actions in terms of a vector map with values $\mathfrak{h}$ and the necessary occurrence of a self-action z. The approach preserves the independence of the balance equations from the constitutive prescriptions.

The results justify not only the viscous-type generalization of the Cahn-Hilliard equation, but also, in the non-isothermal setting treated here, it allows possible non-Fourier effects in the heat propagation (for an account of other hyperbolic-type schemes of heat propagation see [43]). We thus extend the procedure to general complex bodies, paying particular attention to fluids, so we refer in Section 11 to generic manifold-valued phase-fields as descriptors of the material morphology at a micro-scale λ.

For the sake of simplicity, until Section 10 included we will refer to orthonormal frames of reference unless otherwise stated. In Section 11 we will consider general frames of reference, so that we will distinguish between contravariant and covariant tensor components; also we will distinguish between the (spatial) derivative operator D and the gradient ∇, which is the vector-type operator associated with the covector-type operator D, namely $\nabla = D^\sharp$ and $D = \nabla^\flat$. We will also distinguish between transpose (indicated by the superscript $\top$) and adjoint (indicated by the superscript $*$) of seconod-rank 1-contravariant, 1-covariant tensors, the two operations being coincident when we refer to orthonormal frames of reference.

2. Basic fields

Let $\mathcal{B}$ a simply connected open domain in $\mathbb{R}^3$ with surface-like Lipschitz boundary oriented by the outward unit normal n to within a finite number of corners and edges. The domain $\mathcal{B}$ represents here the macroscopic current configuration of a two-phase continuous body; so, $\mathcal{B}$ depends on time. Thus, we adopt an Eulerian representation and do not call upon any reference configuration.

A vector field $v := \tilde{v}(x,t) \in \mathbb{R}^3$ represents at every place $x \in \mathcal{B}$ and time t the *velocity* of material elements. We take $\tilde{v}$ to be *continuous and continuously differentiable*; so, at first we avoid considering the shock set for the sake of simplicity.

A scalar field $(x,t) \longmapsto \mathsf{c} := \tilde{\mathsf{c}}(x,t) \in [0,1]$ indicates the *void volume fraction* density of one phase. We presume that

- $\mathsf{c} := \tilde{\mathsf{c}}(x,t)$ refers at instant t to a spatial window with diameter $\lambda > 0$ and mass center at x, so that λ defines the microscopic scale at which we look at, and
- the field $\tilde{\mathsf{c}}$ is twice continuously differentiable.

We compute

$$\overline{\nabla \mathsf{c}}^{\cdot} = \nabla \dot{\mathsf{c}} - \nabla \mathsf{c} \nabla v \ .$$

Finally, a continuous and continuously differentiable real-valued field $\tilde{\vartheta}$ describes at $x \in \mathcal{B}$ and $t \in \mathbb{R}$ the *absolute temperature* $\vartheta := \tilde{\vartheta}(x,t)$ in Eulerian representation.

3. Mass balance

Let $\rho_{\mathsf{c}} := \tilde{\rho}_{\mathsf{c}}(x,t)$ be the mass density of a phase at x and t, with $\tilde{\rho}_{\mathsf{c}}$ a continuous and continuously differentiable function. We have $\rho_{\mathsf{c}} = \hat{\rho}_{\mathsf{c}}\mathsf{c}$, with $\hat{\rho}_{\mathsf{c}}$ the (positive) constant mass density per unit volume of the pure phase.

Let $\mathfrak{b}$ be any connected subset of $\mathcal{B}$ with non-vanishing volume and surface-like Lipschitz boundary oriented by the outward unit normal n to within a finite number of corners and edges. We call $\mathfrak{b}$ a *part* of $\mathcal{B}$. For the mass balance of a single phase in $\mathfrak{b}$, we thus write

$$\frac{\mathrm{d}}{\mathrm{d}t} \int_{\mathfrak{b}} \rho_{\mathsf{c}} \, \mathrm{d}x = - \int_{\partial \mathfrak{b}} \bar{\mathrm{h}}_{\mathsf{c}} \cdot n \, \mathrm{d}\mathcal{H}^2(x) \ , \tag{3}$$

where $\bar{\mathrm{h}}_{\mathsf{c}}$ is a mass flux depending on x and t. If $\bar{\mathrm{h}}_{\mathsf{c}}(\cdot,t) \in C^1(\mathcal{B},\mathbb{R}^3) \cup C(\bar{\mathcal{B}},\mathbb{R}^3)$ at every t, after using transport and divergence theorems, the arbitrariness of $\mathfrak{b}$ implies

$$\dot{\rho}_{\mathsf{c}} + \rho_{\mathsf{c}} \,\mathrm{div} v = -\mathrm{div} \bar{\mathrm{h}}_{\mathsf{c}} \ .$$

By setting $\mathrm{h}_{\mathsf{c}} = \hat{\rho}_{\mathsf{c}}^{-1} \bar{\mathrm{h}}_{\mathsf{c}}$, we thus get

$$\dot{\mathsf{c}} + \mathsf{c} \,\mathrm{div} v = -\mathrm{div} \mathrm{h}_{\mathsf{c}} \ . \tag{4}$$

The whole mass density is $\rho := \rho_{\mathsf{c}} + \rho_{1-\mathsf{c}}$, where $\rho_{1-\mathsf{c}}$ is the mass density of the complementary phase, with $\bar{\mathrm{h}}_{1-\mathsf{c}}$ the associated flux. If we presume full conservation, that is $\bar{\mathrm{h}}_{\mathsf{c}} = -\bar{\mathrm{h}}_{1-\mathsf{c}}$, we have

$$\dot{\rho} + \rho \,\mathrm{div} v = 0 \ .$$

4. Diffeomorphism-based changes of observer

Observers are frames of reference in all spaces adopted to describe the geometry of a body and its motion.

We consider changes of observer leaving invariant the time scale. We thus take a parameterized family $\{\mathsf{f}_s\}$ of orientation-preserving diffeomorphisms $\mathsf{f}_s \in \mathrm{Diff}(\mathbb{R}^3,\mathbb{R}^3)$, which is differentiable with respect to s and is such that

$$\mathsf{f}_0(x) = x \ ,$$

Write $\mathsf{f}_{t,s}$ for the flux defined by $\mathsf{f}_{t,s} := \mathsf{f}_t \circ \mathsf{f}_s^{-1}$. The vector field with values

$$\bar{\mathsf{v}}(x,t) := \left. \frac{\mathrm{d}\mathsf{f}_{t,s}}{\mathrm{d}t} \right|_{s=t} (x)$$

is the infinitesimal generator of the action of $\{\mathsf{f}_s\}$ at $s = t$.

Let v the velocity evaluated by an observer $\mathcal{O}$ and v' the one recorded by $\mathcal{O}'$, an observer linked with $\mathcal{O}$ by $\mathsf{f}_{s,t}$. We indicate by $v^\diamond$ the pull-back along f_s, at $s = t$, of v' to $\mathcal{O}$; it is given by

$$v^\diamond(x,t) := v(x,t) + \bar{\mathsf{v}}(x,t) \ . \tag{5}$$

Since $\mathsf{f}_{t,s}$ deforms the space, in principle an observer $\mathcal{O}'$ linked to $\mathcal{O}$ by f_s may record a value of c different from the one measured by $\mathcal{O}$. With $\dot{\mathsf{c}}$ and $\dot{\mathsf{c}}'$ the time rates of c recorded by $\mathcal{O}$ and $\mathcal{O}'$, respectively, for the pull-back $\dot{\mathsf{c}}^\diamond$ of $\dot{\mathsf{c}}'$ to $\mathcal{O}$ we write

$$\dot{\mathsf{c}}^\diamond(x,t) := \dot{\mathsf{c}}(x,t) + \mathfrak{v}(x,t) \ , \tag{6}$$

where $\mathfrak{v}(\cdot,\cdot)$ is a differentiable function.

Being associated with the volume measure, c behaves as a pseudo-scalar because it transforms as $(\det \nabla \mathsf{f}_{t,s})\mathsf{c}(\mathsf{f}_{t,s}(x),t)$. Thus, by computing the derivative with respect to t and setting $t = s$, we obtain formula (6).

When f_s is an isometric orientation-preserving map, thus $\bar{\mathrm{v}}(x,t) = \hat{\mathbf{c}}(t)+\mathbf{q}(t)\times(x-x_0)$, with $\hat{\mathbf{c}}(t)$ and $\mathbf{q}(t)$ the values in $\mathbb{R}^3$ of time-dependent smooth maps, and x_0 an arbitrary point, $\mathfrak{v}(x,t)$ vanishes at every x and t. Indeed, c is insensitive to rigid translations in space because at x and t it refers to a property that is inner to the material element at x in the instant t.

Assumption 4.1. We consider admissible those changes of observer such that $\bar{\mathrm{v}}$ and $\mathfrak{v}$ are differentiable and bounded, and their derivatives are also bounded.

5. External power of actions

The fields describing how instantaneously the body morphology changes are $\tilde{v}$ and $\tilde{\mathsf{c}}$. Given any arbitrary part $\mathfrak{b}$ of the current configuration $\mathcal{B}$, we consider bulk and contact actions *external* to $\mathfrak{b}$. They are defined by the power $\mathcal{P}^{ext}_{\mathfrak{b}}(v,\dot{\mathsf{c}})$ that they develop, namely

$$\mathcal{P}^{ext}_{\mathfrak{b}}(v,\dot{\mathsf{c}}) := \int_{\mathfrak{b}} (b^{\ddagger}\cdot v + \beta\dot{\mathsf{c}})\,\mathrm{d}x + \int_{\partial\mathfrak{b}} (\mathsf{t}_{\partial}\cdot v + \tau_{\partial}\dot{\mathsf{c}})\,\mathrm{d}\mathcal{H}^2(x)\,,$$

where $\mathrm{d}\mathcal{H}^2$ is the surface measure. $\mathsf{t}_{\partial} = \tilde{\mathsf{t}}_{\partial}(x,t)$ is a vector-valued density: t_{∂} is a covector, namely it is dual to v; it represents first-neighbor interactions across $\partial\mathfrak{b}$, so it depends on the boundary itself, as indicated by the subscript ∂. $\tau_{\partial} := \tilde{\tau}_{\partial}(x,t)$ is a scalar density representing first-neighbor interactions across $\partial\mathfrak{b}$ due to phase changes, so it depends on $\partial\mathfrak{b}$, as indicated by the subscript ∂. $b^{\ddagger}$ and β represent, respectively, standard bulk forces and a possible scalar (β) external bulk direct action on the phase change. In particular, as usual, $b^{\ddagger}$ is taken to be the sum of inertial b^{in} and non-inertial b components, namely $b^{\ddagger} = b^{in} + b$.

Remark 1. In the general model-building framework for the mechanics of complex materials, fields $\tilde{\nu}$ describing the material morphology at a small scale λ enter the stage [32,36,44]. By maintaining the treatment as general as possible to include a variety of special cases, we select $\tilde{\nu}$ as a map with values $\nu := \tilde{\nu}(x,t)$ on a finite-dimensional, differentiable, geodesic-complete, Riemannian manifold $\mathcal{M}$. (Here the role of ν is played by c.) In that general setting, the above expression of $\mathcal{P}^{ext}_{\mathfrak{b}}$ also holds, provided that the product $\tau_{\partial}\dot{\mathsf{c}}$ be substituted by $\tau_{\partial}\cdot\dot{\nu}$, where $\dot{\nu}$ belongs to the tangent space $T_{\nu}\mathcal{M}$ to $\mathcal{M}$ at $\nu = \tilde{\nu}(x,t)$. In this case τ_{∂} is an element of the cotangent space $T^*_{\nu}\mathcal{M}$, that is the space of linear maps over $T_{\nu}\mathcal{M}$. The interposed dot means duality pairing. When we consider changes of observer determined by rigid-body motions, and $\nu \in \mathcal{M}$ is not a scalar (or a pseudo-scalar), ν is generically affected by rotations. So, asking invariance of the external power alone under this rigid-body-motion-type changes of observer is a reliable way to obtain and justify balances of standard and microstructural interactions, independently of their constitutive structures (see pertinent proofs in [36], [34], [35], where, also, the notion of a *relative power* is introduced to derive from its invariance independent balances of standard, microstructural, and configurational actions, all together from a unique source). Here we cannot follow such a path because c is not sensitive to rigid-body-type changes of observer. This is a reason pushing us to follow the alternative that we discuss.

6. Balance of energy

For any part $\mathfrak{b} \in \mathcal{B}$, we presume that its *internal energy* $\mathcal{E}(\mathfrak{b})$ is a time-dependent Radon measure. Since $\mathbb{R}^3$ is a locally compact topological space, the assumption implies that there exists an *energy density* $e = \tilde{e}(x,t)$ such that

$$\mathcal{E}(\mathfrak{b}) = \int_{\mathfrak{b}} e\,\mathrm{d}x\,.$$

We assume that $\tilde{e}$ is continuous and continuously differentiable, and that the derivatives of $\tilde{e}$ are bounded over $\mathcal{B}$ at every t.

We thus write the *balance of energy* in its Eulerian representation as follows:

$$\frac{\mathrm{d}}{\mathrm{d}t}\int_{\mathfrak{b}} e\,\mathrm{d}x - \int_{\partial\mathfrak{b}} en\cdot v\,\mathrm{d}\mathcal{H}^2(x) - \mathcal{P}^{ext}_{\mathfrak{b}}(v,\dot{\mathsf{c}}) + \int_{\partial\mathfrak{b}} a_{\partial}\,\mathrm{d}\mathcal{H}^2(x) - \int_{\mathfrak{b}} r\,\mathrm{d}x = 0\,, \quad (7)$$

which we presume to hold for *any* choice of v, $\dot{\mathsf{c}}$, and $\mathfrak{b}$. In Eq. (7), a_{∂} is a *scalar heat flux*, which depends on space, time, and the boundary $\partial\mathfrak{b}$, while r is a *heat source*.

Set $v = 0$ and $\dot{\mathsf{c}} = 0$. By using the standard transport theorem on the first integral, the previous balance reduces to

$$\int_{\mathfrak{b}} \dot{e}\,\mathrm{d}x + \int_{\partial\mathfrak{b}} a_{\partial}\,\mathrm{d}\mathcal{H}^2(x) - \int_{\mathfrak{b}} r\,\mathrm{d}x = 0\,.$$

As assumed above, $\dot{e}$ is bounded. Thus, if r is also bounded over $\mathcal{B}(t)$ at every instant and a_{∂} is continuous with respect to x, the classical Cauchy theorem on fluxes implies that a_{∂} depends on $\partial\mathfrak{b}$ only through the normal n at all points where n is well-defined, that is there exist a function $\tilde{a}$ such that $a_{\partial}(x,t) = \tilde{a}(x,t,n) = -\tilde{a}(x,t,-n)$, and also it is linear with respect to n, namely there exist a vector function $\tilde{\mathsf{q}}$ with values $\mathsf{q} := \tilde{\mathsf{q}}(x,t) \in \mathbb{R}^3$ such that

$$a_{\partial}(x,t) = \tilde{a}(x,t,n) = \tilde{\mathsf{q}}(x,t)\cdot n = \mathsf{q}\cdot n\,.$$

So, q is the vector heat flux.

Thus, we rewrite Eq. (7) as

$$\int_{\mathfrak{b}} \dot{e}\,\mathrm{d}x - \mathcal{P}^{ext}_{\mathfrak{b}}(v,\dot{\mathsf{c}}) + \int_{\partial\mathfrak{b}} \mathsf{q}\cdot n\,\mathrm{d}\mathcal{H}(x) - \int_{\mathfrak{b}} r\,\mathrm{d}x = 0\,. \quad (8)$$

We take $\tilde{\mathsf{q}} \in C^1(\mathcal{B},\mathbb{R}^3) \cup C(\bar{\mathcal{B}},\mathbb{R}^3)$. Thus, we get

$$\int_{\mathfrak{b}} \dot{e}\,\mathrm{d}x - \mathcal{P}^{ext}_{\mathfrak{b}}(v,\dot{\mathsf{c}}) - \int_{\mathfrak{b}} (r - \mathrm{div}\mathsf{q})\,\mathrm{d}x = 0\,. \quad (9)$$

7. Entropy inequality

For any $\mathfrak{b}$, we also presume that its *entropy* $\mathsf{H}(\mathfrak{b})$ is a time-dependent Radon measure. Thus, there is a density $\eta = \tilde{\eta}(x,t)$ such that

$$\mathsf{H}(\mathfrak{b}) = \int_{\mathfrak{b}} \eta\,\mathrm{d}x\,.$$

As for the internal energy density, we assume that $\tilde{\eta}$ is continuous and continuously differentiable, and that the derivatives of $\tilde{\eta}$ are bounded over $\mathcal{B}$ at every t. We thus write the entropy inequality as

$$\frac{\mathrm{d}}{\mathrm{d}t}\int_{\mathfrak{b}} \eta\,\mathrm{d}x - \int_{\partial\mathfrak{b}} \eta n\cdot v\,\mathrm{d}\mathcal{H}^2(x) + \int_{\partial\mathfrak{b}} \ell_{\partial}\,\mathrm{d}\mathcal{H}^2(x) - \int_{\mathfrak{b}} s\,\mathrm{d}x \geq 0\,, \quad (10)$$

which we presume to hold for any choice of $\mathfrak{b}$. The boundary term ℓ_{∂} is a *scalar entropy flux*, while s is an *entropy source*. More in detail, ℓ_{∂} depends on x, t, and the boundary $\partial\mathfrak{b}$.

If in addition to $\dot{\eta}$ also s is bounded over $\mathcal{B}(t)$ at every t, and $\ell_{\partial}(\cdot,t)$ is continuous with respect to x at every t, by Cauchy's theorem we obtain that ℓ_{∂} depends on $\partial\mathfrak{b}$ only through n at all places in which n is well-defined, namely there exists a function $\tilde{\ell}$ such that $\ell_{\partial}(x,t) = \tilde{\ell}(x,t,n) = -\tilde{\ell}(x,t,-n)$. Moreover, ℓ is linear in n; it means that there exists a *vector entropy flux* $\tilde{\mathsf{h}}$ with values $\mathsf{h} = \tilde{\mathsf{h}}(x,t)$ such that

$$\ell_{\partial}(x,t) = \tilde{\ell}(x,t,n) = \tilde{\mathsf{h}}(x,t)\cdot n = \mathsf{h}\cdot n\,.$$

Consequently, we write the entropy inequality as

$$\int_{\mathfrak{b}} \dot{\eta}\,\mathrm{d}x + \int_{\partial\mathfrak{b}} \mathsf{h}\cdot n\,\mathrm{d}\mathcal{H}^2(x) - \int_{\mathfrak{b}} s\,\mathrm{d}x \geq 0\,. \quad (11)$$

We take $\tilde{\mathsf{h}}(\cdot,t) \in C^1(\mathcal{B},\mathbb{R}^3) \cup C(\bar{\mathcal{B}},\mathbb{R}^3)$ and assume that both $\dot{\eta}$ and s are continuous; so, due to the arbitrariness of $\mathfrak{b}$, we get the *local entropy inequality*

$$\dot{\eta} \geq s - \mathrm{div}\mathsf{h} \quad (12)$$

in $\mathcal{B}$.

Remark 2. A crucial step in the proof of Cauchy's theorem for fluxes is an estimate for the boundary flux (see common treatises, for example [45, Ch. 1]). Consequently, for the theorem itself an integral balance is not strictly necessary; it may be relaxed, in fact, to an inequality like (10), for example. This circumstance is the key point on which we base the whole argument developed in this paper.

8. The second law in terms of the free energy

We accept the following relations between heat flux, source, and their entropy-type counterparts:

$$s = \frac{r}{\vartheta}\,, \qquad \mathsf{h} = \frac{\mathsf{q}}{\vartheta} + \omega\,,$$

where ω is an extra entropy flux, with respect to what can be attributed to the heat flux q.

By inserting these relations into the local entropy inequality (12), we get

$$\vartheta\dot{\eta} + \vartheta\mathrm{div}\omega - \frac{1}{\vartheta}\mathsf{q}\cdot\nabla\vartheta \geq r - \mathrm{div}\mathsf{q}\,.$$

With ψ the *Helmoltz free energy density* defined by

$$\psi := e - \vartheta\eta,$$

we eventually get

$$\int_{\mathfrak{b}}(\dot{\psi} + \eta\dot{\vartheta})\,\mathrm{d}x - \mathcal{P}^{ext}_{\mathfrak{b}}(v,\dot{\mathsf{c}}) + \int_{\mathfrak{b}}(\vartheta^{-1}\mathsf{q}\cdot\nabla\vartheta - \vartheta\mathrm{div}\omega)\,\mathrm{d}x \leq 0\,, \tag{13}$$

which is a version of *the Clausius-Duhem inequality* that we exploit here as a source of all ingredients describing the motion of bodies with phase transitions.

Remark 3. In non-isothermal setting, still under large strain regime, but with no phase transitions and the extra entropy flux ω, such an inequality has been introduced first by Coleman and Noll [21,22], and exploited for determining constitutive restrictions, admissibility conditions for the shock set, and stability. Here, we extend such a view and assign a further role to the Clausius-Duhem inequality.

9. Structure invariance under the action of diffeomorphism-based changes of observers: derivation of Gurtin's postulate

9.1. Free energy as a density of the volume form

The free energy density ψ is a function of state ς *left unspecified* for the moment. Also, ψ is a density associated with the volume form. Thus, according to a proposal in [46], we assume that ψ varies tensorially under the action of f_s on the ambient space. By interpreting such a tensoriality as in [38], we consider the change $\dot{\psi} \longmapsto \dot{\psi}^{\diamond}$, where

$$\dot{\psi} \longmapsto \dot{\psi}^{\diamond} = \dot{\psi} + \varphi(\varsigma;\nabla\bar{\mathsf{v}},\mathfrak{v},\nabla\mathfrak{v},\dots) \tag{14}$$

and φ is a state function that depends also on $\nabla\bar{\mathsf{v}}$, $\mathfrak{v}$, $\nabla\mathfrak{v}$, and possibly on higher-order derivatives of v and $\mathfrak{v}$, as indicated by the presence of dots. Precisely, $\dot{\psi}^{\diamond}$ is a pull-back to the observer $\mathcal{O}$ of the time rate of ψ evaluated by another observer $\mathcal{O}'$. The relation (14) is a counterpart for $\dot{\psi}$ of (5) and (6).

Also, φ is chosen to be independent of $\bar{\mathsf{v}}$ alone; when f_s is an orientation-preserving isometric map $\varphi = 0$ by assumption.

Remark 4. Imposing $\varphi = 0$ when f_s represents a rigid-body motion is equivalent to require free energy objectivity (that is invariance under the action of $SO(3)$).

Remark 5. Considering φ to be independent of $\bar{\mathsf{v}}$ alone is tantamount to require (superposed) Galilean invariance for φ. Indeed, consider φ to be such that

$$\varphi = \varphi(\varsigma;\bar{\mathsf{v}},\nabla\bar{\mathsf{v}},\mathfrak{v},\nabla\mathfrak{v},\dots)$$

and superpose a further Galilean change of observer so that v becomes $\bar{\mathsf{v}}+a$, with $a \in \mathbb{R}^3$ a constant vector field. Impose now that φ be Galilean invariant under this superposed change of observer. It means that

$$\varphi(\varsigma;\bar{\mathsf{v}},\nabla\bar{\mathsf{v}},\mathfrak{v},\nabla\mathfrak{v},\dots) = \varphi(\varsigma;\bar{\mathsf{v}}+a,\nabla\bar{\mathsf{v}},\mathfrak{v},\nabla\mathfrak{v},\dots)$$

for any a. Thus, $\varphi = \varphi(\varsigma;\nabla\bar{\mathsf{v}},\mathfrak{v},\nabla\mathfrak{v},\dots)$.

Remark 6. The nature of φ is specified when we assign the list of state variables entering ψ. For example, assume $\psi = \tilde{\psi}(x,g,\mathsf{c},\nabla\mathsf{c},\vartheta)$, with g the spatial metric, and require tensoriality to ψ in the sense specified in [46], namely impose that after a change of observer the energy should be the same evaluated over $\mathsf{f}^{*}_{t,s}\circ g$. Consider, in addition, the pertinent changes of c and $\nabla\mathsf{c}$. Also, leave invariant the temperature. Thus, by computing the time derivative of ψ at $t = s$ we get

$$\dot{\psi}^{\diamond} = \dot{\psi} + \frac{\partial\psi}{\partial g}\cdot\mathfrak{L}_{\bar{\mathsf{v}}}g + \frac{\partial\psi}{\partial\mathsf{c}}\mathfrak{v} + \frac{\partial\psi}{\partial\nabla\mathsf{c}}\cdot\nabla\mathfrak{v}\,, \tag{15}$$

where $\mathfrak{L}_{\bar{\mathsf{v}}}g$ is the Lie derivative of g along $\bar{\mathsf{v}}$; so in this specific case

$$\varphi(\varsigma;\nabla\bar{\mathsf{v}},\mathfrak{v},\nabla\mathfrak{v},\dots) = \frac{\partial\psi}{\partial g}\cdot\mathfrak{L}_{\bar{\mathsf{v}}}g + \frac{\partial\psi}{\partial\mathsf{c}}\mathfrak{v} + \frac{\partial\psi}{\partial\nabla\mathsf{c}}\cdot\nabla\mathfrak{v}\,.$$

Since ψ involves also the entropy density, accepting a rule like (14) implies the acceptance of a transformation given by

$$\dot{\eta} \longmapsto \dot{\eta}^{\diamond} = \dot{\eta} + \bar{\varphi}(\varsigma;\nabla\bar{\mathsf{v}},\mathfrak{v},\nabla\mathfrak{v},\dots)\,, \tag{16}$$

where $\bar{\varphi}$ is a different function from φ but with the same properties.

Assumption 9.1. We assume that both φ and $\bar{\varphi}$ are *bounded* over $\mathcal{B}(t)$ at every instant.

We leave invariant the temperature and the whole term $\mathsf{q}\cdot\nabla\ln\vartheta$ appearing in the inequality (13).

Remark 7. Invariance under diffeomorphism-based changes of observer has been taken in [46] for the first law of thermodynamics, while in [38,39] for the second law in isothermal setting. In those cases, however, the list ς of state variables has been specified, while here ς is left unspecified while deriving balance equations. The circumstance maintains conceptually distinguished the balance equations from constitutive laws.

Remark 8. If we think in terms of a discrete-to-continuum view, thus starting from molecular dynamics and reaching a continuum scheme as a coarse-grained representation of the molecular agitation, we may see that the heat flux depends on relative velocities, namely, fluctuations with respect to the average velocity of a molecular cluster (see [47] and the amended translation [48]). Consequently, although the records of velocity can vary from an observer to another, due to the action of f_s, differences of velocities (fluctuations) do not vary.

9.2. Covariance principle in dissipative setting

Write in short the inequality (13) as $\mathfrak{A} \leq 0$ and consider it as referred to a given observer $\mathcal{O}$. For another observer $\mathcal{O}'$ the inequality writes (say) $\mathfrak{A}' \leq 0$. Assume that the change $\mathcal{O} \longrightarrow \mathcal{O}'$ is induced by $\mathsf{f}_s \in \mathrm{Diff}\left(\mathbb{R}^3,\mathbb{R}^3\right)$, with consequences on v, $\dot{\mathsf{c}}$, and $\dot{\psi}$ already described.

The pull-back of $\mathfrak{A}'$ into $\mathcal{O}$ along the action of f_s gives a relation that, according to Eqs. (5), (6), and (14), reads $\mathfrak{A}^{\bullet} \leq 0$, with $\mathfrak{A}^{\bullet} = \mathfrak{A} + \mathfrak{A}^{\dagger}$, where $\mathfrak{A}^{\dagger}$ involves the rates $\bar{\mathsf{v}}$ and $\dot{\mathfrak{v}}$.

If we reverse the process and consider the change $\mathcal{O}' \longrightarrow \mathcal{O}$ as induced by f_s^{-1}, the pull-back of $\mathfrak{A} \leq 0$ into the frame defining $\mathcal{O}'$ reads $\mathfrak{A}' + \mathfrak{A}^{\ddagger} \leq 0$, where $\mathfrak{A}^{\ddagger}$ *is in principle different from* $\mathfrak{A}^{\dagger}$.

We impose the following *covariance principle in dissipative setting*: it states that both $\mathfrak{A}^{\dagger}$ and $\mathfrak{A}^{\ddagger}$ are *always* non-positive.

Axiom 9.1. *In any diffeomorphism-based change of observer, the additional term arising after pulling-back the Clausius-Duhem inequality (13) evaluated by the second observer in a frame defining the first observer is always non positive and vanishes when observer changes are rigid.*

A previous version of this axiom dates back 2013 [38]; it was introduced with reference to finite strain plasticity. Then, it has been rewritten for general classical field theories involving maps between finite-dimensional Riemannian manifolds [39]. In both cases, it has been referred to a non-isothermal Clausius-Duhem inequality written in Lagrangian representation; its expression also involved the so-called *relative power*, which extends the notion of external power to cover possible structural mutations in the body structure, due to the occurrence of evolving defects. In this case, indeed, a Lagrangian representation may profitably exploit a family of infinitely many reference configurations that differ one another only by a (say) defect pattern.

Differences with what has been discussed in [38,39] (see also [40]) are as follows: (i) We refer to a full Eulerian representation of the second law. (ii) We consider a non-isothermal setting. (iii) We do not refer to the relative power because we do not include any reference configuration (however, we could account for it, even by resorting to the inverse motion, when, for example, we would like to describe the relative motion of a solid body embedded into a fluid). (iv) More important: in [38,39] the state variables are specified before stating a rule analogous to (14); at variance, here such a list of state variables is *left unspecified* at first; the specification of state variables enters into play only when we evaluate constitutive restrictions, while it shares no matter with the first consequences of the covariance axiom in dissipative setting. This peculiar aspect allows us—we repeat—to maintain distinguished balance laws from constitutive issues.

9.3. First consequence of the covariance axiom: representation of first-neighbor interactions and local balances

From inequality (13), the covariance axiom under the rules of changes of observers considered implies

$$\int_{\mathfrak{b}} (\varphi + \bar{\varphi})\, \mathrm{d}x - \mathcal{P}^{ext}_{\mathfrak{b}}(\bar{\mathrm{v}}, \mathfrak{v}) \le 0\,. \tag{17}$$

- **Step 1**. Fix $\mathfrak{v} = 0$, leaving $\bar{\mathrm{v}}$ to be arbitrary. The inequality (17) reduces to

$$\int_{\mathfrak{b}} (\varphi + \bar{\varphi})\Big|_{\mathfrak{v}=0} \mathrm{d}x - \int_{\mathfrak{b}} b^{\ddagger} \cdot \bar{\mathrm{v}}\, \mathrm{d}x - \int_{\partial\mathfrak{b}} \mathrm{t}_{\partial} \cdot \bar{\mathrm{v}}\, \mathrm{d}\mathcal{H}^2(x) \le 0\,.$$

Under Assumptions 4.1 and 9.1, if $|b^{\ddagger}|$ is also bounded over $\mathcal{B}$ and t_{∂} is continuous with respect to x, Cauchy's theorem on fluxes, applied to $\hat{\mathrm{t}}_{\partial} := -\mathrm{t}_{\partial}$, assures that t_{∂} depends on $\partial\mathfrak{b}$ only through the normal n at all points where it is well-defined, that is there exists a vector-valued map $\tilde{\mathrm{t}}$ such that $\mathrm{t}_{\partial} = \tilde{\mathrm{t}}(x,t,n) = -\tilde{\mathrm{t}}(x,t,-n)$, which is also linear with respect to n, namely there exists a second-rank tensor-valued map $\tilde{\boldsymbol{\sigma}}$ with values $\boldsymbol{\sigma} = \tilde{\boldsymbol{\sigma}}(x.t)$ such that the standard relation

$$\tilde{\mathrm{t}}(x,t,n) = \tilde{\boldsymbol{\sigma}}(x,t)n = \boldsymbol{\sigma} n$$

holds true. When $\tilde{\boldsymbol{\sigma}}(\cdot,t) \in C^1(\mathcal{B}, \mathbb{R}^3 \otimes \mathbb{R}^3) \cup C(\bar{\mathcal{B}}, \mathbb{R}^3 \otimes \mathbb{R}^3)$, we compute

$$\int_{\mathfrak{b}} (\varphi + \bar{\varphi})\Big|_{\mathfrak{v}=0} \mathrm{d}x - \int_{\mathfrak{b}} ((b^{\ddagger} + \mathrm{div}\boldsymbol{\sigma}) \cdot \bar{\mathrm{v}} + \boldsymbol{\sigma} \cdot \nabla\bar{\mathrm{v}})\, \mathrm{d}x \le 0\,.$$

Thus, the arbitrariness of $\bar{\mathrm{v}}$ and the independence of $(\varphi + \bar{\varphi})$ on $\bar{\mathrm{v}}$ imply the local balance of forces

$$b^{\ddagger} + \mathrm{div}\boldsymbol{\sigma} = 0\,. \tag{18}$$

As already recalled, the standard bulk force $b^{\ddagger}$ is traditionally assumed to be sum of inertial, b^{in}, and non-inertial, b, components, with b^{in} defined to be such that

$$\frac{\mathrm{d}}{\mathrm{d}t}\int_{\mathcal{B}} \frac{1}{2}\rho|v|^2\, \mathrm{d}x - \int_{\partial\mathcal{B}} \frac{1}{2}\rho|v|^2(v\cdot n)\, \mathrm{d}\mathcal{H}^2(x) + \int_{\mathcal{B}} b^{in}\cdot v\, \mathrm{d}x = 0\,,$$

for any choice of compactly supported velocity fields; ρ is mass density. The arbitrariness of v and the standard transport theorem (recall that we are working in Eulerian representation, so $\mathcal{B}$ is the current configuration and depends on time) imply the identification $b^{in} = -\rho\dot{v}$ to within powerless (Corioli's type) terms.

- **Step 2**. Consider $\mathfrak{v} \neq 0$ and arbitrary as $\bar{\mathrm{v}}$. With the results of Step 1, the inequality (17) reads now

$$\int_{\mathfrak{b}} (\varphi + \bar{\varphi})\, \mathrm{d}x - \int_{\mathfrak{b}} (\boldsymbol{\sigma} \cdot \nabla\bar{\mathrm{v}} + \beta\mathfrak{v})\, \mathrm{d}x - \int_{\partial\mathfrak{b}} \tau_{\partial}\mathfrak{v}\, \mathrm{d}\mathcal{H}^2(x) \le 0\,.$$

Under Assumptions 4.1 and 9.1, and the boundedness of $\int_{\mathfrak{b}} \boldsymbol{\sigma} \cdot \nabla\bar{\mathrm{v}}\ \mathrm{d}x$ assured by the results in Step 1, if $|\beta|$ is also bounded over $\mathcal{B}(t)$ at every instant t and τ_{∂} is continuous as a function of x, Cauchy's theorem on fluxes, applied to $\hat{\tau}_{\partial} := -\tau_{\partial}$, allows us to assures that τ_{∂} depends on $\partial\mathfrak{b}$ only through n at all points where n is well-defined, namely there exists a function $\tilde{\tau}$ such that $\tau_{\partial} = \tilde{\tau}(x,t,n) = -\tilde{\tau}(x,t,-n)$, which is also linear with respect to n, so that there exists a vector-valued map $\tilde{\mathfrak{h}}$ with values $\mathfrak{h} = \tilde{\mathfrak{h}}(x.t)$ such that

$$\tilde{\tau}(x,t,n) = \tilde{\mathfrak{h}}(x,t)\cdot n = \mathfrak{h}\cdot n\,.$$

When $\tilde{\mathfrak{h}}(\cdot,t) \in C^1(\mathcal{B}, \mathbb{R}^3) \cup C(\bar{\mathcal{B}}, \mathbb{R}^3)$, we compute

$$\int_{\mathfrak{b}} (\varphi + \bar{\varphi})\, \mathrm{d}x - \int_{\mathfrak{b}} (\boldsymbol{\sigma} \cdot \nabla\bar{\mathrm{v}} + \mathfrak{v}(\beta + \mathrm{div}\mathfrak{h}) + \mathfrak{h}\cdot\nabla\mathfrak{v})\, \mathrm{d}x \le 0\,.$$

Since $(\varphi+\bar{\varphi})$ depend on $\mathfrak{v}$, we can only say that there is a function $\tilde{z}$, with values $z := \tilde{z}(x,t)$ such that

$$\beta + \mathrm{div}\mathfrak{h} = z \tag{19}$$

and the inequality

$$\int_{\mathfrak{b}} (\varphi + \bar{\varphi})\, \mathrm{d}x - \int_{\mathfrak{b}} (\boldsymbol{\sigma} \cdot \nabla\bar{\mathrm{v}} + z\mathfrak{v} + \mathfrak{h}\cdot\nabla\mathfrak{v})\, \mathrm{d}x \le 0 \tag{20}$$

holds true for every choice of $\mathfrak{v}$, $\nabla\mathfrak{v}$, and $\nabla\bar{\mathrm{v}}$. The equality sign holds only when $\bar{\mathrm{v}}$ is determined by an isometry, namely $\bar{\mathrm{v}}(x,t) = \hat{\mathbf{c}}(t) + \mathbf{q}(t)\times(x-x_0)$, where x_0 is fixed and arbitrarily chosen in space, while $\hat{c}(t)$ and $q(t)$ are translational and rotational velocities, so that $\mathfrak{v} = 0$.

We remark once again that in our derivation of Eq. (19), otherwise postulated by Gurtin in [23] (and called a "microforce balance" in that paper), we do not touch constitutive issues.

9.4. Exploiting the invariance requirement for the second law in a different way

We can revisit Step 1 above by restricting $\bar{\mathrm{v}}$ to $\hat{\mathbf{c}}(t) + \mathbf{q}(t)\times(x-x_0)$. In this case $\mathfrak{v} = 0$, $\varphi = 0$, as already assumed, and the inequality (17) reduces to the identity

$$\mathcal{P}^{ext}_{\mathfrak{b}}(\hat{\mathbf{c}}(t) + \mathbf{q}(t)\times(x-x_0), 0) = 0$$

for any choice of $\mathfrak{b}$, $\hat{c}(t)$, and $q(t)$. Thus, we recover the setting described by Noll [49], namely the invariance requirement for the external power of standard forces under rigid-body type changes of observers. The arbitrariness of $\mathfrak{b}$ implies the integral balance of forces

$$\int_{\mathfrak{b}} b^{\ddagger}\, \mathrm{d}x + \int_{\partial\mathfrak{b}} \mathrm{t}_{\partial}\, \mathrm{d}\mathcal{H}^2(x) = 0 \tag{21}$$

and the one of couples, namely,

$$\int_{\mathfrak{b}} (x-x_0)\times b^{\ddagger}\, \mathrm{d}x + \int_{\partial\mathfrak{b}} (x-x_0)\times \mathrm{t}_{\partial}\, \mathrm{d}\mathcal{H}^2(x) = 0\,. \tag{22}$$

Standard regularity assumptions already recalled in the previous sections allow us to derive common results, such as dependence of t_{∂} on $\partial\mathfrak{b}$ only through n, action-reaction principle, linearity with respect to n, which is the existence of a stress tensor $\boldsymbol{\sigma}$, and the pointwise balance

(18), when $b^{\ddagger}(\cdot,t)$ and $\boldsymbol{\sigma}(\cdot,t)$ have the regularity mentioned above. Thus, from Eq. (22) and the local balance of forces, at every t and x we get

$$\boldsymbol{\sigma}\in \mathrm{Sym}(\mathbb{R}^3,\mathbb{R}^3)\ , \tag{23}$$

with $\mathrm{Sym}(\mathbb{R}^3,\mathbb{R}^3)$ the space of symmetric second-rank tensors mapping $\mathbb{R}^3$ onto itself.

An analogous invariance argument cannot be adopted for c because, being a pseudoscalar, it is insensitive to rigid-body type changes of observers. At variance, for different types of microstructural descriptors, the procedure based on external power invariance can be adopted and leads to a nonstandard integral balance of couples, as we summarize in Section 11 (see also [36,37]).

9.5. Symmetry of σ from the inequality (20)

Let us identify $\bar{\mathrm{v}}(x,t)$ with $v(x,t)$ and $\mathfrak{v}$ with $\dot{\mathsf{c}}$. The term $\boldsymbol{\sigma}\cdot\nabla\bar{\mathrm{v}}+z\mathfrak{v}+\mathfrak{h}\cdot\nabla\mathfrak{v}$ in (20) becomes $\boldsymbol{\sigma}\cdot\nabla v+z\dot{\mathsf{c}}+\mathfrak{h}\cdot\nabla\dot{\mathsf{c}}$; it is the internal power density: the power performed in the relative change of place of neighboring material elements and in the development of phase transitions, when first-neighbor interactions are accounted for.

When $\bar{\mathrm{v}}(x,t)=\hat{\mathbf{c}}(t)+\mathbf{q}(t)\times(x-x_0)$, we have $\varphi=0$, $\mathfrak{v}=0$, and the identity sign holds in (20). Thus, arbitrariness of $\mathfrak{b}$ and continuity of $\boldsymbol{\sigma}$ imply

$$\boldsymbol{\sigma}\cdot W=0\ ,$$

where $W=q\times$ is skew-symmetric. Identity to zero and arbitrariness of W imply once again the inclusion (23).

Attributing to the sum $\boldsymbol{\sigma}\cdot\nabla v+z\dot{\mathsf{c}}+\mathfrak{h}\cdot\nabla\dot{\mathsf{c}}$ the role of internal power is justified by the identity

$$\mathcal{P}^{ext}_{\mathfrak{b}}(v,\dot{\mathsf{c}})=\int_{\mathfrak{b}}(\boldsymbol{\sigma}\cdot\nabla v+z\dot{\mathsf{c}}+\mathfrak{h}\cdot\nabla\dot{\mathsf{c}})\,\mathrm{d}x\ , \tag{24}$$

which follows by using the Gauss theorem and exploiting the validity of the pointwise balances.

Remark 9. In other common approaches to multi-field descriptions of non-simple bodies (see, e.g., [33]), the identity (24) is taken as a basic principle. Accepting it, however, implies presuming a priori $\mathfrak{h}$ and z, *without* deriving them. In other words, initial acceptance of (24) would reduce essentially to take Gurtin's postulate expressed in a weak form, which is unnecessary, as we have shown here.

10. Further consequences of the second law

Below, for the sake of simplicity, we restrict the analysis to conducting viscous fluids with phase transitions. Extensions concerning constitutive choices are straightforward. If we develop the analysis in a purely Eulerian representation, so without involving any reference configuration, as we do here, in the case of solids the spatial metric enters the list of state variables (see [46]). However, we leave out this case in the following developments because we just aim at showing skeletal conceptual structures.

Consider the entropy extra flux ω. We assume

$$\omega=\mu\mathsf{h}_{\mathsf{c}}+\varpi\ , \tag{25}$$

where μ is the *chemical potential* given by the difference $\mu=\mu_{\mathsf{c}}-\mu_{1-\mathsf{c}}$ between the chemical potentials pertaining to the phase with concentration c and its complement, respectively. Here μ is taken to be a continuous and continuously differentiable function. ϖ is the remaining part of the entropy extra flux not associated with the transport described by h_{c}, rather possibly determined by further microstructural effects; it requires an appropriate constitutive law.

By taking into account Eqs. (24), (25), and (4), continuity of densities in the volume integrals and arbitrariness of $\mathfrak{b}$ imply from (13) the local inequality

$$\dot{\psi}-\dot{\vartheta}\eta-\boldsymbol{\sigma}\cdot\nabla v-(z+\mu)\dot{\mathsf{c}}-\mathfrak{h}\cdot\nabla\dot{\mathsf{c}}+\frac{1}{\vartheta}\mathsf{q}\cdot\nabla\vartheta-\vartheta\,\mathrm{div}\varpi-\mathsf{h}_{\mathsf{c}}\cdot\nabla\mu-\mathsf{c}\,\mathrm{div}v\le 0\ . \tag{26}$$

We consider volume-preserving flows, a circumstance described by the *internal constraint*

$$\mathrm{div}\,v=0\ . \tag{27}$$

To account for it we adopt the standard additive decomposition of $\boldsymbol{\sigma}$ into active and reactive components, the former taken to be the sum of energetic ($\boldsymbol{\sigma}^e$), meaning determined by ψ, and dissipative ($\boldsymbol{\sigma}^d$) components, the latter indicated by a superscript r. So, we have

$$\boldsymbol{\sigma}=\boldsymbol{\sigma}^r+\boldsymbol{\sigma}^e+\boldsymbol{\sigma}^d\ , \tag{28}$$

with $\boldsymbol{\sigma}^r$ presumed to be powerless, namely

$$\boldsymbol{\sigma}^r\cdot\nabla v=0 \tag{29}$$

for any choice of ∇v. This implies the standard result

$$\boldsymbol{\sigma}^r=-\pi I\ , \tag{30}$$

where $\pi\in\mathbb{R}$ is the pressure, and I the unit tensor (when the frame of reference is not orthonormal, I is substituted by the specific spatial metrics chosen). So, the inequality (26) reduces to

$$\dot{\psi}-\dot{\vartheta}\eta-(\boldsymbol{\sigma}^e+\boldsymbol{\sigma}^d)\cdot\nabla v-(z+\mu)\dot{\mathsf{c}}-\mathfrak{h}\cdot\nabla\dot{\mathsf{c}}+\frac{1}{\vartheta}\mathsf{q}\cdot\nabla\vartheta-\vartheta\,\mathrm{div}\varpi-\mathsf{h}_{\mathsf{c}}\cdot\nabla\mu\le 0\ . \tag{31}$$

We assume that ψ, η, z, μ, $\mathfrak{h}$ all depend on the list

$$(\mathsf{c},\nabla\mathsf{c},\vartheta)\ .$$

We thus distinguish two cases that we think to be of particular prominence. In discussing them, for the sake of simplicity we do not consider viscous-type components for $\mathfrak{h}$ and z. Taking them into account is rather straightforward.

10.1. Case 1: $\varpi=0$

By computing $\dot{\psi}$, the inequality (31) becomes

$$\begin{aligned}\left(\frac{\partial\psi}{\partial\vartheta}+\eta\right)\dot{\vartheta}-\left(\nabla\mathsf{c}\otimes\frac{\partial\psi}{\partial\nabla\mathsf{c}}+\boldsymbol{\sigma}^e\right)\cdot\nabla v+\left(\frac{\partial\psi}{\partial\mathsf{c}}-(z+\mu)\right)\dot{\mathsf{c}}\\ +\left(\frac{\partial\psi}{\partial\nabla\mathsf{c}}-\mathfrak{h}\right)\cdot\nabla\dot{\mathsf{c}}-\boldsymbol{\sigma}^d\cdot\nabla v+\frac{1}{\vartheta}\mathsf{q}\cdot\nabla\vartheta-\mathsf{h}_{\mathsf{c}}\cdot\nabla\mu\le 0\ .\end{aligned} \tag{32}$$

The arbitrariness of time rates involved implies the identities

$$\eta=-\frac{\partial\psi}{\partial\vartheta}\ ,\quad \boldsymbol{\sigma}^e=-\nabla\mathsf{c}\otimes\frac{\partial\psi}{\partial\nabla\mathsf{c}}\ ,\quad z+\mu=\frac{\partial\psi}{\partial\mathsf{c}}\ ,\quad \mathfrak{h}=\frac{\partial\psi}{\partial\nabla\mathsf{c}}\ , \tag{33}$$

and

$$\boldsymbol{\sigma}^d\cdot\nabla v-\frac{1}{\vartheta}\mathsf{q}\cdot\nabla\vartheta+\mathsf{h}_{\mathsf{c}}\cdot\nabla\mu\ge 0\ . \tag{34}$$

This last (reduced) inequality is in general compatible with a structure of $\boldsymbol{\sigma}^d$, q, and h_{c} that is a linear combination of ∇v, $\nabla\vartheta$, and $\nabla\mu$, with coefficients that are different for $\boldsymbol{\sigma}^d$, q, and h_{c}. Here, we accept the simplest option for the sake of simplicity:

$$\boldsymbol{\sigma}^d=\bar{\nu}\nabla v\ ,\qquad \mathsf{q}=-\kappa\nabla\vartheta\ ,\qquad \mathsf{h}_{\mathsf{c}}=\alpha\nabla\mu\ , \tag{35}$$

with $\bar{\nu}$, κ, and α positive constants.

Also, the balance of couples (23) implies that the dyad $\nabla\mathsf{c}\otimes\frac{\partial\psi}{\partial\nabla\mathsf{c}}$ must be symmetric. So, when $\frac{\partial\psi}{\partial\nabla\mathsf{c}}$ is proportional to $\nabla\mathsf{c}$ the symmetry is satisfied and we have

$$\psi=f(\mathsf{c},\vartheta)+\frac{1}{2}\mathsf{a}(x,\mathsf{c},\vartheta)|\nabla\mathsf{c}|^2\ , \tag{36}$$

with $\mathsf{a}(\cdot,\cdot,\cdot)$ a differentiable function. The expression (36) has the Ginzburg–Landau free energy structure. When $\mathsf{a}(x,\mathsf{c},\vartheta)=\bar{\mathsf{a}}=$ cost, the balance of mass (4) becomes

$$\dot{\mathsf{c}}=-\alpha\,\Delta\Big(\frac{\partial f}{\partial\mathsf{c}}-\beta-\bar{\mathsf{a}}\,\Delta\mathsf{c}\Big)\ . \tag{37}$$

In particular, when $\beta=0$ and the process considered is isothermal, so that $\psi=\tilde{\psi}(\mathsf{c},\nabla\mathsf{c})$, Eq. (37) reduces to

$$\dot{\mathsf{c}}=\alpha\,\Delta\big(\bar{\mathsf{a}}\Delta\mathsf{c}-f'\big)\ , \tag{38}$$

which is in essence the Cahn-Hilliard equation, where the prime indicates derivative of f with respect to c. Further viscous regularization is admissible by considering for $\mathfrak{h}$ a dissipative component that we leave out here for the sake of simplicity.

Eq. (38) does not account directly for the activation of the transition. As it is chosen in some standard descriptions of plastic phenomena, we could refer to an activation criterion saying that the right-hand side term of Eq. (38) belongs to the subdifferential of the indicator function of some admissibility set, which in the present case can be $[0,1]$ or some its sub-interval. Details on this (convex analysis) issue, primarily referred to first order phase transitions, can be found in [50, Ch. 11].

Also, if we investigate existence of (at least) weak solutions for (37), coupled with the balance of forces supplemented by pertinent constitutive structures, we need to involve a maximum principle assuring that c remains in $[0,1]$ (see, for example, analyses in [51], although related to a different physical setting).

By taking into account the identity (24) and exploiting the arbitrariness of $\mathfrak{b}$ and the continuity of the integral densities, from the energy balance (9) we get the local form

$$\dot{e}-\boldsymbol{\sigma}\cdot\nabla v-z\dot{\mathsf{c}}-\mathfrak{h}\cdot\nabla\dot{\mathsf{c}}+\mathrm{div}\,\mathsf{q}-r=0\,. \tag{39}$$

Due to the constitutive restrictions (33) and (35), for non-viscous bodies (that is when $\boldsymbol{\sigma}^d=0$), the local balance (39) changes into

$$\frac{\partial e}{\partial\vartheta}\dot{\vartheta}+\vartheta\left(\frac{\partial\eta}{\partial\mathsf{c}}\dot{\mathsf{c}}+\frac{\partial\eta}{\partial\nabla\mathsf{c}}\cdot\nabla\dot{\mathsf{c}}-\nabla\mathsf{c}\otimes\frac{\partial\eta}{\partial\nabla\mathsf{c}}\cdot\nabla v\right)+\mu\dot{\mathsf{c}}+\kappa\,\Delta\vartheta-r=0\,. \tag{40}$$

Since c refers to a spatial scale λ, so it is of order λ, and we write $O(\lambda)$ for this, given a differentiable function $\ell(\mathsf{c},\nabla\mathsf{c})$, its partial derivatives are of the order λ too, namely

$$\frac{\partial\ell}{\partial\mathsf{c}}\sim O(\lambda)\qquad\text{and}\qquad\frac{\partial\ell}{\partial\nabla\mathsf{c}}\sim O(\lambda)\,.$$

Thus, since $\eta=\tilde{\eta}(\mathsf{c},\nabla\mathsf{c},\vartheta)$ and $\mu=\frac{\partial\psi}{\partial\mathsf{c}}-z$, we have

$$\frac{\partial\eta}{\partial\mathsf{c}}\dot{\mathsf{c}}\sim O(\lambda^2)\,,\quad\frac{\partial\eta}{\partial\nabla\mathsf{c}}\cdot\nabla\dot{\mathsf{c}}\sim O(\lambda^2)\,,\quad\nabla\mathsf{c}\otimes\frac{\partial\eta}{\partial\mathsf{c}}\cdot\nabla v\sim O(\lambda^2)\,,\quad\mu\dot{\mathsf{c}}\sim O(\lambda^2)\,.$$

Consequently, to within terms of order $O(\lambda^2)$, Eq. (40) reduces to the standard parabolic description of heat propagation

$$\mathfrak{c}\,\dot{\vartheta}-\kappa\,\Delta\vartheta-r=0\,,$$

where $\mathfrak{c}:=\frac{\partial e}{\partial\vartheta}$ is the specific heat.

Neglecting $O(\lambda^2)$ terms is a condition characterizing a range that we can call the one of *nearly isentropic* flows in the present setting.

10.2. Case 2: $\varpi\neq 0$: emergence of non-Fourier heat propagation

When $\varpi\neq 0$, with the assumptions above we obtain the constitutive restrictions (33), while the inequality (34) changes into

$$\boldsymbol{\sigma}^d\cdot\nabla v-\frac{1}{\vartheta}\mathsf{q}\cdot\nabla\vartheta+\mathsf{h}_{\mathsf{c}}\cdot\nabla\mu\geq\vartheta\,\mathrm{div}\varpi\,, \tag{41}$$

when viscous-type microstructural interactions are absent as in the previous section. The identities $(35)_1$ and $(35)_3$ are once again compatible with the inequality (41), while, under $(35)_1$ and $(35)_3$, the inequality itself is compatible with an extended structure for the heat flux given by

$$\mathsf{q}=-\kappa\nabla\vartheta+\bar{\mathsf{q}}\,, \tag{42}$$

where $\bar{\mathsf{q}}$ is an extra flux such that

$$\bar{\mathsf{q}}\cdot\nabla\vartheta+\vartheta^2\,\mathrm{div}\varpi=0\,.$$

Let us assume $\bar{\mathsf{q}}=\bar{\mathsf{q}}(\vartheta,\dot{\vartheta})$, with $\bar{\mathsf{q}}(\vartheta,0)=0$, meaning that $\bar{\mathsf{q}}$ has non-equilibrium character. Such a choice is minimalist; by Truesdell's equipresence principle we would be free to admit that $\bar{\mathsf{q}}$ depends on history and present values of all state variables and their derivatives; however, we try to maintain a skeletal structure, to sketch only the potentialities of what is discussed here. Thus, with the choice (42), the local energy balance (39) becomes

$$\mathfrak{c}\dot{\vartheta}+\vartheta\left(\frac{\partial\eta}{\partial\mathsf{c}}\dot{\mathsf{c}}+\frac{\partial\eta}{\partial\nabla\mathsf{c}}\cdot\nabla\dot{\mathsf{c}}-\nabla\mathsf{c}\otimes\frac{\partial\eta}{\partial\mathsf{c}}\cdot\nabla v\right)+\mu\dot{\mathsf{c}}-\kappa\,\Delta\vartheta+\frac{\partial\bar{\mathsf{q}}}{\partial\vartheta}\cdot\nabla\vartheta+\frac{\partial\bar{\mathsf{q}}}{\partial\dot{\vartheta}}\cdot\nabla\dot{\vartheta}-r=0\,. \tag{43}$$

In the nearly isentropic regime defined above, Eq. (43) reduces to

$$\mathfrak{a}\dot{\vartheta}-\kappa\,\Delta\vartheta+\mathfrak{a}_1\cdot\nabla\vartheta+\mathfrak{a}_2\cdot\nabla\dot{\vartheta}-r=0\,, \tag{44}$$

where $\mathfrak{a}_1:=\frac{\partial\bar{\mathsf{q}}}{\partial\vartheta}$ and $\mathfrak{a}_2:=\frac{\partial\bar{\mathsf{q}}}{\partial\dot{\vartheta}}$. Eq. (44) describes hyperbolic-type heat propagation. Its analogous has been derived in [44] by neglecting macroscopic strain and attributing the emergence of $\bar{\mathsf{q}}$ to the power due to microstructural interactions in the absence of external bulk actions. The result in [44] is independent of the type of microstructure. The hyperbolic character of Eq. (44) has been analyzed in [52] where the velocities of temperature propagation have been obtained when scalar and vector coefficients are constant. Analyses involving $\bar{\mathsf{q}}$ have been carried out in [53,54].

10.3. Gross-scale interactions

In both cases considered above, the balance of standard forces (18), with the identification $b^{in}=-\rho\dot{v}$, becomes

$$\rho\frac{\partial v}{\partial t}+(v\cdot\nabla)v-\bar{\nu}\Delta v=b-\nabla\pi-(\nabla\mathsf{c})\mathrm{div}\Big(\frac{\partial\psi}{\partial\nabla\mathsf{c}}\Big)-\frac{\partial\psi}{\partial\nabla\mathsf{c}}\Delta\mathsf{c}\,. \tag{45}$$

The last two terms in the previous balance are of the order λ^2, so to within $O(\lambda^2)$ terms, Eq. (45) reduces to the Navier–Stokes system with bulk external force b. When the viscosity $\bar{\nu}$ depends on temperature, Eq. (45) becomes

$$\rho\frac{\partial v}{\partial t}+(v\cdot\nabla)v-\bar{\nu}\Delta v-\frac{\mathrm{d}\bar{\nu}}{\mathrm{d}\vartheta}\nabla v\nabla\vartheta=b-\nabla\pi-(\nabla\mathsf{c})\mathrm{div}\Big(\frac{\partial\psi}{\partial\nabla\mathsf{c}}\Big)-\frac{\partial\psi}{\partial\nabla\mathsf{c}}\Delta\mathsf{c}\,. \tag{46}$$

If we neglect terms of the order $O(\lambda^2)$, the previous equation reduces to

$$\rho\frac{\partial v}{\partial t}+(v\cdot\nabla)v-\bar{\nu}\Delta v-\frac{\mathrm{d}\bar{\nu}}{\mathrm{d}\vartheta}\nabla v\nabla\vartheta+\nabla\pi=b\,. \tag{47}$$

11. Extending the results to a model-building framework for complex fluids

11.1. Morphology and changes of observers

The methodology constructed on the requirement of structure invariance of the Clausius-Duhem inequality under diffeomorphism-based changes of observer has an intrinsic perspective going far beyond what deals with Gurtin's postulate and the Cahn-Hilliard equation

To verify such a claim, consider a generic complex fluid, namely one endowed with *active* microstructure, which we leave unspecified for the sake of generality. The adjective *active* refers to the circumstance that microstructural events (as the phase transition described in the previous sections) occur and are driven by actions hardly representable in terms of standard stresses.

Examples range from fluids with densely scattered polymers or particles of other types (pollutants in general) to those suffering polarization under the action of external fields, to bubbly liquids, or liquid crystals. To account for a variety of different specific cases, we consider a differentiable field

$$\tilde{\nu}:\mathcal{B}\times\mathbb{R}\longmapsto\mathcal{M}\,,$$

where $\mathcal{M}$ is a geodetically complete, differentiable Riemannian manifold with finite dimension differing from an interval of the real line. The field $\tilde{\nu}$, with values $\nu:=\tilde{\nu}(x,t)\in\mathcal{M}$, brings at continuum scale geometrical features of a microstructure at a scale λ (ν can be a vector, a second-rank tensor, an element of the projective plane etc.). Thus, ν collects degrees of freedom that are *relative* to the material element at x in the instant t. So, when we consider a rigid translation of an observer in the physical space, ν is insensitive to it. At variance, when an observer rotates with respect to another, the two observers may record a microstructure as described by different values of ν (consider for example the case in which ν is a $3D$ vector). In this sense, ν is an observable entity.

Consider a change of observer in $\mathbb{R}^3$ due to a diffeomorphism $\mathsf{f}_{s,t}$ that is an isometry so that $\bar{\mathrm{v}}(x,t) = \hat{\mathbf{c}}(t) + \mathbf{q}(t) \times (x - x_0)$. We introduce a (possibly empty) family $\mathcal{F}$ of differentiable homeomorphisms given by

$$\mathcal{F} := \{\phi : SO(3) \times \mathbb{R} \longrightarrow \mathrm{Diff}\,(\mathcal{M}, \mathcal{M})\} \ , \tag{48}$$

where $\mathrm{Diff}\,(\mathcal{M},\mathcal{M})$ is the group of diffeomorphisms mapping $\mathcal{M}$ onto itself. ϕ takes values $\phi(\mathbf{Q}_\epsilon) \in \mathrm{Diff}\,(\mathcal{M},\mathcal{M})$, with $\mathbf{Q}_\epsilon \in SO(3)$, $\epsilon \in \mathbb{R}$, and $\mathbf{Q}_0 = identity$. In particular, ϕ transfers over $\mathcal{M}$ a possible discrepancy on the observation of microstructure between two observers rotating relatively one with respect to the other.

We indicate by ξ the time rate of ν in Eulerian representation and we have $\dot{\overline{D\nu}} = D\xi - D\nu D\upsilon$. After an isometry-based change of observer in $\mathbb{R}^3$, the counterpart of $\upsilon^\diamond$ for ξ is

$$\xi^\diamond := \xi + \mathcal{A}(\nu)\mathbf{q} \ , \tag{49}$$

where $\mathbf{q}$ is the axial vector of the skew-symmetric second-rank tensor $\mathbf{Q}_\epsilon^\top \dot{\mathbf{Q}}_\epsilon\big|_{\epsilon=0}$ and, when the set $\mathcal{F}$ is not empty, with $\nu_{\phi(\mathbf{Q}_\epsilon)}$ the value of ν after the action of $\phi\left(\mathbf{Q}_\epsilon\right) \in \mathrm{Diff}\,(\mathcal{M},\mathcal{M})$, the linear operator $\mathcal{A}\left(\nu\right) \in \mathrm{Hom}\left(\mathbb{R}^3, T_\nu\mathcal{M}\right)$ is given by

$$\mathcal{A}\left(\nu\right) = \frac{\mathrm{d}\nu_{\phi(\mathbf{Q}_\epsilon)}}{\mathrm{d}\mathbf{Q}_\epsilon}\frac{\mathrm{d}\mathbf{Q}_\epsilon}{\mathrm{d}\mathbf{q}_\epsilon}\Big|_{\epsilon=0} \ , \tag{50}$$

after choosing $\epsilon = s - t$ (recall that $\mathbf{Q}_\epsilon = \exp(\mathsf{e}\mathsf{q}_\epsilon)$, with e the third-rank alternating index in $3D$ space) [34,36].

Also, always with $\bar{\mathrm{v}}(x,t) = \hat{\mathbf{c}}(t) + \mathbf{q}(t) \times (x - x_0)$, a counterpart of the above assumptions that φ and $\bar{\varphi}$ vanish under rigid-body motions is

$$\varphi = \varphi(\varsigma, \mathbf{q}\times, \mathcal{A}\mathbf{q}, \dots) = 0 \ , \qquad \bar{\varphi} = \bar{\varphi}(\varsigma, \mathbf{q}\times, \mathcal{A}\mathbf{q}, \dots) = 0 \ ,$$

for any $\mathbf{q}$.

However, besides this special case, the general change of observer in $\mathbb{R}^3$ is described by $\mathsf{f}_{s,t} \in \mathrm{Diff}(\mathbb{R}^3,\mathbb{R}^3)$. Thus, we extend $\mathcal{F}$ to

$$\hat{\mathcal{F}} := \left\{\hat{\phi} : \mathrm{Diff}(\mathbb{R}^3,\mathbb{R}^3) \times \mathbb{R}^2 \longrightarrow \mathrm{Diff}\,(\mathcal{M},\mathcal{M})\right\} \ , \tag{51}$$

where $\hat{\phi}$ tales values $\hat{\phi}(\mathsf{f}_{s,t}) \in \mathrm{Diff}\,(\mathcal{M},\mathcal{M})$. So, the transformation rule (49) becomes

$$\xi^\diamond := \xi + \hat{\upsilon} \ , \tag{52}$$

where $\hat{\upsilon} := \frac{\mathrm{d}}{\mathrm{d}s}\hat{\phi}(\mathsf{f}_{s,t})\big|_{s=t}$.

For the sake of generality, we thus refer to frames of references that are not necessarily orthonormal. So, we will distinguish between covariant and contravariant tensor components, adjoint and transpose of a linear operator, derivative symbol D and gradient ∇, the relation between these two differential operators being $\nabla(\cdot) = D(\cdot)g^{-1}$, where g is a metric in the space where D and ∇ are computed.

11.2. External power in the case of $\mathcal{M}$-valued phase-fields

The external power of standard and microstructural actions on any part $\mathfrak{b}$ is now given by

$$\mathcal{P}_{\mathfrak{b}}^{ext}(\upsilon,\xi) := \int_{\mathfrak{b}} (b^\ddagger \cdot \upsilon + \beta^\ddagger \cdot \xi)\,\mathrm{d}x + \int_{\partial\mathfrak{b}} (\mathrm{t}_\partial \cdot \upsilon + \tau_\partial \cdot \xi)\,\mathrm{d}\mathcal{H}^2(x) \ , \tag{53}$$

where $\beta^\ddagger$ and τ_∂ represent, respectively, bulk and contact microstructural actions and are at x and t elements of the cotangent space $T_\nu^*\mathcal{M}$ so that the interposed dot means duality pairing.

The generality considered does not preclude a decomposition of $\beta^\ddagger$ into the sum of inertial (β^{in}) and non-inertial (β) components, namely $\beta^\ddagger = \beta^{in} + \beta$.

11.3. The dissipation inequality and consequences of the covariance axiom

In the present setting, the inequality (13) changes into

$$\int_{\mathfrak{b}} (\dot{\psi} + \eta\dot{\vartheta})\,\mathrm{d}x - \mathcal{P}_{\mathfrak{b}}^{ext}(\upsilon,\xi) + \int_{\mathfrak{b}} (\vartheta^{-1}\mathrm{q}\cdot\nabla\vartheta - \vartheta\mathrm{div}\omega)\,\mathrm{d}x \le 0 \ , \tag{54}$$

and is presumed to hold for any body part and any choice of the time rates involved.

Axiom 9.1 implies

$$\int_{\mathfrak{b}} (\varphi + \bar{\varphi})\,\mathrm{d}x - \mathcal{P}_{\mathfrak{b}}^{ext}(\bar{\mathrm{v}},\hat{\upsilon}) \le 0 \ , \tag{55}$$

for every choice of $\bar{\mathrm{v}}$, $\hat{\upsilon}$, and $\mathfrak{b}$. When we choose $\bar{\mathrm{v}} = \hat{\mathbf{c}}(t) + \mathbf{q}(t) \times (x - x_0)$ and, consequently, $\hat{\upsilon} = \mathcal{A}(\nu)\mathbf{q}$, we thus get

$$\mathcal{P}_{\mathfrak{b}}^{ext}(\hat{\mathbf{c}}(t) + \mathbf{q}(t) \times (x - x_0), \mathcal{A}(\nu)\mathbf{q}) = 0 \ . \tag{56}$$

This relation emerges directly also from the request of invariance under rigid-body-type change of observer for the external power alone, as adopted in [36] and progressively refined in [34,39]. Thus, the invariance axiom for the external power alone under rigid-body-type changes of observers is included in the covariance axiom for the Clausius-Duhem inequality.

We basically summarize here consequences emerging from the identity (56) (see also [34,39]).

The arbitrariness of $\hat{\mathbf{c}}$ and $\mathbf{q}$ implies the integral balance (21) and a variant of Eq. (22) given by

$$\int_{\mathfrak{b}} ((x - x_0) \times b^\ddagger + \mathcal{A}^*\beta^\ddagger)\,\mathrm{d}x + \int_{\partial\mathfrak{b}} ((x - x_0) \times \mathrm{t}_\partial + \mathcal{A}^*\tau_\partial)\,\mathrm{d}\mathcal{H}^2(x) = 0 \ , \tag{57}$$

where the asterisk in superscript position indicates formal adjoint. The presence of microstructural actions $\beta^\ddagger$ and τ_∂ only in the balance (57) does not means that they are couples per se, rather it means that their projections in $\mathbb{R}^3$ through the linear operator $\mathcal{A}^* \in \mathrm{Hom}(T_\nu^*\mathcal{M},\mathbb{R}^3)$ are couples.

Since $\mathcal{B}$ is assumed to be bounded, we can choose x_0 so that the boundedness of $|b^\ddagger|$ assures the one of $|(x - x_0) \times b^\ddagger|$ and, by the balance (21), the one of $|(x - x_0) \times \mathrm{t}_\partial|$. In addition, if $|\mathcal{A}^*\beta|$ is also bounded and $\tau_\partial(\cdot,t)$ is continuous, Cauchy's theorem applied to Eq. (57) implies the existence of a map $\tilde{\tau}$ such that $\tau_\partial(x,t) = \tilde{\tau}(x,t,n)$ and $\mathcal{A}^*\tilde{\tau}(x,t,n) = -\mathcal{A}^*\tilde{\tau}(x,t,-n)$. Also, $\tilde{\tau}$ results to be linear with respect to n; thus there exists a second-rank tensor $\mathcal{S}$, depending on x and t, which maps n into the cotangent space of $\mathcal{M}$ at ν, namely $\tilde{\tau}(x,t,n) = \mathcal{S}(x,t)n \in T_{\tilde{\nu}(x,t)}^*\mathcal{M}$. We call $\mathcal{S}$ a microstress. The proof of its existence does not require to embed $\mathcal{M}$ into a linear space although the embedding is always available because $\mathcal{M}$ is with finite dimension. Exploiting an embedding can be surely convenient but the embedding itself is not unique and a theory aiming to be intrinsic needs to avoid it, as we do in the present analysis.

When $\mathcal{S}(\cdot,t)$ is C^1 over $\mathcal{B}$ and continuous over $\bar{\mathcal{B}}$ while $\beta^\ddagger$ is also continuous, use of Eq. (18) and arbitrariness of $\mathfrak{b}$ imply the existence of an element $\mathbf{z}$ of $T_\nu^*\mathcal{M}$, defined to within an arbitrary element of $\ker\mathcal{A}^*$, such that

$$\beta^\ddagger - \mathbf{z} + \mathrm{div}\mathcal{S} = 0 \tag{58}$$

and

$$\mathrm{skew}(\boldsymbol{\sigma}) = \frac{1}{2}\mathsf{e}(\mathcal{A}^*\mathbf{z} + (D\mathcal{A}^*)^t\mathcal{S}) \tag{59}$$

(see also [32,36]). So, Cauchy's stress is symmetric only if we neglect $O(\lambda^2)$ terms. Also, the validity of pointwise balances implies the identity

$$\mathcal{P}_{\mathfrak{b}}^{ext}(\upsilon,\xi) = \int_{\mathfrak{b}} (\boldsymbol{\sigma}\cdot D\upsilon + \mathbf{z}\cdot\xi + \mathcal{S}\cdot D\xi)\,\mathrm{d}x \ . \tag{60}$$

The right-hand-side integral is what we call *internal power* and indicate in short it by $\mathcal{P}_{\mathfrak{b}}^{int}(\upsilon,\xi)$.

11.4. Further constraints imposed by the second law

The identity (60) allows us to rewrite the inequality (54) as

$$\int_{\mathfrak{b}} (\dot{\psi} + \eta\dot{\vartheta})\,\mathrm{d}x - \mathcal{P}_{\mathfrak{b}}^{int}(v, \xi) + \int_{\mathfrak{b}} (\vartheta^{-1}\mathsf{q}\cdot\nabla\vartheta - \vartheta \mathrm{div}\varpi)\,\mathrm{d}x \le 0\,. \tag{61}$$

Arbitrariness of $\mathfrak{b}$ and assumed continuity of the integral densities imply the local inequality

$$\dot{\psi} - \dot{\vartheta}\eta - (\boldsymbol{\sigma}^e + \boldsymbol{\sigma}^d)\cdot Dv - \mathbf{z}\cdot\xi - \mathcal{S}\cdot D\xi + \frac{1}{\vartheta}\mathsf{q}\cdot D\vartheta - \vartheta\,\mathrm{div}\varpi \le 0\,. \tag{62}$$

We presume to adopt once again the incompressibility constraint, so that (27), (28), and (29) hold once again and give rise to the emergence of a pressure as in relation (30). Also, we assume that both $\mathbf{z}$ and $\mathcal{S}$ admit additive decompositions into energetic and dissipative components, namely

$$\mathbf{z} = \mathbf{z}^e + \mathbf{z}^d\,, \qquad \mathcal{S} = \mathcal{S}^e + \mathcal{S}^d\,. \tag{63}$$

Then, we consider ψ, η, $\boldsymbol{\sigma}^e$, $\mathbf{z}^e$, and $\mathcal{S}^e$ to depend on the list

$$(\nu, D\nu, \vartheta)$$

with ψ, η, $\boldsymbol{\sigma}^e$, and $\mathcal{S}^e$ that are also assumed to be differentiable. By adopting the same procedure used for deriving and exploiting (32), we get

$$\eta = -\frac{\partial\psi}{\partial\vartheta}\,, \quad \boldsymbol{\sigma}^e = -(D\nu)^*\frac{\partial\psi}{\partial D\nu}\,, \quad \mathbf{z}^e = \frac{\partial\psi}{\partial\nu}\,, \quad \mathcal{S}^e = \frac{\partial\psi}{\partial D\nu} \tag{64}$$

and

$$\boldsymbol{\sigma}^d\cdot Dv + \mathbf{z}^d\cdot\xi + \mathcal{S}^d\cdot D\xi - \frac{1}{\vartheta}\mathsf{q}\cdot D\vartheta + \vartheta\,\mathrm{div}\varpi \ge 0\,, \tag{65}$$

which is required to hold for every choice of the rate fields involved. The inequality (65) is compatible with the choices

$$\boldsymbol{\sigma}^d = a_1 Dv\,, \qquad \mathbf{z}^d = a_2\xi\,, \qquad \mathcal{S}^d = a_3 D\xi\,,$$

with a_i, $i = 1, 2, 3$, positive constants or state functions, and

$$\mathsf{q} = -\kappa D\vartheta + \bar{\mathsf{q}}$$

with $\bar{\mathsf{q}}$ once again such that

$$\bar{\mathsf{q}}\cdot\nabla\vartheta + \vartheta^2\,\mathrm{div}\varpi = 0\,.$$

The inertial components of $b^{\ddagger}$, namely b^{in}, and the one of $\beta^{\ddagger}$, namely β^{in} require to be characterized. A reasonable and rather standard way we can follow is to adapt a prescription that the power developed by inertial terms over a generic body part plus the pertinent kinetic energy vanishes for every part of $\mathcal{B}$.

11.5. Inertia

We consider the kinetic energy density of a complex body to be the sum

$$\frac{1}{2}\rho|v|^2 + \mathfrak{k}(\nu, \xi)\,, \tag{66}$$

where we still consider the constraint $\mathrm{div}v = 0$, and $\mathfrak{k}$ is a twice differentiable non-negative function over the tangent bundle of $\mathcal{M}$, namely the disjoint union $T\mathcal{M} := \bigsqcup_{\nu\in\mathcal{M}} T_\nu\mathcal{M}$, such that $\frac{\partial^2\mathfrak{k}}{\partial\xi\partial\xi}\cdot\xi\otimes\xi > 0$ and $\mathfrak{k}(\nu, 0) = 0$ [32]. We thus consider the identity

$$\begin{aligned}\frac{\mathrm{d}}{\mathrm{d}t}\int_{\mathcal{B}}(\frac{1}{2}\rho|v|^2 + \mathfrak{k}(\nu,\xi))\,\mathrm{d}x - \int_{\partial\mathcal{B}}(\frac{1}{2}\rho|v|^2 + \mathfrak{k}(\nu,\xi))(v\cdot n)\,\mathrm{d}\mathcal{H}^2(x)\\ = \int_{\mathcal{B}}(b^{in}\cdot v + \beta^{\ddagger}\cdot\xi)\,\mathrm{d}x\,,\end{aligned} \tag{67}$$

which is presumed to hold for any choice of the velocity fields involved. Then, we take a function $\chi : T\mathcal{M} \longmapsto \mathbb{R}$, with values $\chi(\nu, \xi)$, such that

$$\mathfrak{k}(\nu, \xi) = \frac{\partial\chi}{\partial\xi}(\nu,\xi)\cdot\xi - \chi(\nu,\xi)\,. \tag{68}$$

Arbitrariness of the time rates involved in the balance (67) and use of a standard transport theorem in evaluating $\frac{\mathrm{d}}{dt}\int_{\mathcal{B}}$ imply that (67) is compatible with the identifications

$$b^{in} = -\rho\dot{v}^{\flat}\,, \quad \beta^{in} = \frac{\partial\chi}{\partial\nu} - \frac{\mathrm{d}}{\mathrm{d}t}\frac{\partial\chi}{\partial\xi}\,, \tag{69}$$

to within powerless terms.

We can do other choices. For example we can accept

$$\frac{1}{2}\rho|v|^2 + \mathfrak{k}(\nu, \xi_r)\,, \tag{70}$$

where

$$\mathfrak{k}(\nu, \xi_r) = \frac{\partial\chi}{\partial\xi_r}\cdot\xi_r - \chi(\nu,\xi_r)\,, \tag{71}$$

and ξ_r is a relative velocity given by $\xi_r := \xi - \mathcal{A}(\mathrm{curl}v)$ so that, by the above procedure, we can have

$$b^{in} = -\rho\dot{v}^{\flat}\,, \quad \beta^{in} = \frac{\partial\chi}{\partial\nu} - \frac{\mathrm{d}}{\mathrm{d}t}\frac{\partial\chi}{\partial\xi_r}\,, \tag{72}$$

to within powerless terms. In this case, when v is the velocity of a rigid-body motion with spin $\mathbf{q}$, the expression of $\mathfrak{k}$ is quadratic ξ_r, namely $\mathfrak{k}(\nu, \xi_r) = \frac{1}{2}(\Omega(\nu)\xi_r)\cdot\xi_r$, with $\Omega(\nu) \in \mathrm{Hom}(T_\nu\mathcal{M}, T_\nu^*\mathcal{M})$, and $\xi = \mathcal{A}\mathbf{q}$, the integral of (70) over $\mathcal{B}$, gives the standard inertial tensor, while with the choice (66), with $\mathfrak{k}(\nu,\xi) = \frac{1}{2}(\Omega(\nu)\xi)\cdot\xi$, the resulting inertia tensor is augmented by a term due to $\mathfrak{k}$, namely $\int_{\mathcal{B}}\mathcal{A}^*\Omega\mathcal{A}\,\mathrm{d}x$. Choosing between the two options is matter of specific physical circumstances.

12. Additional remarks

(1) In addition to the results concerning Gurtin's postulate, the previous analyses shed further (and unusual) light on the role played by the Clausius-Duhem inequality in the construction of continuum models. Indeed, the second law appears to be even a source of the representation of contact actions and their balance besides limiting possible constitutive structures and furnishing admissibility conditions for shock waves or other discontinuities.

(2) Balance of actions at various spatial scales and heat propagation can be expressed in terms of a dissipative-type version of the Poisson brackets. Such an approach involves dissipative pseudo-potentials, which are not always available, and (to an extent) it requires specification of state variables (see [26,55–58]).

(3) Microstructural actions can induce effects of various nature; they may imply hyperbolic-type heat propagation described in terms of balance equations of true interactions (see further analyses in [37,59–61]).

(4) Non-equilibrium states (and pertinent heat propagation) can be described in various ways. In addition to what has been already mentioned above, we can, for example, mention the introduction of internal non-observable variables with postulated pertinent evolution laws. They do not involve true interactions, rather they include thermodynamic affinities, which contribute only to the entropy production and do not play role at equilibrium (see, e.g., [62,63]). Also, looking directly at molecular kinetics, especially when kinetics is dominant, we can look at the Boltzmann equation and consider an expansion of the distribution function in terms of moments. The emerging elegant procedure leads to a cascade of hyperbolic equations, which apply essentially to gases, better if they are in a rarefied state [64,65], while at limit the cascade restores a parabolic character [66].

CRediT authorship contribution statement

Paolo Maria Mariano: Writing – review & editing, Writing – original draft, Validation, Supervision, Methodology, Investigation, Formal analysis, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

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