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ORIGINAL ARTICLE

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Quasi-linear versus potential-based formulations of force–flux relations and the GENERIC for irreversible processes: comparisons and examples

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Abstract An essential part in modeling out-of-equilibrium dynamics is the formulation of irreversible dynamics. In the latter, the major task consists in specifying the relations between thermodynamic forces and fluxes. In the literature, mainly two distinct approaches are used for the specification of force–flux relations. On the one hand, quasi-linear relations are employed, which are based on the physics of transport processes and fluctuation–dissipation theorems (de Groot and Mazur in Non-equilibrium thermodynamics, North Holland, Amsterdam, 1962, Lifshitz and Pitaevskii in Physical kinetics. Volume 10, Landau and Lifshitz series on theoretical physics, Pergamon Press, Oxford, 1981). On the other hand, force–flux relations are also often represented in potential form with the help of a dissipation potential (Šilhavý in The mechanics and thermodynamics of continuous media, Springer, Berlin, 1997). We address the question of how these two approaches are related. The main result of this presentation states that the class of models formulated by quasi-linear relations is larger than what can be described in a potential-based formulation. While the relation between the two methods is shown in general terms, it is demonstrated also with the help of three examples. The finding that quasi-linear force–flux relations are more general than dissipation-based ones also has ramifications for the general equation for non-equilibrium reversible–irreversible coupling (GENERIC: e.g., Grmela and Öttinger in Phys Rev E 56:6620–6632, 6633–6655, 1997, Öttinger in Beyond equilibrium thermodynamics, Wiley Interscience Publishers, Hoboken, 2005). This framework has been formulated and used in two different forms, namely a quasi-linear (Öttinger and Grmela in Phys Rev E 56:6633–6655, 1997, Öttinger in Beyond equilibrium thermodynamics, Wiley Interscience Publishers, Hoboken, 2005) and a dissipation potential–based (Grmela in Adv Chem Eng 39:75–129, 2010, Grmela in J Non-Newton Fluid Mech 165:980–986, 2010, Mielke in Continuum Mech Therm 23:233–256, 2011) form, respectively, relating the irreversible evolution to the entropy gradient. It is found that also in the case of GENERIC, the quasi-linear representation encompasses a wider class of phenomena as compared to the dissipation-based formulation. Furthermore, it is found that a potential exists for the irreversible part of the GENERIC if and only if one does for the underlying force–flux relations.

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1 Introduction

Over the years, a number of approaches to the thermodynamic formulation of models for material behavior have been developed. In the phenomenological realm, one of the most common of these is continuum thermodynamics (e.g., [1]) as based on the Clausius–Duhem inequality and Coleman–Noll dissipation principle (e.g., [2,3]). Another is based on the entropy inequality of Müller–Liu (e.g., [4,5]). Classically, such approaches have been based on the assumption of local thermodynamic equilibrium to formulate models for thermoelastic materials with heat conduction and viscosity. More general approaches such as extended thermodynamics (e.g., [6]) or extended linear irreversible thermodynamics (e.g., [7]) relax this assumption and model the approach of the system to thermodynamic equilibrium. Alternatively, for the case of history-dependent, and in particular inelastic, materials, such models have generally been based on the concepts of strong fading memory and internal variables (e.g., [8]). This concept also lies at the heart of so-called generalized standard or standard dissipative materials (e.g., [9,10]). From the point of view of irreversible thermodynamics, the goal of such formulations is to model the approach of non-equilibrium systems to thermodynamic equilibrium (if it exists) (e.g., [11]). Perhaps the most prominent example of such models is offered by the Ginzburg-Landau equation as based on the free energy.

More recently, an alternative approach to the thermodynamics of solids has been developed as an application of the so-called general equation for non-equilibrium reversible–irreversible coupling (GENERIC: e.g., [12–16]). Originally developed for (complex) fluids, this formalism has been applied to derive models for anisotropic elastic and elasto-(visco)plastic solids in an Eulerian setting [17,18]. An alternative approach to the formulation of GENERIC-based models for inelastic solids was pursued in [19,20], who considered thermoelastic solids with heat conduction and viscosity, as well as the case of viscoplasticity, in a Lagrangian setting. Yet another GENERIC-based approach to formulate models for inelastic materials (e.g., viscoelastic, elastoplastic) has been discussed in [21].

A cornerstone of both continuum thermodynamics and the GENERIC is the modeling of irreversible processes and entropy production via thermodynamic flux–force relations. Via the physics of transport processes (e.g., [11,22]), such relations are derived from fluctuation–dissipation and coarse-graining considerations, resulting in their dependence on transport properties and a mathematical form quasi-linear in the forces. In some cases, such flux–force relations may also be representable in potential form with the help of a dissipation potential (e.g., Chapter 12 in [1]). Formally speaking, such a representation is analogous to that of evolution-constitutive relations for internal variables based on such a potential [23–28] when the internal variable rates involved are interpreted as thermodynamic fluxes. A formulation of the GENERIC based on a dissipation potential has also been advocated in [15,16] and more recently in [21]. On the other hand, it is not clear whether all flux–force relations derived from transport theory are representable in potential form.

One purpose of the current work is to formulate conditions which flux–force relations must satisfy in order for a potential representation of these to exist. A second is the investigation of the connections between the potential representation of flux–force relations and that of the GENERIC for irreversible processes. Among other things, we show that the GENERIC-based model for irreversible processes can be represented in potential form if and only if such a potential form exists for the underlying thermodynamic flux–force relations. To explore the implications of these basic results in more detail, we consider three examples: (i) heat conduction in anisotropic solids, (ii) slippage in complex fluids (Gordon–Schowalter derivative), and (iii) homogeneous chemical reactions. As shown by the application of the general results, the models of (i) and (iii) can be formulated in terms of a dissipation potential under certain conditions. On the other hand, since the irreversible process of slippage is dissipation-free, the dissipation potential for the model of (ii) is identically zero, and hence, the concept of the dissipation potential is inappropriate for its description.

For the purposes of the current work, it is sufficient to work with the purely local form of the GENERIC (Chapters 2 and 3 in [14]) in terms of differential operators rather than generalized functions and integration. As well, this involves working with the energy and entropy densities. Before we begin, a word on notation. For clarity and ease of understanding for continuum mechanicians and physicists alike, a number of results in this work will be expressed in both direct (i.e., symbolic) and (Cartesian) component notation. To this latter end, let upper latin indices $K, L, M, \ldots = 1, 2, 3$, represent Cartesian components of referential or Lagrangian tensors. The summation convention on repeated such indices will be used throughout. Likewise, we use the notation $\nabla_L \varphi = \partial\varphi/\partial r_L$ for the components of the gradient of any field φ defined with respect to the reference configuration of the material in three-dimensional Euclidean point space E^3 with translation vector space V^3. These are functions of referential position $\boldsymbol{r} = \boldsymbol{o} + r_K \boldsymbol{i}_K \in E^3$ with respect to the Cartesian basis vectors $\boldsymbol{i}_1, \boldsymbol{i}_2, \boldsymbol{i}_3 \in V^3$ and origin $\boldsymbol{o} \in E^3$. As is common in solid mechanics for large deformation, all model relations to follow are represented in referential or Lagrangian form relative to some reference configuration. Finally, for a tensor $\mathbf{A}$ of arbitrary rank and two vectors $\mathbf{a}$ and $\mathbf{b}$, the notation $\partial_{\mathbf{a}}\mathbf{A}\,\mathbf{b}$ implies a differentiation of $\mathbf{A}$ and subsequent contraction between the two vectors $\mathbf{a}$ and $\mathbf{b}$.

The paper is organized as follows. In Sect. 2, force–flux relations are discussed, and their quasi-linear and dissipation potential–based formulations are compared. The analogous comparison is made in Sect. 3 for the GENERIC framework, where also both types of formulations exist. The finding that the cases of force–flux relations and the GENERIC are closely related is examined in Sect. 4 in more detail. To illustrate the abstract results, examples are studied in Sect. 5. We close with a discussion in Sect. 6.

2 Flux–force relations

2.1 Basic considerations

For simplicity, attention is restricted in this work to continuous thermodynamic systems containing no discontinuities (e.g., singular surface). In this context, consider the local or “strong” form

$$\dot{\eta} = \pi - \operatorname{div} \boldsymbol{\phi} \tag{1}$$

of referential entropy balance for supply-free processes (e.g., Chapters 3 and 9 in [1]). Here, η represents the referential entropy density, $\boldsymbol{\phi}$ is the referential entropy flux density, and π is the referential entropy production rate density. In particular, $\boldsymbol{\phi}$ represents the (net) flux of entropy per unit area from the environment into the system, and π is the entropy production rate in the system per unit volume. In the current context, the second law is expressed in the local form

$$\pi \geqslant 0 \tag{2}$$

relative to π. Given Gibbs relation and the assumption of local equilibrium (e.g., [1,11,14]), the well-known constitutive form

$$\pi = \mathbf{j} \cdot \mathbf{f} \tag{3}$$

for π follows in terms of thermodynamic fluxes $\mathbf{j}$ (e.g., heat flux) and forces $\mathbf{f}$ (e.g., gradient of reciprocal temperature). Constitutive relations between $\mathbf{j}$ and $\mathbf{f}$ are generally formulated in the form

$$\mathbf{j} = \mathbf{j}(\ldots, \mathbf{f}), \tag{4}$$

where ... indicate a possible dependence on additional quantities besides $\mathbf{f}$. For simplicity, these will be suppressed in the notation and we will just write $\mathbf{j}(\mathbf{f})$ for this relation for the time being; this applies as well to all related forms of this relation to be considered in what follows.

2.2 Quasi-linear transport relation

In the common context of transport theory (e.g., [11,14,22]), for example, the constitutive form

$$\mathbf{j}(\mathbf{f}) = \mathbf{L}(\mathbf{f})\,\mathbf{f} \tag{5}$$

quasi-linear in $\mathbf{f}$ is obtained. In particular, in the classical special case of linear irreversible thermodynamics for systems “near” equilibrium, the transport operator $\mathbf{L}(\mathbf{f})$ is independent of $\mathbf{f}$. In what follows, it will be useful to work with the split

$$\begin{aligned} \mathbf{L} &= \mathbf{L}_{\text{sym}} + \mathbf{L}_{\text{skw}} \\ &= \operatorname{sym}(\mathbf{L}) + \operatorname{skw}(\mathbf{L}) \\ &= \frac{1}{2}(\mathbf{L} + \mathbf{L}^{\mathrm{T}}) + \frac{1}{2}(\mathbf{L} - \mathbf{L}^{\mathrm{T}}) \end{aligned} \tag{6}$$

of $\mathbf{L}$ into symmetric $\mathbf{L}_{\text{sym}}$ and skew-symmetric $\mathbf{L}_{\text{skw}}$ parts. This induces the corresponding split

$$\mathbf{j} = \mathbf{j}_{\mathrm{sym}} + \mathbf{j}_{\mathrm{skw}} = \mathbf{L}_{\mathrm{sym}}\,\mathbf{f} + \mathbf{L}_{\mathrm{skw}}\,\mathbf{f} \tag{7}$$

of $\mathbf{j}$ into dissipative $\mathbf{j}_{\mathrm{sym}}$ and non-dissipative $\mathbf{j}_{\mathrm{skw}}$ parts. Indeed, since

$$\mathbf{j}_{\mathrm{skw}} \cdot \mathbf{f} = \mathbf{L}_{\mathrm{skw}}\,\mathbf{f} \cdot \mathbf{f} = 0 \tag{8}$$

follows via the skew symmetry of $\mathbf{L}_{\mathrm{skw}}$, substitution of (7) into (3) yields

$$\pi = \mathbf{j} \cdot \mathbf{f} = \mathbf{j}_{\mathrm{sym}} \cdot \mathbf{f} = \mathbf{L}_{\mathrm{sym}}\,\mathbf{f} \cdot \mathbf{f}. \tag{9}$$

In the context of (5) and (6), then, clearly only the symmetric part $\mathbf{L}_{\mathrm{sym}}$ of $\mathbf{L}$ contributes to π. On this basis, non-negative entropy production (2) is satisfied sufficiently by requiring $\mathbf{L}_{\mathrm{sym}}(\mathbf{f})$ to be non-negative definite; if $\mathbf{L}_{\mathrm{sym}}$ is in fact independent of $\mathbf{f}$ (i.e., linear irreversible special case), non-negative-definiteness of $\mathbf{L}_{\mathrm{sym}}$ is also necessary for a potential representation to exist.

2.3 Potential-based transport relation

Assume now that a particular form of the flux–force constitutive relation $\mathbf{j}(\mathbf{f})$, for example, the transport form (5), has been derived via physical considerations and is known. As discussed elsewhere [1,29], any variational formulation of the corresponding initial-boundary-value problem is then contingent on whether or not a potential representation for $\mathbf{j}(\mathbf{f})$ can be found. Specifically, this means that the force–flux relation can be written in the form

$$\mathbf{j}(\mathbf{f}) = \partial_{\mathbf{f}}\, p(\mathbf{f}) \tag{10}$$

in terms of the so-called dissipation potential p. In order to ensure a non-negative rate of entropy production, (2), it is sufficient to require that the dissipation potential is non-negative and convex. In this case, one obtains

$$\pi = \mathbf{f} \cdot \partial_{\mathbf{f}}\, p \geqslant p \geqslant 0 \tag{11}$$

as required.

Whether or not a potential representation for $\mathbf{j}(\mathbf{f})$ can indeed be found is basically a mathematical problem (e.g., integrability) for which there may be in general no solution. If the mathematical form of $\mathbf{j}(\mathbf{f})$ satisfies certain conditions, however, then such a potential representation can be found. One possibility in this regard can be formulated with the help of a generalization of the Helmholtz theorem[1] due to [26] (see also [1,31]). To this end, assume that the domain of the flux–force relation $\mathbf{j}(\mathbf{f})$ is convex or "star-shaped." In particular, this implies that there exists a path $\mathbf{c}_{\mathbf{f}}(s) = s\mathbf{f}$ $(0 \leqslant s \leqslant 1)$ in the space of all forces connecting equilibrium $\mathbf{c}_{\mathbf{f}}(0) = \mathbf{0}$ with any $\mathbf{f}$, that is, $\mathbf{c}_{\mathbf{f}}(1) = \mathbf{f}$. On this basis, one can introduce for $\mathbf{j}(\mathbf{f})$ the unique (via linearity and orthogonality) additive split into symmetric and skew-symmetric parts

$$\mathbf{j}(\mathbf{f}) = \partial_{\mathbf{f}}\, p_{\mathbf{j}}(\mathbf{f}) + \mathbf{s}_{\mathbf{j}}(\mathbf{f}), \tag{12}$$

in terms of the scalar-valued non-negative function

$$p_{\mathbf{j}}(\mathbf{f}) = \int_0^1 \mathbf{j}(\mathbf{c}_{\mathbf{f}}(s)) \cdot \mathbf{f}\; \mathrm{d}s \tag{13}$$

(assuming $p_{\mathbf{j}}(\mathbf{0}) = 0$ for simplicity without loss of physical generality) and the vector-valued function

$$\mathbf{s}_{\mathbf{j}}(\mathbf{f}) = \int_0^1 2\,\mathrm{skw}(\partial_{\mathbf{c}_{\mathbf{f}}(s)}\, \mathbf{j}(\mathbf{c}_{\mathbf{f}}(s)))\, \mathbf{c}_{\mathbf{f}}(s)\; \mathrm{d}s \tag{14}$$

which is non-dissipative, that is, $\mathbf{s}_{\mathbf{j}}(\mathbf{f}) \cdot \mathbf{f} = 0$. One thus obtains

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[1] Related to the de Rham decomposition in differential geometry as based on the Poincaré theorem (e.g., [30]).

$$\pi(\mathbf{f}) = \partial_{\mathbf{f}} p_{\mathbf{j}}(\mathbf{f}) \cdot \mathbf{f} = p_{\mathbf{j}}(\mathbf{f}) + \int_0^1 \mathbf{f} \cdot s \, \operatorname{sym}(\partial_{\mathbf{c}_{\mathbf{f}}(s)} \mathbf{j}(\mathbf{c}_{\mathbf{f}}(s))) \, \mathbf{f} \; \mathrm{d}s, \tag{15}$$

where (13) has been employed to derive the second equality. In this form, it is evident that if $\operatorname{sym}(\partial_{\mathbf{f}} \mathbf{j}(\mathbf{f}))$ is non-negative definite, the integral in this last relation is non-negative, and

$$\pi(\mathbf{f}) = \partial_{\mathbf{f}} p_{\mathbf{j}}(\mathbf{f}) \cdot \mathbf{f} \;\geqslant\; p_{\mathbf{j}}(\mathbf{f}) \geqslant 0, \tag{16}$$

is obtained, that is, $p_{\mathbf{j}}(\mathbf{f})$ as given by (13) is convex. If $\partial_{\mathbf{f}} \mathbf{j}(\mathbf{f})$ is in fact symmetric, $\mathbf{s}_{\mathbf{j}}(\mathbf{f})$ vanishes identically, and $p_{\mathbf{j}}(\mathbf{f})$ is a potential for $\mathbf{j}(\mathbf{f})$. Conversely, if a potential for $\mathbf{j}(\mathbf{f})$ exists, $\operatorname{skw}(\partial_{\mathbf{f}} \mathbf{j}(\mathbf{f}))$ vanishes identically (i.e., via Euler's theorem: [30]).

In the context of (12), then, the deviation $\mathbf{s}_{\mathbf{j}}(\mathbf{f})$ of $\mathbf{j}(\mathbf{f})$ from being potential results in no entropy production. Indeed, (12) splits $\mathbf{j}(\mathbf{f})$ into dissipative $\partial_{\mathbf{f}} p_{\mathbf{j}}(\mathbf{f})$ and non-dissipative $\mathbf{s}_{\mathbf{j}}(\mathbf{f})$ parts. As we saw in the previous section, the split (6) of the transport operator induces an analogous split (7) of $\mathbf{j}(\mathbf{f})$ into dissipative $\mathbf{j}_{\mathrm{sym}}(\mathbf{f}) = \mathbf{L}_{\mathrm{sym}}(\mathbf{f})\,\mathbf{f}$ and non-dissipative $\mathbf{j}_{\mathrm{skw}}(\mathbf{f}) = \mathbf{L}_{\mathrm{skw}}(\mathbf{f})\,\mathbf{f}$ parts. To look into this more closely, consider now the representation of (5) via (12). One obtains

$$p_{\mathbf{L}}(\mathbf{f}) = \int_0^1 \mathbf{f} \cdot s \, \mathbf{L}_{\mathrm{sym}}(s\mathbf{f}) \, \mathbf{f} \; \mathrm{d}s \tag{17}$$

and

$$\begin{aligned} \mathbf{a} \cdot \mathbf{s}_{\mathbf{L}}(\mathbf{f}) = {} & \mathbf{a} \cdot \mathbf{L}_{\mathrm{skw}}(\mathbf{f})\,\mathbf{f} \\ & + \int_0^1 s^2 \, \mathbf{a} \cdot (\partial_{\mathbf{c}_{\mathbf{f}}(s)} \mathbf{L}_{\mathrm{sym}}(\mathbf{c}_{\mathbf{f}}(s))\,\mathbf{f})\,\mathbf{f} \; \mathrm{d}s \\ & - \int_0^1 s^2 \, \mathbf{f} \cdot (\partial_{\mathbf{c}_{\mathbf{f}}(s)} \mathbf{L}_{\mathrm{sym}}(\mathbf{c}_{\mathbf{f}}(s))\,\mathbf{a})\,\mathbf{f} \; \mathrm{d}s \end{aligned} \tag{18}$$

for all vectors $\mathbf{a}$ via the skew symmetry of $\mathbf{L}_{\mathrm{skw}}$. In particular, this latter result for $\mathbf{s}_{\mathbf{L}}(\mathbf{f})$ implies that, even if $\mathbf{L}_{\mathrm{skw}}$ is identically zero, assuming non-negative definiteness of $\mathbf{L}_{\mathrm{sym}}(\mathbf{f})$ is necessary, but generally not sufficient, for the transport form (5) of $\mathbf{j}(\mathbf{f})$ to be represented solely by $p_{\mathbf{L}}(\mathbf{f})$. Indeed, the additional condition

$$\mathbf{a} \cdot (\partial_{\mathbf{f}} \mathbf{L}_{\mathrm{sym}}(\mathbf{f})\,\mathbf{f})\,\mathbf{f} = \mathbf{f} \cdot (\partial_{\mathbf{f}} \mathbf{L}_{\mathrm{sym}}(\mathbf{f})\,\mathbf{a})\,\mathbf{f} \tag{19}$$

on the functional form of $\mathbf{L}_{\mathrm{sym}}(\mathbf{f})$ must hold, in which case $\partial_{\mathbf{f}} \mathbf{j}_{\mathrm{sym}}(\mathbf{f})$ is symmetric. Clearly, this represents an additional constitutive restriction on the form of $\mathbf{L}_{\mathrm{sym}}(\mathbf{f})$ going beyond those of Onsager–Casimir symmetry and non-negative definiteness. It also has implications for approaches to the formulation of models for non-equilibrium systems which are based on thermodynamic flux–force relations $\mathbf{j}(\mathbf{f})$. This includes, for example, the case of the GENERIC, to which we turn in Sect. 3.

2.4 Potential-based representations in quasi-linear form

In the previous section, we have shown that not every quasi-linear force–flux relation can be cast into potential form, but that conditions on $\mathbf{L}$ apply, namely $\mathbf{L}_{\mathrm{skw}} = \mathbf{0}$ and the conditions (19). In this section, we prove that in turn any potential-based force–flux relation can be written in quasi-linear form. This implies that the class of constitutive relations from potential-based formulations is a subset of the models captured by quasi-linear relations.

Close to equilibrium, the dissipation potential can be approximated to be quadratic in the force [32,33],

$$p = \frac{1}{2} \mathbf{f} \cdot \left(\partial_{\mathbf{f}} \partial_{\mathbf{f}} p|_{\mathbf{0}} \right) \mathbf{f}, \tag{20}$$

because at $\mathbf{f} = \mathbf{0}$ the general properties of p require $p(\mathbf{0}) = 0$ and $\partial_{\mathbf{f}} p = \mathbf{0}$. Since p is convex, $\partial_{\mathbf{f}} \partial_{\mathbf{f}} p|_{\mathbf{0}}$ is not only symmetric but also non-negative definite. A straightforward calculation leads to the force–flux relation (5) with the constant matrix

$$\mathbf{L} = \mathbf{L}_{\text{sym}} = \partial_{\mathbf{f}} \partial_{\mathbf{f}} p|_{\mathbf{0}} \, . \tag{21}$$

Therefore, any constitutive relation close to equilibrium can both be derived from the dissipation potential and be written in the (quasi-)linear form.

For the general case beyond the proximity to equilibrium, however, the situation requires a more careful discussion. Let us assume that a constitutive relation is written in the form with a dissipation potential p. Then, that same constitutive rule can also be written in the quasi-linear form (5) with the special choice

$$\mathbf{L} = \mathbf{L}_{\text{sym}} = \frac{1}{\pi} \mathbf{j} \otimes \mathbf{j} = \frac{1}{\pi} \, \partial_{\mathbf{f}} p \otimes \partial_{\mathbf{f}} p, \tag{22}$$

with the entropy production rate density π defined above. By construction, $\mathbf{L}$ is not only symmetric, but also non-negative by virtue of the non-negative rate of entropy production (2). The only possible caveat is that (22) may be ill defined mathematically for $\pi = 0$. While the (close to) equilibrium case (with $\pi \to 0$) has already been covered in (21), we need to discuss the possibility of a vanishing dissipation rate out of equilibrium, that is, $\pi = \mathbf{j} \cdot \mathbf{f} = 0$ for a certain value of the driving force vector $\mathbf{f}^\star \neq \mathbf{0}$. If such a non-vanishing driving force really exists, then the dissipation potential assumes its minimum value $p(\mathbf{f}^\star) = p_{\text{min}} = 0$, since p is bracketed between π and 0 according to (11). However, because p is minimal, one obtains $\mathbf{j}^\star \equiv \mathbf{j}(\mathbf{f}^\star) = \partial_{\mathbf{f}} p|_{\mathbf{f}=\mathbf{f}^\star} = \mathbf{0}$. In other words, $\pi = 0$ for a finite $\mathbf{f}^\star$ requires $\mathbf{j}^\star = \mathbf{0}$, rather than $\mathbf{j}^\star \perp \mathbf{f}^\star$ for finite $\mathbf{j}^\star$. Analyzing (22) upon $\mathbf{j} \to \mathbf{0}$, one finds the well-defined limit $\mathbf{L}^\star = \mathbf{0}$ at $\mathbf{f}^\star$. In summary, any constitutive relation written in terms of the dissipation potential can also be written in the quasi-linear form (5). This is also true in the context of the GENERIC (see below), that is, any potential form for the irreversible part of the GENERIC can be expressed in quasi-linear form as well.

For completeness, we point out that the rank of $\mathbf{L}$ in tensor product form (22) is unity. Often, the rank of $\mathbf{L}$ is related on physical grounds to the number of independent irreversible processes that are at play simultaneously. However, such an argument is foreign to a dissipation potential formulation from the start. Since the main goal of this section was to demonstrate the existence of a quasi-linear formulation for any potential form, we do not go into further details about the number of independent processes. We just mention that, using physical arguments, the relation (22) can be generalized to a form with rank larger than unity, that is, with multiple processes.

3 GENERIC-based formulation for irreversible processes

3.1 Basics

In the context of the GENERIC, the total energy E and total entropy S are modeled as functionals of a set of variables (i.e., fields) $\mathbf{x}$ (e.g., temperature) characterizing the system under consideration. Let A represent either E or S, and let a be the density of A. In the current work, attention will be focused on the class of models given by the form

$$A(\mathbf{x}) = \int a(\mathbf{x}, \nabla\mathbf{x}) \, \mathrm{d}v \tag{23}$$

of this functional in which a depends on both $\mathbf{x}$ and (one or more of) their spatial gradients $\nabla\mathbf{x}$. In all what follows, boundary terms are neglected for simplicity which is appropriate if either the boundary conditions are chosen appropriately or the fields vanish at the (infinitely remote) boundary. Since A is a functional of time-dependent fields $\mathbf{x}$,

$$\begin{aligned} \dot{A} &= \int \left(\partial_{\mathbf{x}} a \cdot \dot{\mathbf{x}} + \partial_{\nabla\mathbf{x}} a \cdot \nabla\dot{\mathbf{x}} \right) \, \mathrm{d}v \\ &= \int a_{\mathbf{x}} \cdot \dot{\mathbf{x}} \, \mathrm{d}v \end{aligned} \tag{24}$$

follows for its time rate-of-change via the divergence theorem and neglect of boundary effects as just discussed above, where

$$a_{\mathbf{x}} \equiv \partial_{\mathbf{x}} a - \operatorname{div} \partial_{\nabla \mathbf{x}} a \tag{25}$$

represents the first-order variational derivative of a.

As they embody the physics of transport processes, flux–force relations like (4) lie at the heart of many approaches to the modeling of non-equilibrium systems such as the GENERIC [12–14]. In the spirit of the Ginzburg-Landau equation, this is a model for the evolution of system variables $\mathbf{x}$ (e.g., temperature) in non-equilibrium toward equilibrium. In the context of the GENERIC, the evolution relation

$$\dot{\mathbf{x}} = \dot{\mathbf{x}}_{\mathrm{rev}} + \dot{\mathbf{x}}_{\mathrm{irr}} \tag{26}$$

for $\mathbf{x}$ splits into reversible $\dot{\mathbf{x}}_{\mathrm{rev}}$ and irreversible $\dot{\mathbf{x}}_{\mathrm{irr}}$ parts. In turn, (26) induces the split

$$\begin{aligned} \dot{A} &= \dot{A}_{\mathrm{rev}} + \dot{A}_{\mathrm{irr}} \\ &= \int a_{\mathbf{x}} \cdot \dot{\mathbf{x}}_{\mathrm{rev}}\, \mathrm{d}v + \int a_{\mathbf{x}} \cdot \dot{\mathbf{x}}_{\mathrm{irr}}\, \mathrm{d}v \end{aligned} \tag{27}$$

of $\dot{A}$ from (24). In the current work, attention is focused in particular on $\dot{\mathbf{x}}_{\mathrm{irr}}$ and the corresponding part $\dot{A}_{\mathrm{irr}}$ of $\dot{A}$ for the cases of total energy ($A = E$, $a = e$) and entropy ($A = S$, $a = \eta$). Analogous to the flux–force relation $\mathbf{j}(\ldots, \mathbf{f})$ from (4), a formulation based on the GENERIC works with the constitutive form

$$\dot{\mathbf{x}}_{\mathrm{irr}} = \dot{\mathbf{x}}_{\mathrm{irr}}(\ldots, \eta_{\mathbf{x}}) \tag{28}$$

for $\dot{\mathbf{x}}_{\mathrm{irr}}$; as above in the case of the flux–force relation (4), the dots $\ldots$ indicate a possible dependence on additional quantities (e.g., $\mathbf{x}$) besides the entropy gradient $\eta_{\mathbf{x}}$. For simplicity, these will be suppressed in the notation and we will just write $\dot{\mathbf{x}}_{\mathrm{irr}}(\eta_{\mathbf{x}})$ for this relation for the time being; this applies as well to all related forms of this relation to be considered in what follows.

3.2 Quasi-linear relation

In one version of the GENERIC, advocated by Öttinger [13,14], the irreversible evolution (28) for $\dot{\mathbf{x}}_{\mathrm{irr}}$ is modeled via the transport-theoretic form

$$\dot{\mathbf{x}}_{\mathrm{irr}}(\eta_{\mathbf{x}}) = \mathbf{M}(\eta_{\mathbf{x}})\, \eta_{\mathbf{x}} \tag{29}$$

quasi-linear in the GENERIC-based derivative $\eta_{\mathbf{x}}$ of the entropy density η with respect to $\mathbf{x}$. Here, $\mathbf{M}$ represents the so-called friction operator. Analogous to the case of the flux–force relation (5) above, besides on $\eta_{\mathbf{x}}$, $\dot{\mathbf{x}}_{\mathrm{irr}}$ and related quantities like $\mathbf{M}$ depend in general on additional fields like $\mathbf{x}$. Because they play no direct role in the following, however, we dispense with them in the notation for simplicity. It should be noted that in the "phase-field-like" case, η is a constitutive function of $\mathbf{x}$ and its spatial gradient $\nabla \mathbf{x}$, for example, and thus $\eta_{\mathbf{x}} = \partial_{\mathbf{x}} \eta - \operatorname{div} \partial_{\nabla \mathbf{x}} \eta$ cannot be simply recast in terms of the local fields $\mathbf{x}$ alone. Therefore, $\mathbf{x}$ and $\eta_{\mathbf{x}}$ are in general distinct quantities, of which $\eta_{\mathbf{x}}$ is of prime importance for the relation to the force–flux relations.

The correspondence of the form of (29) with that (5) for transport-based thermodynamic flux–force relations is no coincidence, as will be discussed in more detail below. In the context of the dissipation bracket

$$[A, B] := \int a_{\mathbf{x}} \cdot \mathbf{M}\, b_{\mathbf{x}}\, \mathrm{d}v \tag{30}$$

on functionals A, B of the form (23) induced by (29), consider the split

$$\begin{aligned} \mathbf{M} &= \mathbf{M}_{\mathrm{sym}} + \mathbf{M}_{\mathrm{skw}} \\ &= \operatorname{sym}(\mathbf{M}) + \operatorname{skw}(\mathbf{M}) \\ &= \frac{1}{2}(\mathbf{M} + \mathbf{M}^{\mathrm{T}}) + \frac{1}{2}(\mathbf{M} - \mathbf{M}^{\mathrm{T}}) \end{aligned} \tag{31}$$

of $\mathbf{M}$ into symmetric and skew-symmetric parts, formally analogous to that (6) of the transport operator $\mathbf{L}$ above. In this context, the GENERIC-based form[2]

$$\dot{S}_{\text{irr}} = \int \pi \,\mathrm{d}v = \int \eta_{\mathbf{x}} \cdot \dot{\mathbf{x}}_{\text{irr}} \,\mathrm{d}v = \int \eta_{\mathbf{x}} \cdot \mathbf{M}_{\text{sym}}(\eta_{\mathbf{x}})\, \eta_{\mathbf{x}} \,\mathrm{d}v \tag{32}$$

of the entropy production rate is obtained which depends only on $\mathbf{M}_{\text{sym}}$. This is analogous to the reduced form (9) of π following from split (6) of $\mathbf{L}$ analogous to that (31) of $\mathbf{M}$ just discussed. Note that a non-negative rate of entropy production (32) can be achieved by requiring that $\mathbf{M}_{\text{sym}}$ be positive semi-definite.

3.3 Potential-based formulation

Another form of the GENERIC, alternative to (29), is advocated by Grmela [12,15,16]. It is based on assuming that there exists a potential representation for $\dot{\mathbf{x}}_{\text{irr}}(\eta_{\mathbf{x}})$ *a priori*, that is, from the start. For later convenience, we write this form of the GENERIC as

$$\dot{\mathbf{x}}_{\text{irr}}(\eta_{\mathbf{x}}) = \partial_{\eta_{\mathbf{x}}} p_{\text{irr}}(\eta_{\mathbf{x}}) + \mathbf{s}_{\text{irr}}(\eta_{\mathbf{x}}), \tag{33}$$

where Grmela considers $\mathbf{s}_{\text{irr}}(\eta_{\mathbf{x}}) = \mathbf{0}$. Such a potential-based formulation of the irreversible part of the GENERIC has been studied from a mathematical perspective in [21].

To compare (29) and (33) in more detail, we could proceed analogously to the discussion about the force–flux relations, Sects. 2.3 and 2.4. One would then find that (i) $\mathbf{s}_{\text{irr}}(\eta_{\mathbf{x}})$ is skew-symmetric and thus dissipation-less, analogous to (14), and that (ii) a potential representation exists only for a certain class of relations $\dot{\mathbf{x}}_{\text{irr}}(\eta_{\mathbf{x}})$. An alternative route, demonstrated in the following (Sect. 4), consists in relating the quasi-linear and dissipation potential formulations of the GENERIC to the corresponding formulations of the force–flux relations.

4 Connection between flux–force relations and the GENERIC

The parallels between the formulation of thermodynamic flux–force relations $\mathbf{j}(\mathbf{f})$ in Sect. 2 and the GENERIC-based relation $\dot{\mathbf{x}}_{\text{irr}}(\eta_{\mathbf{x}})$ in Sect. 3 alluded to, and clearly evident, in the development up to this point are no coincidence. Indeed, from a physical point of view, the form of the flux–force relation $\mathbf{j}(\mathbf{f})$ determines that of $\dot{\mathbf{x}}_{\text{irr}}(\eta_{\mathbf{x}})$. In particular, this is the case for the transport-theoretic forms (5) and (29) of these relations. The purpose of the current section is to delve into this in more detail.

To begin, note that any connection between $\mathbf{j}(\mathbf{f})$ and $\dot{\mathbf{x}}_{\text{irr}}(\eta_{\mathbf{x}})$ clearly involves in particular relations between $\eta_{\mathbf{x}}$, $\mathbf{f}$, $\mathbf{j}$, and $\dot{\mathbf{x}}_{\text{irr}}$. Consider, for example, the case of heat conduction in which the internal energy density ε is chosen as an element of $\mathbf{x}$. In this case, the GENERIC-based entropy "gradient" $\eta_{\varepsilon} \equiv \partial_{\varepsilon}\eta = \theta^{-1}$ in (29) is the reciprocal temperature, and its spatial gradient $\mathbf{f}_{\theta} \equiv \nabla\theta^{-1}$ is the thermodynamic force driving heat conduction. Consequently, η_{ε} is "mapped" into $\mathbf{f}_{\theta}$ via the gradient operator ∇. More generally, assume that there exists an operator $\mathbf{C}$ (e.g., Chapters 2 and 3 in [14,34]) independent of $\eta_{\mathbf{x}}$ such that[3]

$$\mathbf{f}(\eta_{\mathbf{x}}) = \mathbf{C}^{\mathrm{T}} \eta_{\mathbf{x}} \tag{34}$$

holds. Since $\mathbf{C}$ is independent of $\eta_{\mathbf{x}}$, $\mathbf{f}(\eta_{\mathbf{x}})$ is linear in $\eta_{\mathbf{x}}$. In terms of operator transposition

$$\int \mathbf{C}\mathbf{j} \cdot a_{\mathbf{x}} \,\mathrm{d}v := \int \mathbf{j} \cdot \mathbf{C}^{\mathrm{T}} a_{\mathbf{x}} \,\mathrm{d}v, \tag{35}$$

the common relation

$$\dot{S}_{\text{irr}} = \int \pi \,\mathrm{d}v = \int \mathbf{j} \cdot \mathbf{f} \,\mathrm{d}v = \int \dot{\mathbf{x}}_{\text{irr}} \cdot \eta_{\mathbf{x}} \,\mathrm{d}v \tag{36}$$

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[2] By orthogonality of reversible and irreversible processes, $\eta_{\mathbf{x}}$ annihilates the reversible part $\dot{\mathbf{x}}_{\text{rev}}$ of $\dot{\mathbf{x}}$ in the context of the GENERIC [12–14].

[3] Using the opposite sign convention to Öttinger (Section 3.1.1 in [14]).

for the entropy production rate density from (3) and (32) induces the basic connection

$$\dot{\mathbf{x}}_{\mathrm{irr}}(\eta_{\mathbf{x}}) = \mathbf{C}\,\mathbf{j}(\mathbf{f}(\eta_{\mathbf{x}})) = \mathbf{C}\,\mathbf{j}(\mathbf{C}^{\mathrm{T}}\eta_{\mathbf{x}}) \tag{37}$$

between $\dot{\mathbf{x}}_{\mathrm{irr}}$ and $\mathbf{j}$ via $\mathbf{C}$.

For quasi-linear force–flux relations (5), the basic connections (34) and (37) imply via the quasi-linear GENERIC (29) the form

$$\mathbf{M}(\eta_{\mathbf{x}}) = \mathbf{C}\,\mathbf{L}(\mathbf{f}(\eta_{\mathbf{x}}))\,\mathbf{C}^{\mathrm{T}} \tag{38}$$

for the friction operator $\mathbf{M}$ in terms of the transport operator $\mathbf{L}$ [14,34–37]. As such, the functional form of $\mathbf{M}(\eta_{\mathbf{x}})$ is clearly induced by that of $\mathbf{L}(\mathbf{f})$.

For force–flux relations of the form (12), (34) and (37) imply the connections

$$\begin{aligned} \partial_{\eta_{\mathbf{x}}} p_{\mathrm{irr}}(\eta_{\mathbf{x}}) &= \mathbf{C}\,\partial_{\mathbf{f}(\eta_{\mathbf{x}})} p_{\mathbf{j}}(\mathbf{f}(\eta_{\mathbf{x}})), \\ \mathbf{s}_{\mathrm{irr}}(\eta_{\mathbf{x}}) &= \mathbf{C}\,\mathbf{s}_{\mathbf{j}}(\mathbf{f}(\eta_{\mathbf{x}})), \end{aligned} \tag{39}$$

via the GENERIC (33). On the basis of this last result, one can conclude that, for general $\mathbf{C}$, $\mathbf{s}_{\mathrm{irr}}(\eta_{\mathbf{x}})$ vanishes iff $\mathbf{s}_{\mathbf{j}}(\mathbf{f})$ does. As such, a potential form for $\dot{\mathbf{x}}_{\mathrm{irr}}(\eta_{\mathbf{x}})$ exists iff one for $\mathbf{j}(\mathbf{f})$ does. In particular, this then applies to the transport-based forms (5) and (29), respectively, of these relations.

Specific expressions for $\mathbf{C}^{\mathrm{T}}$ can be determined in view of the relation (34) between the entropy gradient $\eta_{\mathbf{x}}$ and the thermodynamic force $\mathbf{f}$. For completeness, we mention that an additional condition on $\mathbf{C}^{\mathrm{T}}$ emerges from the GENERIC requirement of the conservation of energy. Specifically, since $\dot{E}_{\mathrm{rev}} = 0$ is determined by Hamiltonian dynamics and vanishes identically in the context of the GENERIC,

$$\dot{E} = \dot{E}_{\mathrm{irr}} = \int \dot{\mathbf{x}}_{\mathrm{irr}} \cdot e_{\mathbf{x}}\,\mathrm{d}v = \int \mathbf{j} \cdot \mathbf{C}^{\mathrm{T}} e_{\mathbf{x}}\,\mathrm{d}v \tag{40}$$

follows from (37) as well. Consequently, conservation of energy $\dot{E} = 0$ is ensured identically if

$$\mathbf{C}^{\mathrm{T}} e_{\mathbf{x}} = \mathbf{0} \tag{41}$$

holds identically [14,34]. Note that this induces a dependence of $\mathbf{C}$ on the components of the GENERIC-based energy gradient $e_{\mathbf{x}}$.

5 Examples

In the following, examples are given to study possible formulations in quasi-linear or potential-based forms. It has been demonstrated above that the GENERIC approach is closely related to the force–flux relations, specifically also with respect to the (non-)existence of a potential representation. Therefore, we concentrate in the following only on the underlying force–flux relations and possible potential representations thereof.

5.1 Example: anisotropic rigid heat conductor

Although not terribly realistic, an anisotropic rigid heat conductor represents perhaps the simplest example of non-isothermal solid behavior. As such, it is ideal for the purpose of illustrating the derivation of specific forms of the general results obtained in the last two sections. As is well known, such a solid deforms via translation and rotation alone; stretch, strain, thermal expansion, and so on are excluded. In this case, the material behavior depends solely on heat conduction, that is, on the temperature θ and its gradient $\nabla\theta$.

As a model for heat conduction, consider the transport-based generalized Fourier relation

$$\boldsymbol{q} = -\boldsymbol{K}(\theta, \nabla\theta)\,\nabla\theta = \theta^2 \boldsymbol{K}(\theta, \nabla\theta^{-1})\,\nabla\theta^{-1} \tag{42}$$

for the heat flux $\boldsymbol{q}$ quasi-linear in the gradient of the (reciprocal) temperature. Since this is the only flux–force relation for the current material class, we have

$$\mathbf{j} = (\mathbf{j}_\theta) := (\boldsymbol{q}), \quad \mathbf{L} = [\mathbf{L}_{\theta\theta}] := [\theta^2 \boldsymbol{K}], \quad \mathbf{f} = (\mathbf{f}_\theta) := (\nabla\theta^{-1}). \tag{43}$$

To discuss the issue of possible potential representations, we proceed as follows. Since $\mathbf{L}_{\theta\theta} = \theta^2 \boldsymbol{K}$ is symmetric and non-negative definite, $\mathbf{L}_{\text{skw}}$ vanishes identically, and $\mathbf{L} = \mathbf{L}_{\text{sym}}$ is symmetric and non-negative definite. On this basis, the general requirement (19) for $\mathbf{s}_{\mathbf{L}}(\mathbf{f}) \equiv \mathbf{s}_{\boldsymbol{K}}(\mathbf{f}_\theta)$ to vanish reduces to

$$\mathbf{a} \cdot (\partial_{\mathbf{f}_\theta} \mathbf{L}_{\theta\theta}(\mathbf{f}_\theta)\, \mathbf{f}_\theta)\, \mathbf{b} = \mathbf{f}_\theta \cdot (\partial_{\mathbf{f}_\theta} \mathbf{L}_{\theta\theta}(\mathbf{f}_\theta)\, \mathbf{a})\, \mathbf{b} \tag{44}$$

for all $\mathbf{a}, \mathbf{b}$. As discussed above, this is clearly a condition going beyond symmetry and non-negative definiteness. For example, viewing $\mathcal{J} = \partial_{\mathbf{f}_\theta} \mathbf{L}_{\theta\theta}$ as a third-order tensor-valued quantity $\mathcal{J} = \mathcal{J}_{KLM}\, \boldsymbol{i}_K \otimes \boldsymbol{i}_L \otimes \boldsymbol{i}_M$, the symmetry of $\mathbf{L}_{\theta\theta} = \theta^2 \boldsymbol{K}$ implies $\mathcal{J}_{KLM} = \mathcal{J}_{LKM}$, whereas $\mathbf{s}_{\boldsymbol{K}}(\mathbf{f}_\theta)$ will vanish if $\mathcal{J}_{KLM} = \mathcal{J}_{MLK}$ holds. This is trivially satisfied of course by the standard Fourier form $\boldsymbol{K}(\theta) = k(\theta)\, \boldsymbol{I}$ for $\boldsymbol{K}$ independent of $\nabla\theta^{-1}$ in terms of the coefficient of thermal conductivity $k(\theta)$. In the Fourier case, then,

$$p_{\mathbf{L}}(\mathbf{f}) = \mathbf{f}_\theta \cdot \int_0^1 s\, \mathbf{L}_{\theta\theta}\, \mathbf{f}_\theta\, \mathrm{d}s = \frac{1}{2}\, \nabla\theta^{-1} \cdot \theta^2 \boldsymbol{K}\, \nabla\theta^{-1} = \frac{1}{2}\, \nabla\theta \cdot \boldsymbol{K}\, \nabla\theta \tag{45}$$

follows from (17) with $p_{\mathbf{L}}(\mathbf{0}) \equiv 0$.

5.2 Example: slippage in complex fluids

Complex fluids consist of discrete constituents (e.g., macromolecules) which can move relative to each other. If one imagines, for example, ellipsoids immersed in a fluid, then this means that their motion is not determined in an affine (i.e., homogeneous) fashion by the (Eulerian) velocity field $\boldsymbol{v}$ of the surrounding fluid. Rather, they may slip relative to one another (e.g., [38–40]). Such slippage is characterized constitutively by a slip parameter ξ which is related to the aspect ratio of ellipsoids. Slippage is also relevant to the modeling of polymeric fluids (e.g., [35,41]). As it turns out, slippage is an irreversible process resulting in no dissipation. In other words, the skew-symmetric part $\mathbf{L}_{\text{skw}}$ of $\mathbf{L}$ does not vanish in this case.

The Eulerian or spatial formulation of complex fluids with slippage (e.g., Section 4.2.1 in [14]) involves the velocity field $\boldsymbol{v}$ or the spatial momentum density $\boldsymbol{m} = \varrho \boldsymbol{v}$, respectively, with ϱ the spatial mass density. In addition, the spatial conformation tensor[4] $\boldsymbol{C}$ is a measure of the (internal) deformation state of the fluid (microstructure) relative to the continuum as a whole. Recall that the time-dependent deformation or flow $\boldsymbol{x} = \boldsymbol{\chi}(\boldsymbol{r}, t)$ of the material determines the deformation gradient $\boldsymbol{F}(\boldsymbol{r}, t) = \nabla \boldsymbol{\chi}(\boldsymbol{r}, t)$, the material velocity field $\dot{\boldsymbol{\chi}}(\boldsymbol{r}, t) = \partial_t \boldsymbol{\chi}(\boldsymbol{r}, t) = \boldsymbol{v}(\boldsymbol{\chi}(\boldsymbol{r}, t), t) = \boldsymbol{v}(\boldsymbol{x}, t)$, and the material velocity gradient $\dot{\boldsymbol{F}}(\boldsymbol{r}, t) = \boldsymbol{L}(\boldsymbol{r}, t)\, \boldsymbol{F}(\boldsymbol{r}, t)$ via the chain rule, with $\boldsymbol{L}(\boldsymbol{x}, t) = \nabla \boldsymbol{v}(\boldsymbol{x}, t)$. In what follows, the usual split $\boldsymbol{L} = \boldsymbol{D} + \boldsymbol{W}$ of $\boldsymbol{L}$ into its symmetric $\boldsymbol{D} = \frac{1}{2}(\boldsymbol{L} + \boldsymbol{L}^{\mathrm{T}})$ and skew-symmetric $\boldsymbol{W} = \frac{1}{2}(\boldsymbol{L} - \boldsymbol{L}^{\mathrm{T}})$ parts is utilized. In particular, this latter quantity is known in general continuum mechanics and in solid mechanics as the spin tensor, and as the vorticity tensor in fluid mechanics.

Let $\boldsymbol{A}$ be a time-dependent spatial second-order tensor field associated with the material. If the evolution of any such tensor is determined solely by the motion or flow of the material as a whole, then its pullback $\boldsymbol{F}^{-1} \boldsymbol{A} \boldsymbol{F}^{-\mathrm{T}}$ to the reference configuration is constant. In the language of rheology due to Oldroyd, such behavior is referred to as upper convected. In this case, $\dot{\boldsymbol{A}} = \boldsymbol{L}\boldsymbol{A} + \boldsymbol{A}\boldsymbol{L}^{\mathrm{T}}$ holds, with $\dot{\boldsymbol{A}}$ the material-time derivative. For example, the left Cauchy-Green deformation tensor $\boldsymbol{B} = \boldsymbol{F}\boldsymbol{F}^{\mathrm{T}}$ from solid mechanics is such a tensor, that is, $\dot{\boldsymbol{B}} = \boldsymbol{L}\boldsymbol{B} + \boldsymbol{B}\boldsymbol{L}^{\mathrm{T}}$. Due to slippage, however, the conformation tensor $\boldsymbol{C}$ deviates from being upper convected in this sense. Indeed, the more general evolution relation

$$\dot{\boldsymbol{C}} = \boldsymbol{L}\boldsymbol{C} + \boldsymbol{C}\boldsymbol{L}^{\mathrm{T}} - \xi\, (\boldsymbol{D}\boldsymbol{C} + \boldsymbol{C}\boldsymbol{D}) \tag{46}$$

holds in terms of the so-called slippage parameter ξ [14,35,41]. The time derivative in (46) depending in particular on ξ is known as the Gordon–Schowalter derivative [42,43]. As discussed by Beris and Edwards [44] and later by Öttinger [14], only in the case of $\xi = 0$ (upper-convected behavior) or $\xi = 2$ (i.e., lower-convected behavior: $\boldsymbol{F}^{\mathrm{T}}\boldsymbol{C}\boldsymbol{F}$ constant) is the slippage process reversible or controllable. Specifically, they have shown that any other value of ξ is inconsistent with the Poisson structure of reversible dynamics because the so-called Jacobi identity is violated. So in general, slippage involves irreversible dynamics. On the other hand,

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[4] Not to be confused with the right Cauchy-Green deformation $\boldsymbol{C} = \boldsymbol{F}^{\mathrm{T}}\boldsymbol{F}$.

since it does not result in an increase of entropy, slippage is not dissipative; for the full details, the reader is referred to [35]. As will be seen in what follows, in the context of the transport-based form (5) of the flux–force relation and (6), this implies that the skew-symmetric part $\mathbf{L}_{\mathrm{skw}}$ of the transport operator $\mathbf{L}$ is non-zero.

The explicit form of $\mathbf{L}_{\mathrm{skw}}$ is discussed in the following. The full Gordon–Schowalter derivative can be split into two contributions,

$$\begin{aligned} \dot{\boldsymbol{C}}_{\mathrm{rev}} &= \boldsymbol{L}\boldsymbol{C} + \boldsymbol{C}\boldsymbol{L}^{\mathrm{T}}, \\ \dot{\boldsymbol{C}}_{\mathrm{irr}} &= -\xi\,(\boldsymbol{D}\boldsymbol{C} + \boldsymbol{C}\boldsymbol{D}) =: -\mathcal{X}\,\nabla\boldsymbol{v}, \end{aligned} \tag{47}$$

and so $\dot{\boldsymbol{C}} = \dot{\boldsymbol{C}}_{\mathrm{rev}} + \dot{\boldsymbol{C}}_{\mathrm{irr}}$, where the last equality in (47) defines the tensor $\mathcal{X}$. For simplicity, all viscous effects, thermal conduction, and diffusion effects will be ignored here and attention will be focused solely on slippage. Since the slippage involves both the conformation tensor $\boldsymbol{C}$ and the momentum density $\boldsymbol{m}$ (or velocity field), there are also force and flux contributions corresponding to these variables. Specifically, one can make the following identifications for the forces and fluxes (see also §4.2.1 in [14]),

$$\begin{aligned} \mathbf{f} &= \begin{pmatrix} \mathbf{f}_{\boldsymbol{m}} \\ \mathbf{f}_{\boldsymbol{C}} \end{pmatrix} = \begin{pmatrix} \theta^{-1}\,\nabla\boldsymbol{v} \\ \partial_{\boldsymbol{C}}\eta \end{pmatrix}, \\ \mathbf{j} &= \begin{pmatrix} \mathbf{j}_{\boldsymbol{m}} \\ \mathbf{j}_{\boldsymbol{C}} \end{pmatrix} = \begin{pmatrix} \theta\,\mathcal{X}\,\partial_{\boldsymbol{C}}\eta \\ -\mathcal{X}\,\nabla\boldsymbol{v} \end{pmatrix} = \mathbf{L}\mathbf{f}. \end{aligned} \tag{48}$$

with the entropy density η. From this, one obtains

$$\mathbf{L} = \begin{bmatrix} \mathbf{0} & \theta\mathcal{X} \\ -\theta\mathcal{X} & \mathbf{0} \end{bmatrix}, \tag{49}$$

which is indeed skew-symmetric.

Given these results, we can now address the issue of a possible potential representation for slippage in complex fluids. Since $\mathbf{L} = \mathbf{L}_{\mathrm{skw}}$ is skew-symmetric, $\mathbf{L}_{\mathrm{sym}}$ is identically zero, according to (17). In this case, $p_{\mathbf{L}}(\mathbf{f}) = p_{\mathbf{L}}(\mathbf{0}) \equiv 0$ follows from (17), and $\mathbf{s}_{\mathbf{L}}(\mathbf{f}) = \mathbf{L}\,\mathbf{f}$ from (18). In conclusion, then, no dissipation potential exists for the force–flux relation representative of the Gordon–Schowalter derivative of a complex fluid with slippage.

5.3 Example: chemical reactions

Our final example represents the prototype of models for non-linear dynamics, namely homogeneous chemical reactions. In particular, we consider a system consisting of n species; for our purposes, it suffices in this context to restrict attention to a single reaction in this system including both forward and reverse reaction. Generalization to multiple reactions is straightforward but lends no new insight into the possible potential representation of the model.

From chemical kinetics (e.g., Chapter 4 in [45]), one has the basic evolution relation

$$\dot{N}_i = \nu_i\,\dot{\xi}_i \tag{50}$$

for N_i in terms of the corresponding extent of reaction ξ_i and stoichiometric coefficient $\nu_i = \partial_{\xi_i} N_i$. In particular, $\nu_i = \beta_i - \alpha_i$ is the difference between the stoichiometric coefficients β_i and α_i of the product and reactant species, respectively, during forward reaction. Again, for simplicity, assume that $\xi_i \equiv \xi$ is the same for all $i = 1, \ldots, n$. Neglecting further changes in the total volume, this system implies the interpretations of

$$\begin{aligned} J &= \dot{\xi}, \\ F &= k_{\mathrm{B}}\,\mathcal{A}, \end{aligned} \tag{51}$$

for the thermodynamic flux and force, respectively. The symbol $\mathcal{A}$ denotes the system chemical affinity in terms of the species chemical potential μ_i,

$$\begin{aligned} \mathcal{A} &= \mathcal{A}_\alpha + \mathcal{A}_\beta, \\ \mathcal{A}_\alpha &= \tfrac{1}{k_{\mathrm{B}}\theta} \sum_{i=1}^{N} \alpha_i \mu_i, \\ \mathcal{A}_\beta &= -\tfrac{1}{k_{\mathrm{B}}\theta} \sum_{i=1}^{N} \beta_i \mu_i, \end{aligned} \tag{52}$$

where $\mathcal{A}_\alpha$ and $\mathcal{A}_\beta$ denote the affinities of the reactant and product species, respectively. The absolute temperature is denoted by θ, and k_B is Boltzmann's constant. Lastly, the quasi-linear flux–force relation (5) then reduces to the scalar relation

$$J(F) = L(F)\, F. \tag{53}$$

On this basis, the potential representation (17) reduces to

$$P_L(F) = F \int_0^1 s\, L(s F)\, F \,\mathrm{d}s, \tag{54}$$

assuming $P_L(0) = 0$, and (18) to $S_L(F) = 0$ identically. Any form for $L(F)$ satisfying the conditions of the representation induces $P_L(F)$ in this fashion. One possibility in this regard is that

$$L(\mathbf{x}, F) = k_\mathrm{B}\, R(\mathbf{x})\, e^{-\mathcal{A}_\beta}\, F^{-1}(e^{F/k_\mathrm{B}} - 1) = R(\mathbf{x})\, \mathcal{A}^{-1}\, (e^{\mathcal{A}_\alpha} - e^{-\mathcal{A}_\beta}) \tag{55}$$

in terms of any non-negative function $R(\mathbf{x})$ of the state variables $\mathbf{x}$. Further,

$$P_L(F) = k_\mathrm{B}\, R\, e^{-\mathcal{A}_\beta} \left\{ k_\mathrm{B}(e^{F/k_\mathrm{B}} - 1) - F \right\} \tag{56}$$

then follows from (54). Assuming that the chemical potentials μ_i depend on N_i as an ideal gas, the mass action law is recovered.

Conversely, Grmela [15] works from the start with a potential of the form

$$\Phi(\mathbf{x}, F) = W(\mathbf{x}) \left\{ e^{F/2k_\mathrm{B}} + e^{-F/2k_\mathrm{B}} - 2 \right\}. \tag{57}$$

The flux derived from this dissipation potential is

$$J = \partial_F \Phi = \frac{W}{2\,k_\mathrm{B}} \left(e^{F/2k_\mathrm{B}} - e^{-F/2k_\mathrm{B}} \right) = \frac{W}{2\,k_\mathrm{B}}\, e^{-\mathcal{A}_\alpha/2}\, e^{-\mathcal{A}_\beta/2} \left(e^{F/k_\mathrm{B}} - 1 \right). \tag{58}$$

This will be compatible with (55) when

$$\frac{W}{2\,k_\mathrm{B}}\, e^{-\mathcal{A}_\alpha/2}\, e^{-\mathcal{A}_\beta/2} = k_\mathrm{B}\, R\, e^{-\mathcal{A}_\beta} \tag{59}$$

holds.

In summary, we observe that highly non-linear chemical reactions can be described equally well both by the quasi-linear flux–force relation (5) and also in terms of the dissipation potential. In the quasi-linear approach, the reaction rate L, (55), has been adjusted by an appropriate function in terms of the state variables $\mathbf{x}$, in order to arrive at the usual form of the reaction equations. Analogously, in the case of the dissipation potential, the function W needed to be chosen appropriately as a function of the state variables $\mathbf{x}$, (59). We close by noting that in the example of chemical reactions, the distinction between a dependence on the state variables $\mathbf{x}$ and the driving force F is blurred, because the latter is only a non-linear function of the former, and hence both potentials, $P_L(F)$ in (56) and $\Phi(F)$ in (57), are equally admissible.

6 Discussion

The relation (37) documents clearly the dependence of the irreversible part (29) of a GENERIC on the transport relation (5). Related to this is the basic dependence (38) of the friction operator $\mathbf{M}$ on the transport "coefficient" $\mathbf{L}$ (e.g., [14]). As also seen in the examples discussed in this work, in particular, this dependence implies that $\mathbf{M}(\eta_\mathbf{x})$ depends on the entropy gradient $\eta_\mathbf{x}$ if and only if $\mathbf{L}(\mathbf{f})$ depends on the thermodynamic force $\mathbf{f}$. In addition, this state of affairs carries over to the case of a potential representation; indeed, as demonstrated by (39), such a representation exists for the GENERIC if and only if one does for the underlying flux–force relations.

The extension of the basic representation (12) for general flux–force relations $\mathbf{j}(\mathbf{f})$ on star-shaped regions in force space to deal with the possibility of non-symmetric transport coefficients $\mathbf{L}(\mathbf{f})$ facilitated the treatment of a broader class of physical models. In particular, these include models for dissipation-free irreversible processes such as the case of slippage in complex fluids, for which the dissipation potential is identically zero (i.e., no dissipation). In the more general case of irreversible and dissipative processes, the existence of a potential representation $p_{\mathbf{L}}(\mathbf{f})$ is contingent on the satisfaction of the higher-order symmetry restrictions (19) on the functional form of $\mathbf{L}_{\mathrm{sym}}(\mathbf{f})$. Again, in the context of (39), (19) are then also necessary for the existence of the analogous potential representation for the irreversible part of the GENERIC. It is worth emphasizing that this represents a mathematical problem which one has to solve if one is interested in deriving such a potential representation for the purpose of a variational formulation of the corresponding initial-boundary-value problem. Indeed, no new physics is involved.

Perhaps not surprisingly, it has been clearly demonstrated above that the class of constitutive relations based on a potential is a subset of the models captured by quasi-linear relations. In other words, by using a potential-based formulation, one uses a more restricted setup as compared to a quasi-linear setting. As stated by Grmela [46], one may deliberately choose to employ the more restrictive procedure, in a similar spirit as one also employs the Hamiltonian structure with the restrictive Jacobi identity [12,13,47] for formulating the reversible dynamics. On the one hand, it should be mentioned that the dissipation potential plays an important role in the formulation of out-of-equilibrium dynamics in the context of differential geometry and so-called "Legendre time evolution" [15]. Furthermore, it has recently been suggested [48] that the potential form of GENERIC emerges from an optimization principle. On the other hand, we point out that the quasi-linear form is a result of projection-operator techniques and of systematically accounting for the separation of timescales [14,49,50], and thus has a firm statistical basis. In addition, the quasi-linear form is closer to experimental procedures than is the potential-based form, as mentioned above. For example, the dynamic behavior of materials is often described in terms of their transport coefficients, that is, in terms of $\mathbf{L}(\mathbf{f})$. In the non-linear case, $\mathbf{L}(\mathbf{f})$ plays no direct role in the dissipation potential, and hence, it is difficult to formalize $\mathbf{L}(\mathbf{f})$ in a dissipation potential. Particularly, the potential $p' = (1/2)\mathbf{f} \cdot \mathbf{L}(\mathbf{f})\mathbf{f}$ eventually results in a matrix of transport coefficients different from $\mathbf{L}$.

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