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REVIEW

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A note on representation-dependent Onsager closures for thermo-diffusive coupling

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Abstract Non-isothermal diffusion can be formulated within different mixture-level approaches that account for diffusion-related transport either through an extended energy flux or through an extended entropy flux. This note compares two prominent approaches: the Gurtin approach, in which diffusion enters the energy balance through an additional diffusive energy flux, and the Müller approach, in which the classical energy balance is retained while diffusion enters through an extended entropy flux. The comparison clarifies how the way diffusion-related transport is represented in each approach and the adopted thermodynamic force basis affect a subsequent Onsager-type closure. In the selected Müller-type force basis, the diffusion-related thermodynamic force contains a temperature-gradient contribution. Consequently, a diagonal Onsager closure in this basis yields a diffusion flux with an apparent Soret-type contribution while the heat flux remains Fourier-like. In the selected Gurtin-type force basis, the corresponding diagonal closure yields uncoupled Fourier and Fick laws, whereas thermo-diffusive coupling appears through non-diagonal Onsager blocks. Thus, the apparent Soret/Dufour structure follows from how diffusion-related transport is represented in the mixture-level approach considered and from the basis of thermodynamic forces used for the Onsager closure. Although diffusion in solids provides the main motivation, the derivation does not rely on a specific constitutive law.

Keywords Continuum thermodynamics · Diffusion · Entropy flux · Energy balance · Dissipation inequality · Onsager relations · Thermodiffusion · Soret effect · Dufour effect · Representation dependence

1 Introduction

Considered thermodynamic approaches
Classical continuum thermodynamics is a common framework for modeling diffusion processes in continua. Over the past few decades, two conceptually different, yet often implicitly conflated, thermodynamic approaches have been widely used to incorporate diffusion into non-isothermal continuum models. These two approaches are closely related to the seminal works by Müller [1] and Gurtin and Vargas [2], cf. also the discussion in Cimmelli et al. [3, p.912]. Therefore, these two approaches are denoted as Müller approach and Gurtin approach, in the present work.

Müller approach
This approach contrasts the procedure discussed in Eckart [4, Eq.(15)], who states the entropy flux $\boldsymbol{\phi}_{\mathcal{V}}$ to be the heat flux vector $\boldsymbol{q}$ over the absolute temperature θ, i.e. $\boldsymbol{\phi}_{\mathcal{V}} = \boldsymbol{q}/\theta$. Instead, the entropy flux is considered as a constitutive quantity, cf. Müller [1, p.118]. In this regard, a modified entropy flux, that still accounts

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for the contribution of $\boldsymbol{q}/\theta$ is introduced in Müller [1, Eq.(2.9)$_2$]. The view of $\boldsymbol{\phi}_{\mathcal{V}}$ as a constitutive quantity, i.e., not prescribed by heat flux over absolute temperature, is also taken by Liu [5, p.134], cf. also Liu [5, Eqs.(4.2) & (4.4)]. While the extended entropy flux is related to a dipolar fluid in Müller [1, Eq.(8.23)], the assumption of the entropy flux as a constitutive quantity is adopted by Liu [5, Eqs.(4.3) & (4.4)] for formulating a general method to exploit the entropy method proposed by Müller [6,7]. This assumption is also considered for mixtures of non-viscous fluids in Müller [8, Eqs.(6.20)-(6.22)], Müller [9, Eq.(2.1)$_2$], where a general entropy flux is introduced. Constitutive relations for this flux are discussed in Müller [8, Eq.(6.52)], which are specified for diffusion in simple mixtures in [8, Eq.(6.111)]. The assumption of an extended entropy flux is frequently used in modern literature, cf., e.g., Bothe and Dreyer [10, Eq.(3.28)]. It is also used for modeling diffusion in the isothermal case, thereby, neglecting the contribution of the entropy flux related to the heat flux vector, cf., e.g., Forest et al. [11, Eq.(52)], Ammar et al. [12, Eq.(14)], de Rancourt et al. [13, Eq.(22)]. A related qualification of the classical heat-flux-over-temperature specification of the entropy flux is discussed by Prahs and Böhlke [14]. There, this specification is treated as a constitutive assumption that is applicable for many classical thermomechanical settings, but may require modification for more advanced material models, in particular when diffusion or mixtures are considered.

Gurtin approach

In contrast to the Müller approach, this approach accounts for the diffusional fluxes by additional energy fluxes. These are manifested in the extension of the balance of internal energy, cf. Gurtin and Vargas [2, Eq.(2.4)], and are, thus, related to an extension of the energy balance of the classical Cauchy continuum, cf. Gurtin et al. [15, p.371]. The extension of the energy flux is structurally similar to the extension due to interstitial working in Dunn and Serrin [16, Eq.(1.9)]. However, this contribution was introduced to account for long range interactions related to a supply of mechanical energy across the boundary of the material volume, beyond traction working and heat flow, cf. Dunn and Serrin [16, p.98]. The Gurtin approach is widely used in recent publications on thermo-mechanically coupled theories that account for diffusion, cf., e.g., Chester and Anand [17, Eq.(6.1)], Anand [18, Eq.6.1], Dyck et al. [19, Eq.(9.1)], Gisy et al. [20, Eq.(5)]. A generalized approach to diffusion based on a micro-force balance is discussed by Gurtin [21].

Other approaches and comparisons

A comprehensive and extensive systematic comparison of continuum thermodynamic theories for chemically reacting fluid mixtures is provided by Bothe and Dreyer [10]. Their work distinguishes different model levels, including class-I and class-II mixture theories, and discusses entropy production, entropy-invariant couplings, Onsager symmetry, and entropy-invariant model reduction. Accordingly, it provides a deeper constituent-based framework than the mixture-level approaches compared in the present note. The present work does not attempt to reproduce or replace such a constituent-based derivation. Instead, it compares two non-isothermal mixture-level approaches to diffusion after the treatment of diffusion-related transport and the thermodynamic force basis used for the Onsager closure have been specified. The view of the entropy flux as a constitutive quantity in mixture theory is classical. In particular, Müller [22] emphasizes that the entropy flux is not specified a priori as heat flux divided by temperature, but is to be determined within the constitutive theory. The present comparison is also consistent with the discussion by Gurtin and Vargas [2, p. 181, note 3], where the Gurtin approach is related to Müller's viewpoint under suitable additional assumptions. Therefore, the present note does not claim a general thermodynamic inequivalence between both viewpoints, but focuses on the Onsager closure structures obtained after the treatment of diffusion-related transport and the thermodynamic force basis have been specified. In contrast, the Coleman–Noll procedure uses the Clausius–Duhem inequality as a restriction on admissible constitutive equations, but it does not by itself prescribe a specific linear force–flux closure [23]. Further comparisons and related formulations can be found in the literature on Standard Non-Equilibrium Thermodynamics, cf. de Groot and Mazur [24], GENERIC [25,26], and extended irreversible thermodynamics [27–29]. These works represent only a small portion of the literature on continuum thermodynamics and irreversible processes. The novelty of the present work is therefore not a new thermodynamic principle. Rather, it is a concise side-by-side clarification of how two mixture-level approaches to diffusion are associated with different apparent Onsager closure structures in a specified thermodynamic force basis.

Motivation for comparing the Müller and Gurtin approaches

The preceding literature discussion shows that diffusion can be incorporated into continuum thermodynamics in different ways. Among these possibilities, the Müller and Gurtin approaches provide a particularly instructive pair for a focused comparison, because they account for diffusion-related transport through different thermodynamic fluxes. This makes them suitable for illustrating how such modeling choices affect the subsequent Onsager closure.

On the thermo-diffusive coupling contributions
The thermo-diffusive coupling contributions, present in both approaches, are referred to as Soret effect [30] and Dufour effect [31]. The Soret effect describes diffusion driven by thermal gradients, while the Dufour effect describes heat flow induced by diffusive driving forces often associated with concentration gradients, cf., e.g., de Groot and Mazur [24, p.274, Eqs.(212)-(213)], [32, p.2516]. In solids, thermo-diffusive coupling effects are commonly discussed in terms of the heat of transport, cf., e.g., [33–35], and assessed through thermotransport measurements, cf., e.g., [36,37]. Representative experimental studies on interstitial solutes in metals provide reference data for transport directions relative to the temperature gradient and for heats of transport, cf., e.g., [38,39]. From a theoretical perspective, thermal diffusion in crystals has been discussed using mechanism-based models, including semi-empirical alloy theories [40], lattice-dynamical considerations [41], and random-walk formulations [42]. Further discussions for concentrated solid solutions and crystals are given by [43,44]. In summary, the above-mentioned contributions demonstrate that thermo-diffusive couplings are an experimentally accessible aspect of diffusion in solids. Consequently, these couplings motivate a dedicated structural comparison of admissible continuum-thermodynamic closures in coupled heat and mass transport.

Application of thermo-diffusive coupling contributions
Early treatments already incorporated such coupling contributions in boundary-value problems for solid diffusion/thermodiffusion and coupled heat–mass transport descriptions, cf., e.g., [45,46]. Thermal diffusion in solids, formulated in terms of Soret/Dufour-type coupling, was also addressed early on, cf., e.g., [47]. More recent works address thermo-diffusive couplings mainly within coupled multi-physics models and simulations. Prominent applications include (i) thermomigration-driven degradation and reliability considerations in microelectronic interconnects and micro-joints [48–53], (ii) coupled ionic–thermal transport (thermotransport) in doped fluorite-structured oxide-ion conductors and related solid electrolytes [54,55], and (iii) thermally biased mass transport during processing and microstructure evolution [56–59].

Objectives of the current work This work neither advocates for one approach over another nor proposes a new diffusion theory. Its objective is to provide a structural comparison of two mixture-level continuum-thermodynamic approaches to non-isothermal diffusion. To this end, it formulates the mixture-level balance equations (i) within the Gurtin approach, where an additional diffusion-related energy flux is introduced, and (ii) within the Müller approach, where the classical energy balance is combined with an extended entropy flux. Based on these two approaches, the work clarifies how diffusion-related transport is treated in the thermodynamic formulation and how this affects the thermodynamic force basis and, consequently, the apparent Onsager-type closure format. All statements on Soret- and Dufour-type couplings are therefore conditional on this treatment and on the diagonal or non-diagonal closure adopted in the corresponding force basis.

Scope of the comparison
The present derivation does not rely on a specific constitutive law. Instead, it addresses how the treatment of diffusion-related transport at mixture level affects the resulting dissipation inequalities and the corresponding Onsager closures. A deeper derivation from partial constituent balances, as in constituent-based class-II mixture theories, cf. [10], can provide additional structural restrictions on the fluxes and entropy production at mixture level. In contrast, the purpose of the present comparison is to clarify how the treatment of diffusion-related transport and the choice of thermodynamic force basis affect the apparent Onsager closure format in non-isothermal diffusion.

Originality
This work provides a non-isothermal, side-by-side comparison of two mixture-level approaches to diffusion and the Onsager force bases used for their closure. The comparison in this work is restricted to the level of Onsager-type closure structures and does not propose a new thermodynamic principle. Rather, this work

- identifies the repartition of diffusion-related transport between energy flux and entropy flux as the source of different reduced dissipation formats,
- separates the thermodynamic restriction imposed by the dissipation inequality from the additional linear Onsager closure used for constitutive modeling,
- shows that the Müller approach leads to a diffusion-related thermodynamic force containing a temperature-gradient contribution, whereas the Gurtin approach leads to a force basis in which the diffusion-related thermodynamic force is given by the gradient of the relative diffusion potential,
- shows that a diagonal Onsager closure in this shifted Müller-type force basis yields an apparent Soret-type term in the diffusion flux, whereas a diagonal closure in the Gurtin-type force basis yields uncoupled Fourier and Fick laws,

- emphasizes that diagonal and non-diagonal Onsager structures are not invariant under general changes of thermodynamic force basis.

Outline
The balance equations and the dissipation inequality of the Gurtin approach and the Müller approach are derived in Section 2 and 3, respectively. The relation between both approaches regarding the thermo-diffusional coupling and the implications for the Onsager constitutive modeling are presented in Section 4. The work is concluded in Section 5.

Notation
Throughout the manuscript, a direct tensor notation is used. Thus, first and second order tensors are written as $\boldsymbol{a}$ and $\boldsymbol{A}$, respectively. Moreover, $\boldsymbol{a} \cdot \boldsymbol{b}$ denotes the scalar product between two vectors. The material time derivative of a given quantity $\boldsymbol{\alpha}$ is denoted by $\dot{\boldsymbol{\alpha}}$.

2 Gurtin approach - Diffusion modeled via energy fluxes

2.1 Energy balance and related balances

Remark on the Gurtin approach The approach discussed in this section uses arguments that are inherent to the approach discussed by Gurtin and Vargas [2], Gurtin et al. [15, Sect. (64)]. However, in contrast to Gurtin and Vargas [2] and Gurtin et al. [15] the balance laws for the mixture are derived based on invariance considerations. Moreover, in contrast to Gurtin et al. [15], we consider not only an isothermal behavior. Thus, the starting point of this section is given by a discussion of the corresponding energy balance. In this work, mixture-level approaches to diffusion are compared. These approaches are not derived from partial constituent momentum or partial constituent energy balances and are not claimed to be more fundamental than class-II or class-III mixture theories, as discussed, for example, by Bothe and Dreyer [10]. A constituent-based derivation would provide additional structural information about the fluxes and the corresponding entropy production at mixture level. Neither the Gurtin approach nor the Müller approach is presented as the preferred approach. Rather, both are prominent mixture-level approaches to diffusion. Since they account for diffusion-related transport through different thermodynamic fluxes, they constitute a particularly instructive pair for a focused comparison regarding the Onsager closure. The mixture-level setting is appropriate when the resolved fields are mixture fields and when the partial constituent momentum and energy exchange processes are not modeled explicitly. This choice is deliberate because the aim of the present note is not to derive a constituent-based mixture theory, but to compare the closure structures obtained after the two non-isothermal mixture-level approaches have been selected.

Balance of total energy for a chemically open system
For the Gurtin approach, a material volume is considered that allows for a chemical energy flux, related to diffusional fluxes, in addition to the traction working and the heat flow. Subsequently, this continuum is referred to as mechanically closed but chemically open. The corresponding energy balance is that of a material volume extended by additional flux terms, cf. Gurtin et al. [15, p.371], reading

$$\frac{\mathrm{d}}{\mathrm{d}t}\int_{\mathcal{V}} \rho \left(e + \frac{1}{2}\boldsymbol{v}\cdot\boldsymbol{v} \right) \mathrm{d}v = \int_{\mathcal{V}} \rho \left(\boldsymbol{b}\cdot\boldsymbol{v} + r \right) \mathrm{d}v + \int_{\partial\mathcal{V}} \left(\boldsymbol{t}\cdot\boldsymbol{v} + h + \Pi^{\mathrm{ch}} \right) \mathrm{d}a. \tag{1}$$

Here, ρ denotes the mass density, e the specific internal energy, $\boldsymbol{v}$ the spatial velocity field, $\boldsymbol{b}$ the specific body force, r the specific heat supply, $\boldsymbol{t}$ the traction vector, h the heat flux. All these quantities are with respect to the mixture and not the components, cf., e.g., Gurtin and Vargas [2, p.179]. Moreover, Π^{ch} denotes the energy flux due to diffusion, cf. Gurtin and Vargas [2, p.179], Gurtin et al. [15, Eq.(64.1)]. This contribution extends the classical energy balance of a material volume, cf., e.g., Prahs and Böhlke [60, Eq.(1)], Marsden and Hughes [61, p.143].

Open system, material volume
In the work at hand, the energy balance is considered for a material volume moving with the barycentric velocity field $\boldsymbol{v}$. Thus, the system boundary coincides with that of the material volume, i.e., the boundary of the considered system moves with the velocity field $\boldsymbol{v}$. In this case, the standard Reynolds' transport theorem, cf., e.g., Truesdell and Toupin [62, Eq.(81.3)], Slattery [63, Eq.(1.3.2-9)], can be applied for localizing the

integral balance stated in Eq. (1). Nevertheless, the system is chemically open since the constituent velocities $\boldsymbol{v}_\omega$, $\omega = 1, \ldots, K$ (with K denoting the number of constituents), generally satisfy $\boldsymbol{v}_\omega \neq \boldsymbol{v}$, so that diffusion fluxes may cross $\partial\mathcal{V}$ even though the volume is material with respect to $\boldsymbol{v}$. Accordingly, term 'open' is used, here, solely in a chemical–energetic sense, i.e., diffusional fluxes entail an additional transport of energy across $\partial\mathcal{V}$, in structural analogy to the interstitial working introduced by Dunn and Serrin [16, p.98]. This differs from considering a non-material volume whose boundary moves with a velocity different from that of the contained solid or fluid. In this particular case, the application of an extension of Reynolds' transport theorem, as discussed by, cf., e.g., Truesdell and Toupin [62, Eq.(81.4)], Slattery [63, Eq.(1.3.2-12)], Cermelli et al. [64, Eq.(1.3)], would be required. However, this is not considered, in the work at hand.

Invariance considerations and derived balance equations

Equation (1) is structurally similar to the balance of total energy stated in Dunn and Serrin [16, Eq.(1.9)] and that in Prahs and Böhlke [60, Eq.(6)], which is formulated for an extended continuum. The apparent difference lies in how the extension of the energy flux is interpreted. This allows to transfer the discussion regarding the invariance consideration of the energy balance from [60] to Eq. (1). Since (Π^{ch}) is a scalar, it is invariant under the change of observer, and the existence of the Cauchy stress tensor along with the standard balances of mass, linear momentum, and angular momentum is obtained, reading

$$\boldsymbol{\sigma}\boldsymbol{n}_{\mathcal{V}} = \boldsymbol{t}, \quad \dot{\rho} + \rho \operatorname{div}(\boldsymbol{v}) = 0, \quad \rho\boldsymbol{a} = \rho\boldsymbol{b} + \operatorname{div}(\boldsymbol{\sigma}), \quad \boldsymbol{\sigma} = \boldsymbol{\sigma}^{\mathsf{T}}. \tag{2}$$

Here, $\boldsymbol{n}_{\mathcal{V}}$ denotes the outward unit normal vector and $\boldsymbol{a} = \dot{\boldsymbol{v}}$ the acceleration. Accounting for Eq. (2), Eq. (1) reads

$$\int_{\mathcal{V}} \dot{\rho} e - \rho r - \boldsymbol{\sigma} \cdot \operatorname{grad}(\boldsymbol{v}) \, \mathrm{d}v - \int_{\partial\mathcal{V}} h + \Pi^{\mathrm{ch}} \, \mathrm{d}a = 0. \tag{3}$$

The application of Cauchy's Theorem, cf., e.g., Marsden and Hughes [61, p.127], implies the application of Eq. (3) to an infinitesimal tetrahedron yielding

$$\int_{\partial\mathcal{V}} h + \Pi^{\mathrm{ch}} \, \mathrm{d}a = 0, \tag{4}$$

similar to Prahs and Böhlke [60, Eq.(33)]. It can be proven that a flux term $\boldsymbol{k}(\boldsymbol{x}, t)$ exists for which

$$\boldsymbol{k}(\boldsymbol{x}, t) \cdot \boldsymbol{n}_{\mathcal{V}} = h(\boldsymbol{x}, t, \boldsymbol{n}) + \Pi^{\mathrm{ch}}(\boldsymbol{x}, t, \boldsymbol{n}) \tag{5}$$

holds. To reflect the additive composition, the flux term $\boldsymbol{k}(\boldsymbol{x}, t)$ is also additive decomposed such that

$$\boldsymbol{k}(\boldsymbol{x}, t) = \boldsymbol{h}(\boldsymbol{x}, t) + \boldsymbol{l}^{\mathrm{ch}}(\boldsymbol{x}, t), \quad h = \boldsymbol{h} \cdot \boldsymbol{n}_{\mathcal{V}}, \quad \Pi^{\mathrm{ch}} = \boldsymbol{l}^{\mathrm{ch}} \cdot \boldsymbol{n}_{\mathcal{V}} \tag{6}$$

holds. Based on Eq. (6), the heat flux is introduced as

$$\boldsymbol{q}^{\mathrm{G}} = -\boldsymbol{h}, \quad \text{with} \quad \boldsymbol{q}^{\mathrm{G}} \cdot \boldsymbol{n}_{\mathcal{V}} = -h. \tag{7}$$

Moreover, considering K species the chemical fluxes are introduced as

$$\boldsymbol{l}^{\mathrm{ch}} = -\sum_{\omega=1}^{K} \mu_\omega \boldsymbol{j}^\omega. \tag{8}$$

Remark on independent concentrations and diffusion fluxes

For a mixture of K species with the partial mass densities ρ_ω and the partial velocities $\boldsymbol{v}_\omega$, the mixture density and the mass averaged velocity, subsequently denoted as barycentric velocity, are defined as

$$\rho = \sum_{\omega=1}^{K} \rho_\omega, \quad \rho\boldsymbol{v} = \sum_{\omega=1}^{K} \rho_\omega \boldsymbol{v}_\omega, \tag{9}$$

cf., e.g., Ubachs et al. [65, Eqs.(4)&(5)], Slattery [63, p.428]. While this work explicitly employs the diffusion fluxes $\boldsymbol{j}^{\omega}$, they are formally defined as $\boldsymbol{j}^{\omega} := \rho_{\omega}\,(\boldsymbol{v}_{\omega} - \boldsymbol{v})$ and are therefore taken relative to $\boldsymbol{v}$, cf., e.g., de Groot and Mazur [24, p.13, Eq.(9)], Ubachs et al. [65, Eq.(7)]. This yields the constraint regarding the diffusional fluxes via

$$\sum_{\omega=1}^{K} \boldsymbol{j}^{\omega} = \sum_{\omega=1}^{K} \rho_{\omega}\,(\boldsymbol{v}_{\omega} - \boldsymbol{v}) = \sum_{\omega=1}^{K} \rho_{\omega}\boldsymbol{v}_{\omega} - \boldsymbol{v}\sum_{\omega=1}^{K} \rho_{\omega} = \rho\boldsymbol{v} - \boldsymbol{v}\rho = \boldsymbol{0}. \tag{10}$$

Rewriting Eq. (10) yields

$$\sum_{\omega=1}^{K} \boldsymbol{j}^{\omega} = \boldsymbol{j}^{K} + \sum_{\omega=1}^{K-1} \boldsymbol{j}^{\omega} = \boldsymbol{0} \quad \rightsquigarrow \quad \boldsymbol{j}^{K} = -\sum_{\omega=1}^{K-1} \boldsymbol{j}^{\omega}. \tag{11}$$

Consequently, only $K-1$ diffusion fluxes are independent of each other. Moreover, reformulating Eq. $(9)_1$ as

$$1 = \sum_{\omega=1}^{K} c_{\omega}, \quad c_{\omega} := \frac{\rho_{\omega}}{\rho}. \tag{12}$$

yields an additional constraint regarding the concentrations c_{ω} leading to

$$1 = c_K + \sum_{\omega=1}^{K-1} c_{\omega} \quad \rightsquigarrow \quad c_K = 1 - \sum_{\omega=1}^{K-1} c_{\omega}. \tag{13}$$

Thus, also only $K-1$ concentrations are independent of each other. Accordingly,

$$\sum_{\omega=1}^{K} \mu_{\omega}\boldsymbol{j}^{\omega} = \sum_{\omega=1}^{K-1} \mu_{\omega}\boldsymbol{j}^{\omega} + \mu_K\,\boldsymbol{j}^{K} = \sum_{\omega=1}^{K-1} \mu_{\omega}\boldsymbol{j}^{\omega} - \mu_K \sum_{\omega=1}^{K-1} \boldsymbol{j}^{\omega} = \sum_{\omega=1}^{K-1} (\mu_{\omega} - \mu_K)\,\boldsymbol{j}^{\omega} \tag{14}$$

holds true. Introducing the relative potentials $\tilde{\mu}_{\omega}$ as

$$\tilde{\mu}_{\omega} = \mu_{\omega} - \mu_K \tag{15}$$

Eq. (8) can be written as

$$\boldsymbol{l}^{\mathrm{ch}} = -\sum_{\omega=1}^{K-1} \tilde{\mu}_{\omega}\boldsymbol{j}^{\omega}. \tag{16}$$

Balance of internal energy

Accounting for Eqs. (7) and (16), the application of the divergence theorem to Eq. (3) and subsequent localization yields the balance of internal energy as

$$\rho\dot{e} = \boldsymbol{\sigma} \cdot \operatorname{grad}(\boldsymbol{v}) + \rho r - \operatorname{div}\left(\boldsymbol{q}^{\mathrm{G}}\right) - \sum_{\omega=1}^{K-1} \operatorname{div}\left(\tilde{\mu}_{\omega}\boldsymbol{j}^{\omega}\right). \tag{17}$$

Extension of Eq. (17) and accounting for the diffusion equation

$$\rho\dot{c}_{\omega} = -\operatorname{div}\left(\boldsymbol{j}^{\omega}\right) \quad \forall\,\omega \in [1, K-1] \tag{18}$$

cf., e.g., Ubachs et al. [65, Eq.(7)], Eq. (17) can be written as

$$\rho\dot{e} = \boldsymbol{\sigma} \cdot \operatorname{grad}(\boldsymbol{v}) + \rho r - \operatorname{div}\left(\boldsymbol{q}^{\mathrm{G}}\right) + \sum_{\omega=1}^{K-1} \tilde{\mu}_{\omega}\rho\dot{c}_{\omega} - \sum_{\omega=1}^{K-1} \nabla\tilde{\mu}_{\omega} \cdot \boldsymbol{j}^{\omega}. \tag{19}$$

The two last terms that are related to the diffusion extend the balance of energy of a classical Cauchy continuum in a closed system and are discussed, e.g., in Gurtin et al. [15, Eq. (64.3)]. The extension of the balance of internal energy is already discussed in Gurtin and Vargas [2].

2.2 Entropy balance and dissipation inequality

Entropy balance

The balance of entropy for a material volume is given by

$$\frac{\mathrm{d}}{\mathrm{d}t}\int_{\mathcal{V}} \rho\eta \,\mathrm{d}v = -\int_{\partial\mathcal{V}} \boldsymbol{\phi}^{\eta}_{\mathcal{V}} \cdot \boldsymbol{n}_{\mathcal{V}} \,\mathrm{d}a + \int_{\mathcal{V}} \rho\, p^{\eta}_{\mathcal{V}} + s^{\eta}_{\mathcal{V}} \,\mathrm{d}v, \tag{20}$$

cf., e.g., Müller [8, Table 3.1]. Here, η denotes the specific entropy, $\boldsymbol{\phi}^{\eta}_{\mathcal{V}}$ the entropy flux, $p^{\eta}_{\mathcal{V}}$ the specific entropy production, and $s^{\eta}_{\mathcal{V}}$ the entropy supply. Application of the divergence theorem to Eq. (20) and subsequent localization yield the local form of the entropy balance, reading

$$\rho\dot{\eta} = -\mathrm{div}\left(\boldsymbol{\phi}^{\eta}_{\mathcal{V}}\right) + \rho p^{\eta}_{\mathcal{V}} + s^{\eta}_{\mathcal{V}}. \tag{21}$$

Dissipation inequality

Multiplication of Eq. (21) with the absolute temperature θ and rearrangement yields the dissipation inequality as

$$\rho\delta = \rho\theta\dot{\eta} + \theta\mathrm{div}\left(\boldsymbol{\phi}^{\eta}_{\mathcal{V}}\right) - \theta s^{\eta}_{\mathcal{V}} \geq 0, \quad \text{with} \quad \delta := \theta p^{\eta}_{\mathcal{V}}. \tag{22}$$

Following the Gurtin approach, the entropy flux and the entropy supply are considered to be given as

$$\boldsymbol{\phi}^{\eta}_{\mathcal{V}} = \frac{\boldsymbol{q}^{\mathrm{G}}}{\theta}, \quad s^{\eta}_{\mathcal{V}} = \frac{\rho r}{\theta}, \tag{23}$$

cf., e.g., Gurtin and Vargas [2, Eq.(2.5)]. Taking into account the Legendre transformation, i.e., $\psi = e - \theta\eta$, cf., e.g., [66], the dissipation inequality takes the form

$$\rho\delta = \rho\dot{e} - \rho\dot{\psi} - \rho\dot{\theta}\eta - \rho r + \mathrm{div}\left(\boldsymbol{q}^{\mathrm{G}}\right) - \frac{1}{\theta}\boldsymbol{q}^{\mathrm{G}} \cdot \boldsymbol{g} \geq 0, \tag{24}$$

with the temperature gradient $\boldsymbol{g} = \mathrm{grad}\,(\theta)$, cf., e.g., Coleman and Gurtin [67, eq.(2.5)]. Inserting the balance of internal energy according to Eq. (19) yields

$$\rho\delta = \boldsymbol{\sigma} \cdot \mathrm{grad}\,(\boldsymbol{v}) - \rho\dot{\psi} - \rho\dot{\theta}\eta - \frac{1}{\theta}\boldsymbol{q}^{\mathrm{G}} \cdot \boldsymbol{g} + \sum_{\omega=1}^{K-1} \rho\tilde{\mu}_{\omega}\dot{c}_{\omega} - \sum_{\omega=1}^{K-1} \nabla\tilde{\mu}_{\omega} \cdot \boldsymbol{j}^{\omega} \geq 0. \tag{25}$$

For the following comparison, the reduced dissipation is split into a contribution associated with the selected transport fluxes, subsequently denoted as δ_{flux}, and a contribution related to constitutive material modeling through the free energy, denoted as δ_{const}. This split is used only to organize the subsequent comparison. It is not unique and is not introduced as an additional thermodynamic principle. Accordingly, the subsequent Onsager closure is conditional on this particular identification of the flux-related part. In this regard,

$$\rho\delta = \rho\delta_{\mathrm{const}} + \rho\delta_{\mathrm{flux}} \geq 0 \tag{26}$$

holds true, with the contributions

$$\rho\delta_{\mathrm{const}} = \boldsymbol{\sigma} \cdot \mathrm{grad}\,(\boldsymbol{v}) - \rho\dot{\psi} - \rho\dot{\theta}\eta + \sum_{\omega=1}^{K-1} \rho\tilde{\mu}_{\omega}\dot{c}_{\omega}, \quad \rho\delta_{\mathrm{flux}} = -\frac{1}{\theta}\boldsymbol{q}^{\mathrm{G}} \cdot \boldsymbol{g} - \sum_{\omega=1}^{K-1} \nabla\tilde{\mu}_{\omega} \cdot \boldsymbol{j}^{\omega}. \tag{27}$$

Subsequently,

$$\rho\delta_{\mathrm{const}} \geq 0, \quad \rho\delta_{\mathrm{flux}} \geq 0 \tag{28}$$

is imposed here as a sufficient condition to fulfill $\rho\delta \geq 0$. Other constitutive choices could ensure non-negative total dissipation without requiring the two identified contributions to be non-negative separately. It is noteworthy that, due to the constraint in Eq. (13), the specific free energy has to be formulated in terms of the independent concentrations $c_1, \ldots c_{K-1}$, and the chemical driving forces can equivalently be expressed using the relative potentials $\tilde{\mu}_1, \ldots \tilde{\mu}_{K-1}$, with $\tilde{\mu}_{\omega}$ according to Eq. (15).

3 Müller approach - Diffusion modeled via entropy fluxes

3.1 Energy balance and related balances

Balance of total energy for a closed system
For the Müller approach, the energy balance of a material volume for a Cauchy continuum is considered. The diffusion is not accounted for by an additional energy flux but by a modified entropy flux. Thus, the considered energy balance corresponds to Eq. (1) without the contribution Π^{ch}, reading

$$\frac{\mathrm{d}}{\mathrm{d}t}\int\limits_{\mathcal{V}} \rho\left(e+\frac{1}{2}\boldsymbol{v}\cdot\boldsymbol{v}\right)\,\mathrm{d}v = \int\limits_{\mathcal{V}} \rho\left(\boldsymbol{b}\cdot\boldsymbol{v}+r\right)\,\mathrm{d}v + \int\limits_{\partial\mathcal{V}} \left(\boldsymbol{t}\cdot\boldsymbol{v}+h\right)\,\mathrm{d}a. \tag{29}$$

Invariance considerations and derived balance equations
As in Sect. (2.1), the discussion regarding the invariance considerations of [60] can be directly applied to Eq. (29). This yields the balances as stated in Eq. (2), while in contrast to Eq. (17) the balance of internal energy is obtained in its standard form, i.e., without the additional contributions related to Π^{ch}, reading

$$\rho\dot{e} = \boldsymbol{\sigma}\cdot\operatorname{grad}\left(\boldsymbol{v}\right) + \rho r - \operatorname{div}\left(\boldsymbol{q}^{\mathrm{M}}\right). \tag{30}$$

As in the Gurtin approach, Cauchy's Theorem is used to represent the surface heat flux h by a heat flux vector. For the Müller approach, this heat flux vector is denoted by $\boldsymbol{q}^{\mathrm{M}}$, with the sign convention $h = -\boldsymbol{q}^{\mathrm{M}}\cdot\boldsymbol{n}_{\mathcal{V}}$, which leads to Eq. (30). The superscript M is introduced to distinguish this heat flux vector from $\boldsymbol{q}^{\mathrm{G}}$, which was introduced in Eq. (7) for the Gurtin approach.

3.2 Entropy balance and dissipation inequality

Entropy balance
The entropy balance in integral and local form corresponds to that stated in Eq. (20) and Eq. (21), since the entropy flux and supply are not yet specified.

Dissipation inequality
Following the Müller approach, the entropy flux and the entropy supply are considered to be given as

$$\boldsymbol{\phi}^{\eta}_{\mathcal{V}} = \frac{\boldsymbol{q}^{\mathrm{M}}}{\theta} - \sum_{\omega=1}^{K}\frac{\mu_{\omega}}{\theta}\boldsymbol{j}^{\omega}, \quad s^{\eta}_{\mathcal{V}} = \frac{\rho r}{\theta}. \tag{31}$$

In accordance with the discussion by Eqs. (9) - (16), the entropy flux is reformulated in terms of the relative potentials, cf. Eq. (15), reading

$$\boldsymbol{\phi}^{\eta}_{\mathcal{V}} = \frac{\boldsymbol{q}^{\mathrm{M}}}{\theta} - \sum_{\omega=1}^{K-1}\frac{\tilde{\mu}_{\omega}}{\theta}\boldsymbol{j}^{\omega}, \quad s^{\eta}_{\mathcal{V}} = \frac{\rho r}{\theta}. \tag{32}$$

In the present Müller approach, the diffusion-related contribution that is accounted for by the additional energy flux in Eq. (16) is instead assigned to the entropy flux in Eq. (32). Thus, the two formulations differ here by a repartition of the same type of $\tilde{\mu}_{\omega}\boldsymbol{j}^{\omega}$ transport between energy flux and entropy flux. The fluxes $\boldsymbol{q}^{\mathrm{G}}$ and $\boldsymbol{q}^{\mathrm{M}}$ should therefore not be interpreted as identical heat flux vectors. With the sign conventions used here, the flux entering the classical energy balance in the Müller approach is related to the Gurtin heat flux by

$$\boldsymbol{q}^{\mathrm{M}} = \boldsymbol{q}^{\mathrm{G}} + \sum_{\omega=1}^{K-1}\tilde{\mu}_{\omega}\boldsymbol{j}^{\omega}. \tag{33}$$

This relation means that, at the level of the energy balance, the diffusion-related energetic transport that appears as the additional energy flux $\sum_{\omega=1}^{K-1}\tilde{\mu}_{\omega}\boldsymbol{j}^{\omega}$ in the Gurtin approach is accounted for through $\boldsymbol{q}^{\mathrm{M}}$ in the Müller approach, rather than through a separate energy flux term. Conversely, inserting Eq. (33) into the Müller

entropy flux in Eq. (32) recovers the standard entropy flux $\boldsymbol{q}^{\mathrm{G}}/\theta$ used in the Gurtin approach. Taking into account Eq. (32) as well as the Legendre transformation, Eq. (21) reads

$$\rho\delta = \rho\dot{e} - \rho\dot{\psi} - \rho\dot{\theta}\eta - \rho r + \operatorname{div}\left(\boldsymbol{q}^{\mathrm{M}}\right) - \frac{1}{\theta}\boldsymbol{q}^{\mathrm{M}}\cdot\boldsymbol{g} - \sum_{\omega=1}^{K-1}\operatorname{div}\left(\tilde{\mu}_{\omega}\boldsymbol{j}^{\omega}\right) + \sum_{\omega=1}^{K-1}\frac{\tilde{\mu}_{\omega}}{\theta}\boldsymbol{j}^{\omega}\cdot\boldsymbol{g} \geq 0. \tag{34}$$

Moreover, accounting for Eq. (30) and Eq. (18) and applying the product rule, Eq. (34) is expressed as

$$\rho\delta = \boldsymbol{\sigma}\cdot\operatorname{grad}(\boldsymbol{v}) - \rho\dot{\psi} - \rho\dot{\theta}\eta - \frac{1}{\theta}\boldsymbol{q}^{\mathrm{M}}\cdot\boldsymbol{g} - \sum_{\omega=1}^{K-1}\nabla\tilde{\mu}_{\omega}\cdot\boldsymbol{j}^{\omega} + \sum_{\omega=1}^{K-1}\rho\tilde{\mu}_{\omega}\dot{c}_{\omega} + \sum_{\omega=1}^{K-1}\frac{\tilde{\mu}_{\omega}}{\theta}\boldsymbol{j}^{\omega}\cdot\boldsymbol{g} \geq 0. \tag{35}$$

In line with Eq. (26), the dissipation is decomposed in the two contributions δ_{const} and δ_{flux}, reading

$$\rho\delta_{\mathrm{const}} = \boldsymbol{\sigma}\cdot\operatorname{grad}(\boldsymbol{v}) - \rho\dot{\psi} - \rho\dot{\theta}\eta + \sum_{\omega=1}^{K-1}\rho\tilde{\mu}_{\omega}\dot{c}_{\omega}, \quad \rho\delta_{\mathrm{flux}} = -\frac{1}{\theta}\boldsymbol{q}^{\mathrm{M}}\cdot\boldsymbol{g} - \sum_{\omega=1}^{K-1}\nabla\tilde{\mu}_{\omega}\cdot\boldsymbol{j}^{\omega} + \sum_{\omega=1}^{K-1}\frac{\tilde{\mu}_{\omega}}{\theta}\boldsymbol{j}^{\omega}\cdot\boldsymbol{g}. \tag{36}$$

While the contributions in Eq. $(27)_1$ and Eq. $(36)_1$ coincide, Eq. $(36)_2$ exhibits the thermo-diffusional coupling term $\sum_{\omega=1}^{K-1}\tilde{\mu}_{\omega}/\theta\,\boldsymbol{j}^{\omega}\cdot\boldsymbol{g}$ in contrast to Eq. $(27)_2$. This additional term should not be interpreted as an additional physical mechanism that is independent of the chosen basis of thermodynamic forces. It results from assigning diffusion-related transport to the entropy flux rather than to an additional energy flux. Equivalently, the flux-related dissipation can be written with a shifted thermodynamic force for diffusion, as shown below.

4 Relation between both approaches regarding thermo-diffusivity

4.1 Exploitation of Gurtin approach

Thermodynamic restrictions and Onsager closure

The exploitation of the contribution δ_{const}, cf. Eq. $(28)_1$, is commonly associated with the Coleman–Noll procedure [23,67]. This procedure provides restrictions on admissible constitutive equations by requiring the dissipation inequality to hold for all admissible processes. It does not, by itself, prescribe a specific linear relation between fluxes and thermodynamic forces. The Onsager-type relations used below are therefore an additional constitutive closure assumption imposed on the flux-related part δ_{flux} in a selected thermodynamic force basis. Such linear Onsager relations are sufficient for non-negative flux dissipation if the corresponding Onsager operator is positive semidefinite. However, they are not the only possible closure construction, since the entropy inequality can also be satisfied by other admissible constitutive choices, as discussed by Bothe and Dreyer [10, pp. 1759, 1790]. The present work concentrates on this flux contribution, which can be discussed independently of any particular material behavior modeled by δ_{const}. Thus, the detailed exploitation of Eq. $(28)_1$ is omitted here.

Exploitation of flux terms

To fulfill the non-negativity demanded in Eq. $(28)_2$, one simple sufficient closure in the present thermodynamic force basis is given by Fourier's law of heat conduction and Fick's law of diffusion, reading

$$\boldsymbol{q}^{\mathrm{G}} = -\boldsymbol{\kappa}\boldsymbol{g}, \quad \boldsymbol{j}^{\omega} = -\boldsymbol{M}_{\omega}^{\mathrm{G}}\nabla\tilde{\mu}_{\omega}, \tag{37}$$

respectively. Here, $\boldsymbol{\kappa} \in SPD$ denotes Fourier's tensor of heat conduction and $\boldsymbol{M}_{\omega}^{\mathrm{G}} \in SPD$ Fick's diffusivity tensor. In this regard, SPD denotes the set of symmetric, positive definite tensors. Accounting for Eq. (37), Eq. $(27)_2$ reads

$$\rho\delta_{\mathrm{flux}} = \frac{1}{\theta}\boldsymbol{g}\cdot(\boldsymbol{\kappa}\boldsymbol{g}) + \sum_{\omega=1}^{K-1}\nabla\tilde{\mu}_{\omega}\cdot\left(\boldsymbol{M}_{\omega}^{\mathrm{G}}\nabla\tilde{\mu}_{\omega}\right) \geq 0, \tag{38}$$

which fulfills the requirement of non-negativity. The closure according to Eq. (37) results in no coupling between thermal and diffusion fluxes in this selected thermodynamic force basis. This is a common modeling assumption, cf., e.g., Anand [18, footnote 8], but it is not the only thermodynamically admissible closure.

4.2 Exploitation of Müller approach

Dissipation inequality in standard form

The direct Müller approach analogue of the uncoupled closure in Eq. (37), obtained by replacing $\boldsymbol{q}^{\mathrm{G}}$ with $\boldsymbol{q}^{\mathrm{M}}$ and $\boldsymbol{M}_{\omega}^{\mathrm{G}}$ with $\boldsymbol{M}_{\omega}^{\mathrm{M}}$, does not guarantee non-negativity of Eq. $(36)_2$ due to the thermo-diffusional coupling term $\boldsymbol{j}^{\omega} \cdot \boldsymbol{g}$. Specifically, applying an analogous uncoupled diffusion law, $\boldsymbol{j}^{\omega} = -\boldsymbol{M}_{\omega}^{\mathrm{M}} \nabla \tilde{\mu}_{\omega}$, yields the cross contribution $-\tilde{\mu}_{\omega}/\theta \left(\boldsymbol{M}_{\omega}^{\mathrm{M}} \nabla \tilde{\mu}_{\omega}\right) \cdot \boldsymbol{g}$, which cannot be guaranteed to be non-negative in general. To circumvent this issue, it is necessary to write the flux contribution $\rho \delta_{\mathrm{flux}}$ according to Eq. $(36)_2$. To this end, following de Groot and Mazur [24, p.33, Eq.(13)], the thermodynamic forces $\boldsymbol{X}^{q}$ and $\boldsymbol{X}^{\omega}$ are introduced as

$$\boldsymbol{X}^{q} = \operatorname{grad}\left(\frac{1}{\theta}\right) = -\frac{1}{\theta^2}\boldsymbol{g}, \quad \boldsymbol{X}^{\omega} = -\operatorname{grad}\left(\frac{\tilde{\mu}_{\omega}}{\theta}\right) = \frac{\tilde{\mu}_{\omega}}{\theta^2}\boldsymbol{g} - \frac{1}{\theta}\nabla\tilde{\mu}_{\omega}. \tag{39}$$

Consequently, Eq. $(36)_2$ reads

$$\rho\delta_{\mathrm{flux}} = \theta\left(\boldsymbol{q}^{\mathrm{M}} \cdot \boldsymbol{X}^{q} + \sum_{\omega=1}^{K-1} \boldsymbol{j}^{\omega} \cdot \boldsymbol{X}^{\omega}\right). \tag{40}$$

For a better comparability with de Groot and Mazur [24, p.33, Eq.(13)], the identity $\operatorname{grad}(\tilde{\mu}_{\omega})/\theta = \operatorname{grad}(\tilde{\mu}_{\omega}/\theta) - \tilde{\mu}_{\omega}\operatorname{grad}(1/\theta)$ can be inserted in Eq. (40).

Exploitation of flux terms

To fulfill Eq. $(36)_2$, the linear relation between thermodynamic fluxes, written compact as $\underline{j}$, and thermodynamic forces, abbreviated by $\underline{X}$, is introduced, cf., e.g., de Groot and Mazur [24, p.30] such that

$$\underline{j} = \underline{\underline{\mathcal{L}}}\,\underline{X}, \quad \underline{j} = \begin{pmatrix} [q_i^{\mathrm{M}}] \\ [j_i^{1}] \\ \vdots \\ [j_i^{\omega}] \\ \vdots \\ [j_i^{K-1}] \end{pmatrix} \in \mathbb{R}^{3K}, \quad \underline{X} = \begin{pmatrix} [X_i^{q}] \\ [X_i^{1}] \\ \vdots \\ [X_i^{\omega}] \\ \vdots \\ [X_i^{K-1}] \end{pmatrix} \in \mathbb{R}^{3K}, \tag{41}$$

$$\underline{\underline{\mathcal{L}}} = \begin{pmatrix} [\mathcal{L}_{ij}^{00}] & [\mathcal{L}_{ij}^{01}] & \cdots & [\mathcal{L}_{ij}^{0K-1}] \\ [\mathcal{L}_{ij}^{10}] & [\mathcal{L}_{ij}^{11}] & \cdot & [\mathcal{L}_{ij}^{1K-1}] \\ \vdots & \vdots & \ddots & \vdots \\ [\mathcal{L}_{ij}^{K-10}] & [\mathcal{L}_{ij}^{K-11}] & \cdots & [\mathcal{L}_{ij}^{K-1K-1}] \end{pmatrix} \in \mathbb{R}^{3K\times 3K}. \tag{42}$$

Here, $[q_i^{\mathrm{M}}]$, $[j_i^{\omega}]$, $[X_i^{q}]$, and $[X_i^{\omega}]$ denote the column-matrices of $\boldsymbol{q}^{\mathrm{M}}$, $\boldsymbol{j}^{\omega}$, $\boldsymbol{X}^{q}$, and $\boldsymbol{X}^{\omega}$, respectively, i.e., the matrices collect the Cartesian components in a fixed spatial basis. Moreover, $[\mathcal{L}_{ij}^{\alpha\beta}]$ denote the corresponding matrices of the Onsager coefficients $\boldsymbol{\mathcal{L}}^{\alpha\beta}$ in that basis. Since the thermodynamic fluxes and forces are vector-valued, the Onsager coefficients are tensors of second order. Regarding Equation (41), $\underline{\underline{\mathcal{L}}}$ is referred to as the Onsager operator. Finally, Eq. $(36)_2$ can be written as

$$\rho\delta_{\mathrm{flux}} = \theta\left(\underline{\underline{\mathcal{L}}}\,\underline{X}\right) \cdot \underline{X} = \theta\left(\underline{X}^{\mathsf{T}}\underline{\underline{\mathcal{L}}}\,\underline{X}\right) = \theta\left(\sum_{\alpha=0}^{K-1}\sum_{\beta=0}^{K-1} \mathbf{X}^{\alpha} \cdot \left(\boldsymbol{\mathcal{L}}^{\alpha\beta}\mathbf{X}^{\beta}\right)\right) \geq 0. \tag{43}$$

To ensure the non-negativity of δ_{flux}, i.e. $\delta_{\mathrm{flux}} \geq 0$, the Onsager operator $\underline{\underline{\mathcal{L}}}$ needs to be positive semidefinite, i.e., $\underline{X}^{\mathsf{T}}\underline{\underline{\mathcal{L}}}\,\underline{X} \geq 0\ \forall \underline{X}$. This is achieved by requiring the diagonal Onsager blocks to be symmetric and positive semidefinite. In this work, they are chosen symmetric positive definite, i.e., $[\mathcal{L}_{ij}^{00}] \in SPD$ and $[\mathcal{L}_{ij}^{\omega\omega}] \in SPD$ for $\omega = 1, \ldots, K-1$. Moreover, the off-diagonal blocks satisfy Onsager reciprocity in the block sense,

i.e., $[\mathcal{L}_{ij}^{\alpha\beta}] = [\mathcal{L}_{ij}^{\beta\alpha}]^{\mathsf{T}}$, and are chosen such that the assembled Onsager operator $\underline{\underline{\mathcal{L}}}$ remains positive semidefinite, cf. Bhatia [68, Theorem 1.3.3]. Equation (41) can also be written as

$$\mathbf{j}^{\alpha} = \sum_{\beta=0}^{K-1} \boldsymbol{\mathcal{L}}^{\alpha\beta}\mathbf{X}^{\beta}, \quad \alpha = 0, \ldots, K-1 \tag{44}$$

cf. de Groot and Mazur [24, p.30, Eq.(1)]. Consequently, the linear relation between thermodynamic fluxes and forces can be written as

$$\boldsymbol{q}^{\mathrm{M}} = -\frac{1}{\theta^2}\boldsymbol{\mathcal{L}}^{00}\boldsymbol{g} + \sum_{\beta=1}^{K-1}\frac{\tilde{\mu}_{\beta}}{\theta^2}\boldsymbol{\mathcal{L}}^{0\beta}\boldsymbol{g} - \sum_{\beta=1}^{K-1}\frac{1}{\theta}\boldsymbol{\mathcal{L}}^{0\beta}\nabla\tilde{\mu}_{\beta}, \tag{45}$$

$$\boldsymbol{j}^{\omega} = -\frac{1}{\theta^2}\boldsymbol{\mathcal{L}}^{\omega 0}\boldsymbol{g} + \sum_{\beta=1}^{K-1}\frac{\tilde{\mu}_{\beta}}{\theta^2}\boldsymbol{\mathcal{L}}^{\omega\beta}\boldsymbol{g} - \sum_{\beta=1}^{K-1}\frac{1}{\theta}\boldsymbol{\mathcal{L}}^{\omega\beta}\nabla\tilde{\mu}_{\beta}, \quad \omega = 1, \ldots, K-1 \tag{46}$$

Remark on the symmetry of the Onsager coefficients
In the present work, thermodynamic fluxes are restricted to the heat flux $\boldsymbol{q}^{\mathrm{M}}$ and the diffusion fluxes $\boldsymbol{j}^{\omega}$, cf. Eqs. (40) - (41). According to de Groot and Mazur [24], these fluxes exhibit the same time-reversal invariance, implying the block sense symmetry $[\mathcal{L}_{ij}^{\alpha\beta}] = [\mathcal{L}_{ij}^{\beta\alpha}]^{\mathsf{T}}$. See the note on even functions on particle velocities in de Groot and Mazur [24, p.35].

Reduction to diagonal Onsager matrix
Regarding Eq. (41), the diagonal elements are given by

$$\boldsymbol{\mathcal{L}}^{00} = \theta^2\boldsymbol{\kappa}, \quad \boldsymbol{\mathcal{L}}^{\omega\omega} = \boldsymbol{M}_{\omega}^{\mathrm{M}}, \quad \forall\omega \in [1, K-1], \tag{47}$$

with $\boldsymbol{\kappa} \in SPD$ and $\boldsymbol{M}_{\omega}^{\mathrm{M}} \in SPD$. The tensor $\boldsymbol{M}_{\omega}^{\mathrm{M}}$ is the counterpart of $\boldsymbol{M}_{\omega}^{\mathrm{G}}$ for the Müller approach. The tensor $\boldsymbol{M}_{\omega}^{\mathrm{G}}$ was introduced in Eq. (37) for the diagonal closure in the thermodynamic force basis of the Gurtin approach. Therefore, the subscripts G and M indicate the thermodynamic force basis in which the respective diagonal closure is imposed. In particular, $\boldsymbol{M}_{\omega}^{\mathrm{G}}$ and $\boldsymbol{M}_{\omega}^{\mathrm{M}}$ are not identified unless an additional constitutive assumption is introduced. The off-diagonal coefficients $\boldsymbol{\mathcal{L}}^{\alpha\beta}$ are related to the so called Soret-Dufour effect of thermodiffusion, cf. de Groot and Mazur [24, p.274]. The full coupling in Eq. (43) can be reduced by neglecting the off-diagonal coefficients, i.e., choosing $\boldsymbol{\mathcal{L}}^{\alpha\beta} = \mathbf{0}, \forall\,\alpha \neq \beta$. This yields the following relations for the heat flux $\boldsymbol{q}^{\mathrm{M}}$ and the diffusion flux $\boldsymbol{j}^{\omega}$

$$\boldsymbol{q}^{\mathrm{M}} = \theta^2\boldsymbol{\kappa}\boldsymbol{X}^{q} = -\boldsymbol{\kappa}\boldsymbol{g}, \quad \boldsymbol{j}^{\omega} = \boldsymbol{M}_{\omega}^{\mathrm{M}}\boldsymbol{X}^{\omega} = -\boldsymbol{M}_{\omega}^{\mathrm{M}}\mathrm{grad}\left(\frac{\tilde{\mu}_{\omega}}{\theta}\right) = -\frac{1}{\theta}\boldsymbol{M}_{\omega}^{\mathrm{M}}\nabla\tilde{\mu}_{\omega} + \frac{\tilde{\mu}_{\omega}}{\theta^2}\boldsymbol{M}_{\omega}^{\mathrm{M}}\boldsymbol{g}. \tag{48}$$

Equation $(48)_1$ corresponds to the classical Fourier law of heat conduction, whereas Eq. $(48)_2$ contains an additional term proportional to $\boldsymbol{g}$. This term appears because, in the Müller approach considered here, the diffusion-related thermodynamic force is chosen according to Eq. $(39)_2$ and therefore already contains a contribution proportional to $\boldsymbol{g}$. Consequently, a diagonal Onsager closure in this thermodynamic force basis still yields a temperature-gradient contribution in the diffusion flux. This should not be interpreted as an additional physical mechanism that is independent of the thermodynamic force basis used for the Onsager closure. The coupling of the diffusion flux to the temperature gradient is referred to as Soret effect, while a coupling of the heat flux to diffusion-related driving forces is denoted as Dufour effect [24, p.274]. In this restricted sense, the Müller approach considered here exhibits an apparent "Soret-without-Dufour" structure for vanishing off-diagonal Onsager coefficients in the chosen force basis.

4.3 Gurtin approach combined with Onsager exploitation

Exploitation of flux terms
For establishing a relation between the Gurtin approach and the Müller approach, Eq. $(27)_2$ is written in the standard form as well, reading

$$\rho\delta_{\text{flux}} = \boldsymbol{q}^{\text{G}} \cdot \boldsymbol{X}^{q,\text{G}} + \sum_{\omega=1}^{K-1} \boldsymbol{j}^{\omega} \cdot \boldsymbol{X}^{\omega,\text{G}}, \tag{49}$$

with the contributions

$$\boldsymbol{X}^{q,\text{G}} = -\frac{1}{\theta}\boldsymbol{g}, \quad \boldsymbol{X}^{\omega,\text{G}} = -\nabla\tilde{\mu}_{\omega}. \tag{50}$$

Similar to Eq. (41), the linear relation between the thermodynamic fluxes $\underline{j}^{\text{G}}$ and forces $\underline{X}^{\text{G}}$ is written as

$$\underline{j}^{\text{G}} = \underline{\underline{\mathcal{L}}}^{\text{G}}\,\underline{X}^{\text{G}}, \quad \underline{j}^{\text{G}} = \begin{pmatrix} [q_i^{\text{G}}] \\ [j_i^{1}] \\ \vdots \\ [j_i^{\omega}] \\ \vdots \\ [j_i^{K-1}] \end{pmatrix} \in \mathbb{R}^{3K}, \quad \underline{X}^{\text{G}} = \begin{pmatrix} [X_i^{q,\text{G}}] \\ [X_i^{1,\text{G}}] \\ \vdots \\ [X_i^{\omega,\text{G}}] \\ \vdots \\ [X_i^{K-1,\text{G}}] \end{pmatrix} \in \mathbb{R}^{3K}, \tag{51}$$

$$\underline{\underline{\mathcal{L}}}^{\text{G}} = \begin{pmatrix} [\mathcal{L}_{ij}^{\text{G},0\,0}] & [\mathcal{L}_{ij}^{\text{G},0\,1}] & \cdots & [\mathcal{L}_{ij}^{\text{G},0\,K-1}] \\ [\mathcal{L}_{ij}^{\text{G},1\,0}] & [\mathcal{L}_{ij}^{\text{G},1\,1}] & \cdot & [\mathcal{L}_{ij}^{\text{G},1\,K-1}] \\ \vdots & \vdots & \ddots & \vdots \\ [\mathcal{L}_{ij}^{\text{G},K-1\,0}] & [\mathcal{L}_{ij}^{\text{G},K-1\,1}] & \cdots & [\mathcal{L}_{ij}^{\text{G},K-1\,K-1}] \end{pmatrix} \in \mathbb{R}^{3K\times 3K}. \tag{52}$$

Similar to the Müller approach, the column-matrices of $\boldsymbol{q}^{\text{G}}$, $\boldsymbol{j}^{\omega}$, $\boldsymbol{X}^{q,\text{G}}$, and $\boldsymbol{X}^{\omega,\text{G}}$ are referred to as $[q_i^{\text{G}}]$, $[j_i^{\omega}]$, $[X_i^{q,\text{G}}]$, and $[X_i^{\omega,\text{G}}]$, respectively. In addition, the corresponding matrices of the Onsager coefficients $\boldsymbol{\mathcal{L}}^{\text{G},\alpha\,\beta}$, with respect to that basis, are referred to as $[\mathcal{L}_{ij}^{\text{G},\alpha\,\beta}]$. Consequently, Eq. $(27)_2$ can be written as

$$\rho\delta_{\text{flux}} = \left(\underline{\underline{\mathcal{L}}}^{\text{G}}\,\underline{X}^{\text{G}}\right)\cdot\underline{X}^{\text{G}} = \left(\underline{X}^{\text{G}^{\mathsf{T}}}\,\underline{\underline{\mathcal{L}}}^{\text{G}}\,\underline{X}^{\text{G}}\right) = \left(\sum_{\alpha=0}^{K-1}\sum_{\beta=0}^{K-1}\mathbf{X}^{\text{G},\alpha}\cdot\left(\boldsymbol{\mathcal{L}}^{\text{G},\alpha\,\beta}\mathbf{X}^{\text{G},\beta}\right)\right) \geq 0, \tag{53}$$

which fulfills the non-negativity requirement demanded in Eq. $(28)_2$ if $\underline{\underline{\mathcal{L}}}^{\text{G}} \in \mathit{SPSD}$, i.e., if $\underline{\underline{\mathcal{L}}}^{\text{G}}$ is symmetric positive semidefinite. This requires $[\mathcal{L}_{ij}^{\text{G},\omega\,\omega}] \in \mathit{SPSD}$, for $\omega = 0, \ldots, K-1$, the Onsager reciprocity in the block sense, i.e., $[\mathcal{L}_{ij}^{\text{G},\alpha\,\beta}] = [\mathcal{L}_{ij}^{\text{G},\beta\,\alpha}]^{\mathsf{T}}$ for $\alpha \neq \beta$, and choosing $[\mathcal{L}_{ij}^{\text{G},\alpha\,\beta}]$ such that $\underline{\underline{\mathcal{L}}}^{\text{G}}$ remains *SPSD*. In this work, $[\mathcal{L}_{ij}^{\text{G},\omega\,\omega}] \in \mathit{SPD}$ is considered. Equation (51) can also be written as

$$\mathbf{j}^{\text{G},\alpha} = \sum_{\beta=0}^{K-1}\boldsymbol{\mathcal{L}}^{\text{G},\alpha\,\beta}\mathbf{X}^{\text{G},\beta}, \quad \alpha = 0, \ldots, K-1. \tag{54}$$

Thus, the relations between fluxes and forces read

$$\boldsymbol{q}^{\text{G}} = -\boldsymbol{\mathcal{L}}^{\text{G},0\,0}\frac{1}{\theta}\boldsymbol{g} - \sum_{\omega=1}^{K-1}\boldsymbol{\mathcal{L}}^{\text{G},0\,\omega}\nabla\tilde{\mu}_{\omega}, \tag{55}$$

$$\boldsymbol{j}^{\omega} = -\boldsymbol{\mathcal{L}}^{\text{G},\omega\,0}\frac{1}{\theta}\boldsymbol{g} - \sum_{\beta=1}^{K-1}\boldsymbol{\mathcal{L}}^{\text{G},\omega\,\beta}\nabla\tilde{\mu}_{\beta}, \quad \omega = 1, \ldots, K-1. \tag{56}$$

Reduction to diagonal Onsager matrix
Neglecting the off-diagonal Onsager coefficients, i.e., considering $\mathcal{L}^{\mathrm{G},\alpha\beta} = \mathbf{0}\,\forall\,\alpha \neq \beta$ and choosing $\mathcal{L}^{\mathrm{G},00} = \theta\boldsymbol{\kappa}$ and $\mathcal{L}^{\mathrm{G},\omega\omega} = \boldsymbol{M}^{\mathrm{G}}_{\omega}$ yields

$$\boldsymbol{q}^{\mathrm{G}} = -\boldsymbol{\kappa}\boldsymbol{g}, \quad \boldsymbol{j}^{\omega} = -\boldsymbol{M}^{\mathrm{G}}_{\omega}\nabla\tilde{\mu}_{\omega}, \tag{57}$$

which corresponds to Eq. (37).

4.4 Representation dependence of thermodynamic force bases and diagonal closures

Balance-level formulation and thermodynamic force bases
Before comparing the two approaches, it is useful to distinguish between three levels. First, the present work adopts a mixture-level description rather than a constituent-based theory with separate partial mass, momentum, energy, and entropy balances for each constituent. Second, within this mixture-level setting, diffusion-related transport can be incorporated into the balance structure in different ways. In the Gurtin approach considered here, this contribution is represented by an additional energy flux and the corresponding governing equations are obtained from the invariance of the extended energy balance. In the Müller approach considered here, the classical energy balance is retained, whereas the corresponding diffusion-related contribution enters through the extended entropy flux. Third, these balance-level choices lead to different forms of the flux-related dissipation. For the subsequent Onsager closure, each form of the flux-related dissipation suggests a natural thermodynamic force basis. This force basis, however, is not unique. Alternative admissible choices of thermodynamic forces are possible and would transform the corresponding Onsager operator.

Thermodynamic forces in a selected representation
In the Onsager closure, the word "force" is used in the restricted sense of the quantity that multiplies a flux in the chosen bilinear representation of δ_{flux}. Such factors are commonly referred to as thermodynamic forces [69, pp. 25–26]. This choice is not unique. Different definitions of fluxes may lead to different forms of the entropy production [69, p. 27]. Consequently, whether an Onsager operator appears diagonal or non-diagonal depends on the adopted basis of thermodynamic forces. Specifically, a closure that is diagonal in one basis of thermodynamic forces may appear non-diagonal in another admissible basis.

Consequence for the present comparison
For comparing the thermodynamic force bases considered for the Müller and Gurtin approaches, it is useful to rescale the Müller-type forces in Eq. (39) by the temperature θ. This rescaling is not used to introduce a new closure. However, it explicitly illustrates the relation to the Gurtin-type force basis. Using Eq. (50), one obtains

$$\theta\boldsymbol{X}^{q} = -\frac{1}{\theta}\boldsymbol{g} = \boldsymbol{X}^{q,\mathrm{G}}, \tag{58}$$

$$\theta\boldsymbol{X}^{\omega} = -\nabla\tilde{\mu}_{\omega} + \frac{\tilde{\mu}_{\omega}}{\theta}\boldsymbol{g} = \boldsymbol{X}^{\omega,\mathrm{G}} + \frac{\tilde{\mu}_{\omega}}{\theta}\boldsymbol{g}. \tag{59}$$

Thus, after rescaling, the Müller-type thermal force coincides with the Gurtin-type thermal force, whereas the Müller-type force associated with diffusion contains an additional temperature-gradient contribution. Since a diagonal Onsager closure relates the diffusion flux directly to this diffusion-related force, this temperature-gradient contribution also appears in the resulting diffusion flux. It should not be interpreted as an additional physical mechanism that is independent of the thermodynamic force basis used for the Onsager closure. The flux repartition in Eq. (33) and the force transformation in Eqs. (58) and (59) show that both the flux vector and the thermodynamic force basis used for the Onsager closure change between the two representations. Consequently, a diagonal Onsager operator in one representation is generally not diagonal in the other.

4.5 Comparing thermo-diffusion for both approaches

Side-by-side comparison of both approaches
Having established the Onsager-based flux–force relations for the two approaches considered here, this subsection provides a concise side-by-side comparison with a focus on the apparent Soret/Dufour structure obtained

Table 1 Comparison of the Gurtin and Müller approaches considered here with respect to the balance of internal energy, the entropy flux, the flux-related dissipation, the thermodynamic force basis used for the Onsager closure, the resulting thermo-diffusive laws for heat flux and diffusion flux, and the special case of a diagonal Onsager closure in the respective thermodynamic force basis. The distinction between diagonal and non-diagonal Onsager structures depends on the chosen basis of thermodynamic forces and is not invariant under a general transformation of these forces

	Gurtin approach	**Müller approach**
Balance of internal energy	$\rho\dot{e} = \boldsymbol{\sigma} \cdot \operatorname{grad}(\boldsymbol{v}) + \rho r - \operatorname{div}\left(\boldsymbol{q}^{\mathrm{G}}\right) + \sum_{\omega=1}^{K-1} \tilde{\mu}_\omega \rho \dot{c}_\omega - \sum_{\omega=1}^{K-1} \nabla\tilde{\mu}_\omega \cdot \boldsymbol{j}^\omega$	$\rho\dot{e} = \boldsymbol{\sigma} \cdot \operatorname{grad}(\boldsymbol{v}) + \rho r - \operatorname{div}\left(\boldsymbol{q}^{\mathrm{M}}\right)$
Entropy flux	$\boldsymbol{\phi}^\eta_{\mathcal{V}} = \dfrac{\boldsymbol{q}^{\mathrm{G}}}{\theta}$	$\boldsymbol{\phi}^\eta_{\mathcal{V}} = \dfrac{\boldsymbol{q}^{\mathrm{M}}}{\theta} - \sum_{\omega=1}^{K} \dfrac{\mu_\omega}{\theta} \boldsymbol{j}^\omega$
Flux related dissipation	$\rho\delta_{\mathrm{flux}} = -\dfrac{1}{\theta}\boldsymbol{q}^{\mathrm{G}} \cdot \boldsymbol{g} - \sum_{\omega=1}^{K-1} \nabla\tilde{\mu}_\omega \cdot \boldsymbol{j}^\omega$	$\rho\delta_{\mathrm{flux}} = -\dfrac{1}{\theta}\boldsymbol{q}^{\mathrm{M}} \cdot \boldsymbol{g} - \sum_{\omega=1}^{K-1} \nabla\tilde{\mu}_\omega \cdot \boldsymbol{j}^\omega + \sum_{\omega=1}^{K-1} \dfrac{\tilde{\mu}_\omega}{\theta} \boldsymbol{j}^\omega \cdot \boldsymbol{g}$
Thermodynamic force basis for Onsager closure	$\boldsymbol{X}^{q,\mathrm{G}} = -\dfrac{1}{\theta}\boldsymbol{g}, \quad \boldsymbol{X}^{\omega,\mathrm{G}} = -\nabla\tilde{\mu}_\omega$	$\boldsymbol{X}^{q} = -\dfrac{1}{\theta^2}\boldsymbol{g}, \quad \boldsymbol{X}^{\omega} = \dfrac{\tilde{\mu}_\omega}{\theta^2}\boldsymbol{g} - \dfrac{1}{\theta}\nabla\tilde{\mu}_\omega$
Thermo-diffusion	$\boldsymbol{q}^{\mathrm{G}} = -\boldsymbol{\kappa}\boldsymbol{g} - \sum_{\omega=1}^{K-1} \boldsymbol{\mathcal{L}}^{\mathrm{G},0\,\omega} \nabla\tilde{\mu}_\omega$	$\boldsymbol{q}^{\mathrm{M}} = -\dfrac{1}{\theta^2}\boldsymbol{\mathcal{L}}^{00}\boldsymbol{g} + \sum_{\beta=1}^{K-1} \dfrac{\tilde{\mu}_\beta}{\theta^2}\boldsymbol{\mathcal{L}}^{0\beta}\boldsymbol{g} - \sum_{\beta=1}^{K-1} \dfrac{1}{\theta}\boldsymbol{\mathcal{L}}^{0\beta}\nabla\tilde{\mu}_\beta$
	$\boldsymbol{j}^\omega = -\boldsymbol{\mathcal{L}}^{\mathrm{G},\omega\,0}\dfrac{1}{\theta}\boldsymbol{g} - \sum_{\beta=1}^{K-1} \boldsymbol{\mathcal{L}}^{\mathrm{G},\omega\,\beta}\nabla\tilde{\mu}_\beta$	$\boldsymbol{j}^\omega = -\dfrac{1}{\theta^2}\boldsymbol{\mathcal{L}}^{\omega 0}\boldsymbol{g} + \sum_{\beta=1}^{K-1} \dfrac{\tilde{\mu}_\beta}{\theta^2}\boldsymbol{\mathcal{L}}^{\omega\beta}\boldsymbol{g} - \sum_{\beta=1}^{K-1} \dfrac{1}{\theta}\boldsymbol{\mathcal{L}}^{\omega\beta}\nabla\tilde{\mu}_\beta$
Diagonal closure in the respective thermodynamic force basis	$\boldsymbol{q}^{\mathrm{G}} = -\boldsymbol{\kappa}\boldsymbol{g}, \quad \boldsymbol{j}^\omega = -\boldsymbol{M}^{\mathrm{G}}_\omega \nabla\tilde{\mu}_\omega$	$\boldsymbol{q}^{\mathrm{M}} = -\boldsymbol{\kappa}\boldsymbol{g}, \quad \boldsymbol{j}^\omega = -\frac{1}{\theta}\boldsymbol{M}^{\mathrm{M}}_\omega \nabla\tilde{\mu}_\omega + \frac{\tilde{\mu}_\omega}{\theta^2}\boldsymbol{M}^{\mathrm{M}}_\omega \boldsymbol{g}$

in the corresponding thermodynamic force bases. The comparison is conditional on the mixture-level formulation of each approach and on the Onsager closures introduced above. Both approaches are compared in Table 1 with respect to the balance of internal energy, entropy flux, flux-related dissipation, thermo-diffusion, and the special case of a diagonal Onsager operator in the respective thermodynamic force basis.

Comparison between Onsager relations for both approaches

The preceding sections illustrate that the different treatments of diffusion-related transport at mixture level lead to different flux-related dissipation formats, cf. Eq. $(27)_2$ and Eq. $(36)_2$. These dissipation formats suggest different thermodynamic force bases for the subsequent Onsager closure, cf. Eqs. (39) and (50). This difference should be understood relative to the thermodynamic force bases adopted here. In particular, a diagonal closure in one force basis does not generally remain diagonal after an admissible change of thermodynamic forces. The comparison of Eq. (48) and Eq. (57) yields the following conditional statements:

- In the thermodynamic force basis used for the Müller approach, a diagonal Onsager operator yields a Fourier-type heat flux and a diffusion flux containing an additional temperature-gradient term. This term appears because the diffusion-related thermodynamic force contains a contribution proportional to $\boldsymbol{g}$, cf. Eq. $(39)_2$ and Eq. (59). In this restricted sense, the Müller approach considered here exhibits an apparent "Soret-without-Dufour" structure.
- In the thermodynamic force basis used for the Gurtin approach, a diagonal Onsager operator yields uncoupled Fourier and Fick laws. Thermo-diffusive coupling in this basis requires non-diagonal Onsager blocks. With Onsager reciprocity imposed in this basis, such non-diagonal blocks couple the heat flux and the diffusion fluxes simultaneously.

- These statements do not exclude alternative admissible closures. In particular, non-diagonal closures or different thermodynamic force bases can lead to different apparent Soret/Dufour structures while still satisfying the entropy inequality.

5 Concluding remarks

Balances and dissipation inequality
Two mixture-level continuum-thermodynamic approaches to non-isothermal diffusion have been compared side by side. In the Gurtin approach considered here, diffusion-related energetic transport is accounted for through an additional energy flux, while the entropy flux is taken in its standard heat-flux-over-temperature form. In the Müller approach considered here, the classical Cauchy-continuum energy balance is retained, while diffusion-related transport is accounted for through an extended entropy flux. Both approaches lead to admissible dissipation inequalities, but they yield different flux-related bilinear forms for the subsequent Onsager closure.

Thermodynamic force bases and Onsager closures
The main conclusion is that the apparent Soret/Dufour structure depends on how diffusion-related transport is accounted for in the mixture-level approach considered and on the thermodynamic force basis used for the Onsager closure. In the Müller approach considered here, the diffusion-related thermodynamic force contains a temperature-gradient contribution. Therefore, a diagonal Onsager closure in this force basis yields a Fourier-type heat flux and a diffusion flux containing an apparent Soret-type term. In this restricted sense, the formulation exhibits a "Soret-without-Dufour" structure. In the thermodynamic force basis used for the Gurtin approach considered here, a diagonal Onsager closure yields uncoupled Fourier and Fick laws. Thermodiffusive cross-effects then require non-diagonal Onsager blocks, which couple heat and diffusion fluxes simultaneously in that basis. This difference should not be interpreted as an additional physical distinction that is independent of the thermodynamic force basis used for the Onsager closure, since a diagonal Onsager operator is not invariant under a general change of thermodynamic forces. The central message is that the apparent Soret/Dufour structure is a closure-level property. It depends on how diffusion-related transport is accounted for at mixture level and on the thermodynamic force basis used for the Onsager closure.

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